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POLYCONDENSATION STATISTICS

by

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ABSTRACT

The classical theory of polycondensation statistics is generalized to include the two major sources of non-randomness;

- (a) substitution effects arising from the influence of neighbouring groups on the rate of reaction of a functionality
- (b) intramolecular condensation.

The theory of branching processes is used as a common mathematical framework and the statistical theory is set out with reference to f -functional polycondensation. The non-random model is used to analyse the two extreme cases of polycondensation, i.e. thermodynamically and kinetically controlled reactions.

The simple equilibrium system $\text{POCl}_3/\text{P}_2\text{O}_5$ is examined and excellent agreement of nmr data in the literature is obtained. There are found to be negligible substitution effects and the amount of cyclization agrees reasonably with that predicted by random-flight statistics. As an example of a kinetically controlled system, the uncatalysed polyesterification of pentaerythritol and its homologue, trimethylol ethane, was studied experimentally at 175°C . The rate of the reaction was followed in a closed system using a transducer to measure the pressure of water vapour above the reaction mixture. The concentration dependence of the gel points was also studied. The analysis of the results showed the uncatalysed polyesterification to be third-order. This is masked by the non-random effects which falsely

indicate an apparent $2\frac{1}{2}$ -order reaction; this situation has probably deceived previous investigators of related systems. From the measurements of the gel points for mixtures containing different ratios of polyol to acid, the substitution parameter for each component and the one cyclization parameter required by theory were determined. Finally the experimental rate curves were compared with the theoretical ones and excellent agreement obtained for the equivalent mixtures of polyol to acid. Once again the cyclization parameter was in reasonable agreement with random-flight statistics. A small cumulative substitution effect was found on the polyols which progressively favoured the reaction of free functionalities according to the number of reacted functionalities already borne by the unit to which they were attached.

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CHAPTER 1

INTRODUCTION

The aim of this work was to make the necessary theoretical generalizations to the classical schemes for random condensation reactions (Flory 1953), so as to include in the theory the two major non-random influences: (i) substitution effects and (ii) intramolecular (cyclization) reactions. These generalizations are of importance for the scientific and technological understanding of processes and products of several industries (resins, paints, varnishes, plastics), and while this work was in progress, other workers have published parallel attempts to come to grips with these problems (e.g. Van Wazer 1962, Keller 1962).

The technical need for this work may be exemplified by the following remarks. Classical polycondensation theory led to a satisfactory account of the gel point phenomenon, which is of great practical significance. Yet no quantitative applications appear to have been made to gel points of such industrial systems as phenol - or melamine-formaldehyde resins, and it may safely be surmised that this could not be done until chemical substitution and cyclization effects could be taken into account. Thus the present work was started with the aim in mind of providing a basis for a more complete chemical understanding of such important systems.

This study attempts to test kinetic schemes concerning the

reaction mechanism of polycondensation reactions against statistical quantities which can be measured as a function of conversion. The work is chiefly concerned with polyfunctional polymerizations and thus the gel point is one of the most convenient and easily measured statistical parameter that can be used to test these schemes. The earlier work on the calculation of molecular weight distributions from the mechanism of polymerization was pioneered by Flory (1953). Later studies by Case (1957, 1958, 1959, 1960) extended this work of Flory on f-functional monomers to mixtures of functionalities of unequal reactivity. These authors derive the molecular weight distributions from probability arguments, but Inoue (1953) uses the complementary method of solving the appropriate differential rate equations. In practice, it is often more fruitful to characterize distributions roughly by averages such as the number average (DP_n) or weight average (DP_w) degree of polymerization which are experimentally accessible.

The calculation of statistical quantities from postulated kinetic mechanisms fits admirably into the general framework of the stochastic theory of branching processes (Harris 1963), especially as developed by Good (1955, 1960, 1963) and applied to polymer distributions by Gordon (1962). A more general use of the theory of branching processes to equilibrium statistics of clustering processes in the uncondensed phase has recently been published by Whittle (1965a, 1965b). Chapter 2 briefly describes the principles

involved and defines the statistical parameters in terms of generating functions. The method only uses differential calculus, and for copolymerization, the elements of matrix algebra. It has the advantage over previous statistical methods (Flory 1953; Stockmayer 1944) of reducing the use of probability theory to essentially one equation, and the summation of algebraic series is usually avoided. This is because this method does not depend on obtaining an explicit algebraic expression for the molecular weight distribution, although it would, in principle, be able to do so (cf. Good 1960). But the method gives directly the statistical parameters which can be experimentally measured. Hence the theory of branching processes provides a unified method for kinetic and thermodynamic studies of polymer reactions and for the calculation of statistical parameters for theories of physical properties.

The theory of branching processes has already been extended by Dobson and Gordon (1964) to compute configurational statistics and to the calculation of the number and length of active network chains in polymer networks (Dobson and Gordon 1965). The work of Gordon (1962) is here extended to take into account deviations from non-random behaviour in polycondensation reactions. The classical model (Flory 1953) postulates that pairs of functionalities react at random to produce links between the f-functional (repeat) units. Two major sources of deviations are recognized:

- (1) Substitution Effects. These consist of changes in the

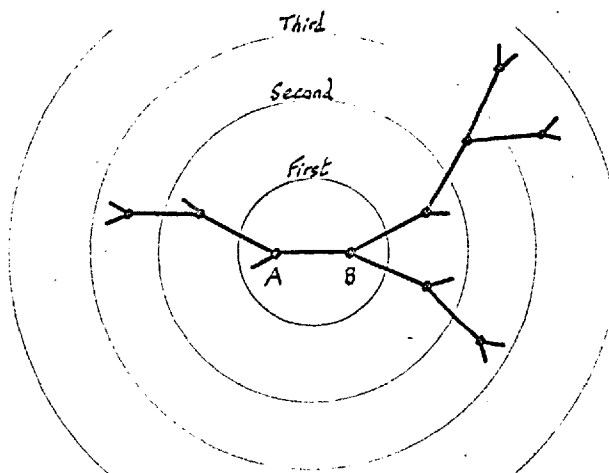


Fig. 1.1 Schematic diagram showing arrangement of links in successive shells about the link A-B in a particular decamer. There are 3 first shell, 3 second shell and 2 third shell links.

rate of forming or breaking a link (such as A-B in Fig. (1.1)) induced by the presence of other links in the same molecule. This general substitution effect may be controlled thermodynamically or kinetically, and links in the first shell (Fig. (1.1)) are, of course, expected to exert the strongest effects of this type. These first shell substitution effects (FSSE) are treated theoretically in Chapter 3. The substitution effect of a given functionality on others borne on distant units (second shell, third shell, etc.) will, fortunately, be of much smaller magnitude and is neglected in the treatment. Although general effects on the reaction rates and equilibria by the fate of other functional groups on the same

molecule are usually considered negligible, they must always occur in practice. The special case of a linear FSSE, whose magnitude is proportional to the sum of the number of links already borne by the two units to be bonded, is treated exactly in section (3.3).

(ii) Cyclization. In linear polycondensation ($f=2$) the only opportunity in any x-mer molecule for the formation of an intramolecular link arises between the pair of terminal functionalities of the chain. The statistical mechanics of this process was derived exactly, using Gaussian statistics for the chain conformation, by Jacobson and Stockmayer (1950); applications to polydecamethylene adipate were made by Jacobson, Beckmann and Stockmayer (1950). A similar model, using a discrete state approximation to calculate the probability of ring closure, was proposed by Carmichael and Kinsinger (1964) for the polydimethylsiloxane system and recently the two models have been tested on this system (Carmichael and Winger 1965), (see section (4.1)). In polyfunctional polycondensations ($f>2$) the combinatorial problem of evaluating the numbers and distances of possible reaction partners for a given functionality to close a ring with another on the same molecule presents much greater difficulty. Harris (1955) tackled this problem with rather drastically simplified models. Kilb (1958) used an extension of Flory's method to calculate the extent of reaction and the concentration dependence of the gel point. Hoeve (1956) followed the lines of Jacobson and Stockmayer (1950) in his contribution to the statistics of intramolecular

condensation. The theory of branching processes provides the proper mathematical framework for combinatorial problems and is used in Chapter 4 to estimate the effect of intramolecular condensation.

The experiments of Kienle and his co-workers (1939) on the condensation of glycerol with dibasic acids have shown that intramolecular reaction proceeds to an appreciable degree in competition with intermolecular condensation. If esterification were exclusively intermolecular, the number of molecules present should decrease by one for each ester group formed. Kienle (1939a) observed that the cryoscopically determined number of particles decreased less than the increase in the extent of the esterification; this discrepancy amounted to about 5% of the total esterification.

Both substitution and cyclization effects become more prominent the more closely the functionalities are spaced within the repeat units. Publication by Groenweghe, Payne and Van Wazer (1960) of measurements of statistical parameters in the simple equilibrium system phosphorus oxychloride/phosphorus pentoxide, in which the chlorine-functionalities are directly attached to the same phosphorus atom in a given unit, is used as a test-case in Chapter 6 for assessing the rôle of deviations from randomness in an equilibrium polycondensation.

Finally, the kinetically controlled polyesterification system pentaerythritol/adipic acid is studied in detail and the measured statistical quantities compared with that predicted by the non-random

model. The kinetics of this polyesterification reaction are measured by following the evolution of water from the reaction mixture in a closed system with a pressure transducer. The construction and method of using this apparatus is discussed and details given for following the course of such reactions up to and past the gel point. In this way conversion-time plots are obtained for various mole ratios of alcohol to acid. A homologue of pentaerythritol, trimethylolethane, is also studied in this apparatus. The concentration dependence of the gel point for this polycondensation reaction is measured. The data obtained are tested against kinetic reaction schemes (Chapter 8).

This work illustrates the use of the theory of branching processes in polymer statistics and shows how non-random effects fit into this common framework. By using these models to analyse the data from both equilibrium and kinetically controlled polycondensation, it is hoped that the calculations can be extended with confidence to other polycondensation systems.

CHAPTER 2

THE THEORY OF BRANCHING PROCESSES

2.1 Introduction

The theory of branching processes stems from the work of Galton and Watson (1874) on human heridity. They used a simple model to discuss the probability that a family is still in existence after a large finite number of generations. The original Galton-Watson process and its generalizations are connected with work dating back to Neils Abel (1881) on functional equations and the iteration of functions, and with various lines of development in the theory of stochastic processes. More recently the model has been developed for cascade processes by Good (1955, 1960) and applied to the statistics of polymer distributions by Gordon (1962). (For a general reference see Harris 1963).

The convential approach to calculating statistical parameters is based on distributions such as molecular weight distributions (Flory 1953). In the scheme based on the theory of branching processes everything is derived from the so-called link probability distribution (lpd), which is always closely related to the chemical mechanisms of synthesis, and which in favourable cases is open to direct experimental measurement (section (6.2)). Repeated use is made of the probability generating function (pgf). This is a function of the probability distribution defined so that the coefficient P_i

of θ^i in the Taylor series expansion of the pgf is the probability for the occurrence of the i^{th} event, i.e.

$$G(\theta) = \sum_{i=0}^{\infty} P_i \theta^i \quad (2.1)$$

where θ is a dummy variable. Normalization of probabilities implies that

$$G(1) = \sum_{i=0}^{\infty} P_i = 1 \quad (2.2)$$

Operating on this dummy variable, the statistical parameters can be derived from the pgf; thus, the mean of the distribution is given by

$$\left[dG(\theta)/d\theta \right]_{\theta=1} = G'(1) = \sum_{i=0}^{\infty} P_i \cdot i \quad (2.3)$$

where the prime denotes differentiation with respect to θ .

The method for the simplest case of a single type of repeat unit is now described; extension to copolymerization of s different types ($s > 1$) is to some extent a formal procedure involving vectorial generating functions and will be discussed in section (2.5).

2.2 Statement of the Method

Having chosen a unit at random in the system, one may consider one of its f - functionalities; if this has a chance γ of being reacted (cross-linked to another unit), then it has a chance $(1 - \gamma)$ of not being reacted. For random polycondensation (whose parameters will be given a superscript star in this thesis) this statement exhausts the combinatorial theory required, all the remaining manipulation being of a general type. Thus the pgf of the number of bonds formed by the

functionality in question is

$$f^*(\theta) = 1 - \gamma^* + \gamma^* \theta \quad (2.4)$$

By definition of randomness, the corresponding pgf for all the f -functionalities on the chosen unit is

$$F_o^f(\theta) = (1 - \gamma^* + \gamma^* \theta)^f \quad (2.5)$$

For example, we may consider the etherification of pentaerythritol ($f = 4$). The probability that a unit chosen at random has 3 cross-links is merely the coefficient of θ^3 in eq. (2.5) when f is set to 4. This coefficient is $4(1 - \gamma^*)(\gamma^*)^3$; the term $(1 - \gamma^*)$ reflects the chance that one of the functionalities is free while $(\gamma^*)^3$ is the chance that three of the functionalities are cross-linked, the factor 4 is the combinatorial term arising from the different combinations of 3 cross-links and 1 free functionality.

In general, if P_i denotes the chance of finding i links (reacted functionalities) on a randomly chosen unit, then the P_i are said to form the link distribution and its pgf is (cf eq. (2.1))

$$F_o(\theta) = \sum_{i=0}^f P_i \theta^i \quad (2.6)$$

From this pgf all the other statistical parameters are derived by standard formulae (section 2.4).

The general procedure in this work is based on the construction of an ensemble M of graphs or trees. To this end each unit in the molecular system is chosen in turn to form the root or zeroth

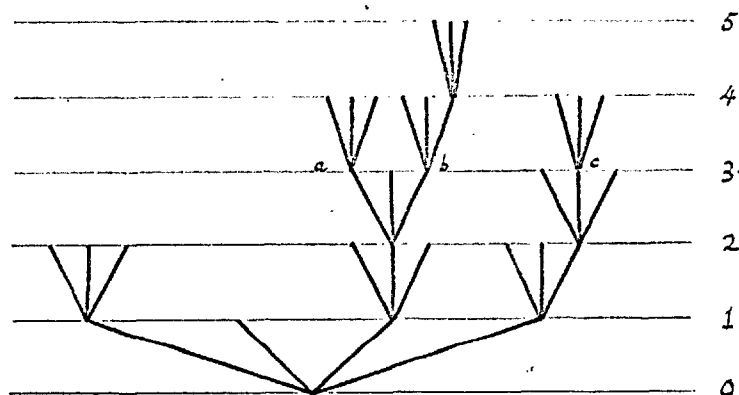


Fig. 2.1 Schematic representation of poly (pentaerythritol) molecule as a tree with conventional numbering of generations. The root of the tree is on the zeroth generation; and on the third generation, a is a brother unit of b, but not of c.

generation of one family tree (fig. (2.1)); the other units in the same molecule are then unambiguously assigned to the first generation, second generation, etc. To each x-mer molecule in the molecular system there accordingly corresponds x trees in the ensemble; each such tree has one of its x units as its root. The mean size of the ensemble is the weight average DP_w of the molecular system. A second ensemble of trees can be formally generated using the generating functions $F_0(\theta)$, $F_1(\theta)$, $F_2(\theta)$, etc. for the probabilities of the number of children borne by a unit belonging to the zeroth, first, second, etc. generation of the ensemble respectively. For random polycondensation systems the ensembles M and G are identical and if one can formulate the generating functions $F_j(\theta)$ these will describe

the molecular system uniquely and can therefore be used to evaluate the statistical parameters of the system.

2.3 The Probability Generating Function

The pgf $F_1(\theta)$ of the number of children borne by a unit belonging to the first generation is completely determined by $F_0(\theta)$ (the pgf for the offsprings of a unit on the zeroth generation) in virtue of a consistency condition:

$$F_1(\theta) = F_0'(\theta) / F_0'(1) \quad (2.7)$$

This follows from the manner in which the ensemble is constructed; i.e. $F_1(\theta)$ must be the pgf for the number of offsprings borne by $(f-1)$ functionalities on a unit of which the remaining functionality is known to be reacted.

In other words, a given i -substituted monomer unit appears on the zeroth generation once, the first generation i times, each time producing $(i-2)$ offsprings in the second. This result is illustrated in figure (2.2) for a tetra-functional unit A with three cross-links.

Regarding the higher $F_g(\theta)$ ($g > 1$), their structure depends on the degree of randomness of the polymerization and depolymerization reactions which have produced the system. Fortunately, most practical cases lead to the following simple state of affairs:

$$F_1(\theta) = F_2(\theta) = F_3(\theta) = \dots \quad (2.8)$$

These are cases where the rate of formation or breakage of links is subject (at most) to a first shell substitution effect (FSSE), (see section (3.2)). The random polycondensation reaction does not even depend on the first shell. The thermodynamics and kinetics of the

FSSE are discussed in section (3.3)

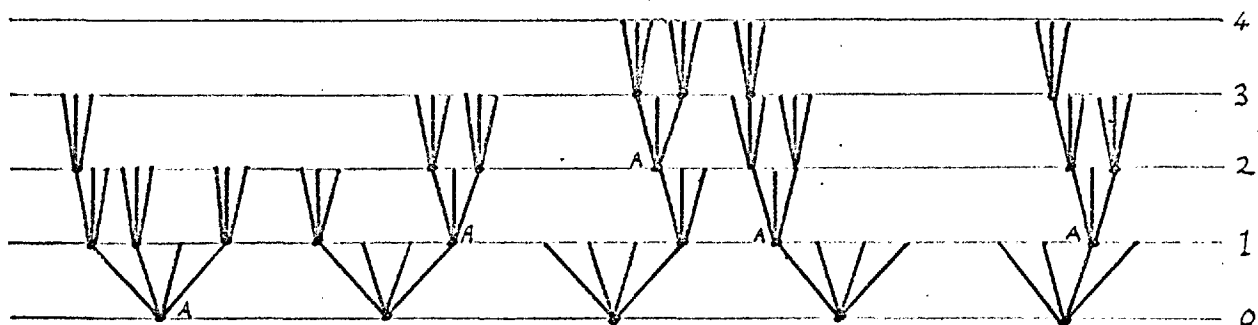
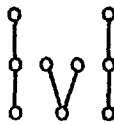
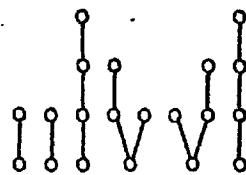
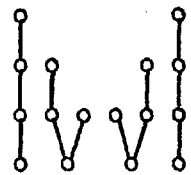
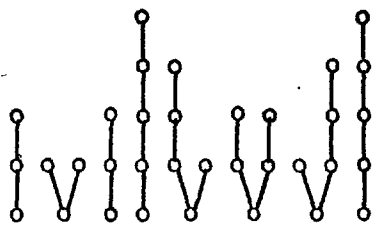


Fig. 2.2. Schematic representation of the assignment of a pentamer molecule of a tetrafunctional monomer in the ensemble of trees. The labelled unit A bearing three cross-links appears once in the zeroth and thrice in the first generation.

To illustrate the use of generating functions and the relationships between them we can consider a mixture of paraffins. These may be treated as ensembles of trees in a similar manner. Although the relationship (eq. (2.7)) between $F_0(\theta)$ and $F_1(\theta)$ is universally valid it is easily demonstrated that $F_2(\theta)$ is independent of $F_1(\theta)$ and hence of $F_0(\theta)$. Four systems are discussed; A, 100% propane; B, equimolar mixture of ethane and butane; c, 100% n-butane; D, equimolar mixture of propane and n-pentane. The pgf for these systems are shown in Table (2.1). Although the $F_0(\theta)$ (and hence $F_1(\theta)$) are identical

TABLE 2.1

Probability Generating Functions and Mean Size (DP_w)
for mixtures of Paraffins

	A propane	B equimolar mixture ethane & n-butane	C n-butane	D equimolar mixture propane & n-pentane
Ensemble				
$F_0(\theta)$	$\frac{2}{3}\theta + \frac{1}{3}\theta^2$	$\frac{2}{3}\theta + \frac{1}{3}\theta^2$	$\frac{1}{2}\theta + \frac{1}{2}\theta^2$	$\frac{1}{2}\theta + \frac{1}{2}\theta^2$
$F_1(\theta)$	$\frac{1}{2} + \frac{1}{2}\theta$	$\frac{1}{2} + \frac{1}{2}\theta$	$\frac{1}{3} + \frac{2}{3}\theta$	$\frac{1}{3} + \frac{2}{3}\theta$
$F_2(\theta)$	1	$\frac{1}{2} + \frac{1}{2}\theta$	$\frac{1}{2} + \frac{1}{2}\theta$	$\frac{1}{2} + \frac{1}{2}\theta$
$F_3(\theta)$	-	1	1	$\frac{1}{2} + \frac{1}{2}\theta$
$F_4(\theta)$	-	-	-	1
DP_w	3.00	3.60	4.00	4.47
DP_w (eq. 2.13)	3.67	3.67	5.50	5.50

for the systems A-B, and C-D, the $F_2(\theta)$ for A and B are not the same although $F_2(\theta)$ for C and D are still identical. In this latter case the $F_3(\theta)$ differ. The mean size (DP_w) for these systems is also shown in Table (2.1), together with a value computed (eq. 2.13) on the assumption that the $F_g(\theta)$ for $g > 1$ are identical. The agreement in these extreme examples is surprisingly good considering the crudeness of this approximation, which replaces the given systems by distributions of x-mers with x ranging from one to infinity. The approximate validity of this relationship (eq. (2.8)) between the higher pgf in the presence of intramolecular reactions in polycondensation is discussed in section (4.3).

All statistical parameters can, therefore, in principle, be calculated from $F_1(\theta)$ alone for FSSE systems without cyclization. This link probability generating function forms the keystone of the edifice.

2.4. Statistical Parameters

The statistical parameters discussed in this section are for systems with at most a first shell substitution effect, i.e. those systems for which the relationship (eq. (2.8)) between the higher pgf is valid (the validity of eq. (2.8) in the presence of a FSSE is discussed in section (3.2)). The first statistical parameter to be discussed for any polycondensing units of functionality f is the mean degree of reaction α , i.e. the fraction of all functionalities which have reacted intermolecularly, and which is a measure of the degree of chemical advancement of the polymerization reaction. It

is always given by

$$\alpha = F_0'(1)/f \quad (2.9)$$

which in the random case (eq. (2.5)) leads to

$$\gamma^* = \alpha \quad (2.10)$$

Thus the pgf for the offsprings of a unit on generation g can be written down for the random reaction using eq. (2.5), (2.7), (2.8), (2.10)

$$F_g^*(\theta) = (1 - \alpha + \alpha\theta)^{f-1}, \quad g \geq 1 \quad (2.11)$$

The number degree of polymerization (DP_n) can be written down from stoichiometry

$$DP_n = 1/(1 - f\alpha/2) \quad (2.12)$$

The weight average degree of polymerization (DP_w) is most easily formulated in terms of $F_0(\theta)$ and $F_1(\theta)$, though $F_1(\theta)$ can be eliminated using eq. (2.7), thus:

$$DP_w = 1 + F_0'(1)/(1 - F_1'(1)) \quad (2.13)$$

This equation is formally derived below, but is confirmed by simply expanding the RHS:

$$DP_w = 1 + F_0'(1) + F_0'(1)F_1'(1) + F_0'(1)[F_1'(1)]^2 + \dots \quad (2.14)$$

It is apparent and it can be rigorously proved (Good 1955, Corollary 6)

that successive terms on the right of eq. (2.14) are merely the mean number per tree in the ensemble of units on the zeroth, first, second, etc. generation, respectively. Since the mean size tree is just the sum of the mean number of units contributed by the zeroth, first, second, etc. generations, eq. (2.14) is confirmed. It is also readily shown that (cf Good 1963, eq. (7))

$$DP_z = 1 + \frac{1}{1 - F_1'(1) + F_0'(1)} \left(\frac{2F_0'(1) + F_0''(1)}{1 - F_1'(1)} + \frac{F_1''(1)}{(1 - F_1'(1))} \right) \quad (2.15)$$

The number fraction of the trees in the ensemble which consist of x units is also the weight fraction of x -mer in the corresponding system of molecules and is given (Good 1963) by

$$w_x = (x-1)! (f_x)^{1-x} C(\theta^{x-2}) [F_0'(\theta)]^x \quad (2.16)$$

where $C(\theta^{x-2})$ denotes the coefficient of θ^{x-2} in the Taylor expansion of what follows. The original form of this equation is derived (Good 1963) by Lagrange's expansion applied to the weight fraction generating function which is obtained by the iterative process

$$W(\theta) = \theta F_0 \left(F_1 \left\{ \theta F_1 \left[\theta F_1 (\dots) \right] \right\} \right) \quad (2.17)$$

This may be written

$$W(\theta) = \theta F_0 (u(\theta)) \quad (2.18)$$

in terms of $u(\theta)$, which is a generating function obeying

$$u(\theta) = \theta F_1 (u(\theta)) \quad (2.19)$$

It should be noted that by definition the coefficient of θ^x in $W(\theta)$ is the weight fraction w_x of x-mer, i.e.

$$W(\theta) = \sum_{x=1}^{\infty} w_x \theta^x \quad (2.20)$$

The function $u(\theta)$ has been described (Dobson and Gordon 1964) as a pgf of a size distribution in two distinct ways by referring either to the ensemble of trees or to the original molecular system;

- a) $u(\theta)$ is the pgf of the sizes of proper subtrees of the ensemble. A proper subtree is obtained by choosing any unit from generations 1, 2, 3, ... (but not from generation zero) together with all the descendants of the unit chosen.
- b) $u(\theta)$ is the pgf of the sizes of molecular moieties produced by splitting a link chosen at random in the system of molecules.

In systems subject to at most a FSSE, there is no correlation between the probabilities of the sizes of the two moieties produced by splitting a randomly chosen link.

The weight average degree of polymerization (DP_w), the z-average (DP_z) and higher averages are obtained from the weight average generating function (eq. (2.18)) by successive differentiations;

$$DP_w = \left[dW(\theta)/d\theta \right]_{\theta=1} \quad (2.21)$$

$$DP_z = (d(\theta dW(\theta)/d\theta)/d\theta)_{\theta=1} / (dW(\theta)/d\theta)_{\theta=1} \quad (2.22)$$

For the calculation of DP_w , differentiation of eq. (2.18) and eq. (2.19), followed by elimination of $du(\theta)/d\theta$, which is given by

$$du(\theta)/d\theta = F_1(u(\theta)) / [1 - \theta F_1'(u(\theta))] \quad (2.23)$$

between the two resulting equations leads to

$$dW(\theta)/d\theta = F_0(u(\theta)) + [\theta F_1(u(\theta)) F_0'(u(\theta))] / [1 - \theta F_1'(u(\theta))] \quad (2.24)$$

Putting both $u(\theta)$ and θ equal to unity yields

$$DP_w = 1 + F_0'(1) / [1 - F_1'(1)] \quad (2.25)$$

which formally derives eq. (2.13). By substituting the generating function for f -functional polycondensation (eq. (2.11)) into eq. (2.25), one immediately arrives at the well known formula of Flory

$$DP_w = (1 + \alpha) / [1 - (f - 1)\alpha] \quad (2.26)$$

Since DP_w diverges when $F_1'(1)$ is unity (eq. (2.25)), this can be used as the gel point condition, hence from eq. (2.26)

$$\alpha_c = 1/(f - 1) \quad (2.27)$$

where subscript c will be used to denote the critical value of any statistical parameter at the gel point.

Further statistical parameters will be defined in terms of the pgf $F_s(\theta)$ as the model is developed to include a FSSE and intramolecular condensation (chapters 3 and 4). In particular the generating function $u(\theta)$ will be used in chapter 5 in which post-gel parameters are discussed.

2.5 Extension To Copolymerization

The full power of the theory of branching processes becomes apparent only when cases of copolymerization of different repeat units are examined. A full treatment for these cases is given by Gordon (1962) and it is sufficient here only to give those equations which will be used in subsequent chapters. As an example, the polyesterification of pentaerythritol and adipic acid is used. It is convenient to label the two types of unit as follows



The vectorial generating function for the offsprings on the zeroth generation can be written for the random reaction,

$$\begin{aligned}
 F_s(\theta) &= \left[(1 - \alpha_1 + \alpha_1 \theta_1)^4, (1 - \alpha_2 + \alpha_2 \theta_1)^2 \right] \\
 &= [F_{s1}(\theta), F_{s2}(\theta)]
 \end{aligned}
 \tag{2.28}$$

where α_s is the fractional conversion of units of type s . The coefficient of $(\theta_1)^i (\theta_2)^j$ in $F_{s1}(\theta)$ is, by definition of the pgf, the probability that a unit of type s in the zeroth generation of the molecular tree has i units of type 1 and j units of type 2 in

the following (i.e. first) generation among its offsprings. Thus $\mathbb{F}_{s,1}(\theta)$ deals with the probabilities for various offsprings when a type 1 unit (pentaerythritol) is present in the zeroth generation; the absence of a dummy variable θ_1 in $\mathbb{F}_{s,1}(\theta)$ (eq. (2.28)) correctly reflects the knowledge that a pentaerythritol unit in the zeroth generation can only give rise to a unit of type 2 (adipic acid) in the first generation.

The universal relation (eq. (2.7)) between the pgf for units on the first and those of the zeroth still applies to the vectorial pgf and may be generalized to copolymers:

$$/F \quad \mathbb{F}_{1s}(\theta) = \sum_j \mathbb{F}_{s,j}^j(\theta) / \sum_j \mathbb{F}_{s,j}^j(1) \quad (2.29)$$

where

$$/F \quad \mathbb{F}_{i,j}^{p,p}(\theta) = d\mathbb{F}_{i,j}^p(\theta) / d\theta_p \quad (2.30)$$

thus using eq. (2.29) on eq. (2.28) we have for the pentaerythritol/adipic acid system

$$\begin{aligned} /F \quad \mathbb{F}_1(\theta) &= [(1 - \alpha_1 + \alpha_1 \theta_2)^3, (1 - \alpha_2 + \alpha_2 \theta_1)] \\ &= [\mathbb{F}_{11}(\theta), \mathbb{F}_{12}(\theta)] \end{aligned} \quad (2.31)$$

/F where the coefficient of $(\theta_1)^i (\theta_2)^j$ in $\mathbb{F}_{1s}$ is the probability that a unit of type s, occurring in the first generation, has i units of type 1 and j units of type 2 among its offspring in the following generation.

The relationship between the vectorial pgf for higher generations

is subject to the same restrictions as discussed for the homopolymerization of single types of repeat units in section (2.3), i.e. to those systems with at most a FSSE and no cyclization.

$$\bar{F}_1(0) = \bar{F}_2(0) = \bar{F}_3(0) \quad (2.32)$$

is the appropriate generalization of eq. (2.8) for copolymerization.

The only remaining generalization that is required here is the gel point condition which is proved (Gzedon 1962) to take the form

$$\text{/F} \quad \left| \delta_i^j - \bar{F}_{ii}^j(1) \right| = 0 \quad (2.33)$$

where δ_i^j is the kronecker delta. For the pentaerythritol/adipic acid system we have from eq. (2.30), (2.31):

$$\text{/F} \quad \bar{F}_{11}^1(1) = \bar{F}_{12}^2(1) = 0 \quad (2.34)$$

$$\text{/F} \quad \bar{F}_{11}^2(1) = 3 \alpha_1 \quad (2.35)$$

$$\text{/F} \quad \bar{F}_{12}^1(1) = \alpha_2 \quad (2.36)$$

substituting eq. (2.34), (2.35), (2.36) into eq. (2.33) and solving we arrive at

$$3 \alpha_{1c} \alpha_{2c} = 1 \quad (2.37)$$

as the gel point condition.

Stoichiometry, of course, determines the relationship between α_1 and α_2 ; for the pentaerythritol/adipic acid system we have

$$2 \alpha_1 = m_2 M_1 \alpha_2 / m_1 M_2 \quad (2.38)$$

where m_s^0 , M_s are the initial weight fractions of the whole system and molecular weight of the s^h type of unit respectively. Thus α_1 can be used as a representative parameter of the progress of the copolymerization.

CHAPTER 3

STATISTICAL THEORY OF THE SUBSTITUTION EFFECT

3.1 Introduction

The theory of random f-functional polycondensation is now generalized to cases in which the rate of forming or breaking a bond between units A and B is influenced by the number of links already borne by A and B (to further units). For instance, when two links have already been formed on a given unit, its resulting substitution pattern may then induce a bias against the formation of further bonds on the same unit. This particular substitution effect actually dominates large tracts of the chemistry of phosphorus-containing polymers, where it has been called the 'anti-branching' rule (Van Wazer 1958). Though often found negligible in the past, general effects on the reaction rates and equilibria by the bonds already formed on a given unit in a polymerization must always occur in practice. The influences of reacted neighbours may be of steric or electronic origin.

Links in the first shell (see fig. 1.1) are, of course, expected to exert the strongest influence on non-random polycondensation, these are called first shell substitution effects (FSSE). The substitution effect of a given reacted functionality on others borne on distant units (second shell, third shell, etc.) will, fortunately, be of much smaller magnitude and is neglected in this treatment.

Matula, Groenweghe and Van Wazer (1964) have discussed how the i^{th} shell substitution effect (called by them $2i^{\text{th}}$ reorganization heat order) falls in importance when i increases beyond unity. They found some evidence for FSSE in the free energy data available for branched hydrocarbons, and for higher order effects in phosphate glasses.

The FSSE will be analysed in terms of the chance of forming a link between two units which have already acquired i_1 and i_2 links respectively to $(i_1 + i_2)$ other units. A special case of a linear FSSE whose magnitude is proportional to $(i_1 + i_2)$ serves as a first approximation to the more general FSSE and is treated in exact detail in section (3.3). The effect of intramolecular condensation is neglected in this treatment, but will be included into the scheme in the next chapter (4). The treatment is once again set out with reference to f-functional polycondensation. Homopolymerization of a single type of repeat unit is discussed for simplicity, since the method of extension to copolymerization has been discussed (section (2.5)).

The molecular weight distributions in presence of a substitution effect (but not the purely random reaction) depend on the relative rates of the forward (bond-forming) and backward (bond-breaking) reactions, in addition to their dependence on the extent of reaction α . Only the two extreme cases will be considered:

- (i) thermodynamic control (forward and backward rates equal)

(ii) kinetic control (backward rate negligible)

A series of papers (Keller 1962, Alfrey and Lloyd 1963, Arends 1963, Keller 1963) on the kinetically controlled FSSE for the condensation of bifunctional monomers have been published. These are concerned with the sequence of unreacted groups on long-chain molecules, each segment of which carries a reactive group.

Firstly the effect of FSSE on the generating function of the link probability distribution and on the statistical parameters that have been defined in section (2.4) is discussed.

3.2 The Link Probability Generating Function in the Presence of a First-Shell Substitution Effect

The lpgf $F_i(\theta)$ is of course independent of a FSSE as it can be defined (eq. (2.6)) in terms of the probability (P_i) that a unit chosen at random in the system has i links to other units and the fate of the functionalities on these units has no influence on P_i . Similarly from the way that the ensemble is constructed we still have the relation (eq. (2.7))

$$F_i(\theta) = F'_i(\theta)/F'_i(1) \quad (3.1)$$

It now only requires for the relation between the higher generations (eq. (2.8))

$$F_1(\theta) = F_2(\theta) = F_3(\theta) = \dots \quad (3.2)$$

to be shown to be still valid for FSSE in order that the definitions of statistical parameters given in chapter 2 to be applicable.

It is simple to prove that $F_g(\theta)$ is independent of g ($g \geq 1$) when the substitution effect affects at most the first shell. The

selection of a unit on the g^{th} generation implies that there exists exactly one path of g links back from the selected unit to the zeroth generation (root). Of these g links only the one linking the selected unit directly to its parent is relevant to the chances of finding the selected unit to have various numbers of offspring (as in this respect the other $(g - 1)$ links belong to higher shells than the first). Thus the relevant a priori knowledge is the same irrespective of g , provided $g > 1$. For a second shell substitution effect the scheme is seriously affected, because there is then a correlation between the probability distribution for the number of offsprings of a given unit on any generation (after the zeroth) and the number of brother units it happens to have (see Fig. (2.1)). (This point is treated by Harris 1963, pp 3-4). However, in the presence of the second shell substitution effect, the mean size (DP_w) of the ensemble is still given correctly by the generalization of eq. (2.14).

$$DP_w = 1 + F'_0(1) + F'_0(1)F'_1(1) + F'_0(1)F'_1(1)F'_2(1) + \dots \quad (3.3)$$

even though the correlation between brothers invalidates the corresponding generalization of eq. (2.17) for the size distribution as a whole, i.e.

$$W(\theta) \neq \theta F_0 \{ \theta F_1 [\theta F_2 (\dots)] \} \quad (3.4)$$

3.3. Thermodynamics of the First Shell Substitution Effect

Let ΔG° be the standard free energy of a reaction which forms a specific link between some given x-mer species and some given y-mer species. Let the unit A in the x-mer which is to acquire the new link already bear i_1 links, and the unit B concerned in the y-mer bear already i_2 links (fig. 3.1).

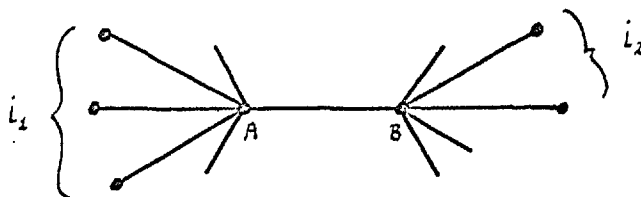


Fig. 3.1 Local situation for formation of link A-B between x-mer (containing unit A) and y-mer (containing unit B). Unit A bears $i_1 = 3$ first shell links, and unit B bears $i_2 = 2$ first shell links.

Then

$$\Delta G^\circ = \Delta G^{\circ*} + F(i_1, i_2) \quad (3.5)$$

expresses the most general FSSE we wish to consider. Here $\Delta G^{\circ*}$ is the free energy of forming the same link in absence of a FSSE (i.e. in the random reaction), and $F(i_1, i_2)$ is some function, on the form of which thermodynamics exercises a specific restriction

now to be deduced. Firstly, it is noted that

$$F(0, 0) = 0 \quad (3.6)$$

This means there is no substitution effect in reaction between unsubstituted species (formation of dimer from two monomers).

Secondly, for symmetric links (e.g. ether links from two hydroxyls) we have

$$F(i_1, i_2) = F(i_2, i_1) \quad (3.7)$$

Extension of the argument to reactions of pairs of dissimilar functionalities to form unsymmetrical links (e.g. esterification) is trivial. Finally, consider two methods of synthesising the species (fig. 3.1) from its $(i_1 + i_2 + 2)$ monomer units by (a) forming the link between A and B first and then attaching successively i_1 units to A and i_2 units to B, and (b) forming first the attachments of i_1 units to A, and i_2 units to B and then making the A-B link as the last step.

The total ΔG° and total $\Delta G^{\circ'}$ must be identical for both syntheses: Thus

$$\begin{aligned} F(0,0) + \sum_{k=1}^{i_1} F(0,k) + \sum_{k=1}^{i_2} F(k,0) \\ = \sum_{k=1}^{i_1-1} F(0,k) + \sum_{k=1}^{i_2-1} F(k,0) + F(i_1, i_2) \end{aligned} \quad (3.8)$$

Using (3.5) and (3.6) this reduces to

$$F(i_1, i_2) = F(i_1, 0) + F(i_2, 0) \quad (3.9)$$

which may be written

$$F(i_1, i_2) = \gamma(i_1) + \gamma(i_2) \quad (3.10)$$

with

$$\gamma(0) = 0 \quad (3.11)$$

Thus eq. (3.5) reduces to

$$\Delta G^\circ = \Delta G^{\circ*} + \gamma(i_1) + \gamma(i_2) \quad (3.12)$$

That there are no further thermodynamic restrictions of $F(i_1, i_2)$ beside (3.10) follows because in terms of (3.10) the FSSE contribution to the standard free energy of forming any species from its constituent monomer units is given, irrespective of the order in which the required links are made, by summing the contributions attributable to the individual units: for a unit bearing i links in any species ($2 \leq i \leq f$), this contribution is $\sum_{m=1}^{i-1} \gamma(m)$. Matula, Groenweghe and Van Wazer (1964) state that for FSSE (their case $\rho = 2$) the heats of formation are formed additively from the units; but the above argument clearly applies more generally to the free energies and to all extensive property changes of formation.

By passing from the standard free energy to the equilibrium constant, the ratio $\phi(i)$ of the concentrations of units with i links in the FSSE system to that in the random system (when both are in equilibrium) is seen to be

$$\phi(i) = \exp - \sum_{m=1}^{i-1} \gamma(m)/RT \quad (2 \leq i \leq f) \quad (3.13)$$

Thus $f-1$ constants $\phi(i)$ govern the whole of the FSSE on any equilibrium state arising for a given overall concentration of functionalities. If we define

$$\phi(0) = \phi(1) = 1 \quad (3.14)$$

the FSSE is allowed for in $F_0(\theta)$ thus:

$$F_0(\theta) = N_0 \sum_{i=0}^f f C_i \gamma^i (1-\gamma)^k \phi(i) \theta^i \quad (3.15)$$

with

$$i + k = f \quad (3.16)$$

N_0 is the normalizer and γ a conversion parameter (see section (2.2)) measuring the degree of advancement of the condensation reaction at equilibrium. The corresponding lpgf for the random reaction is (cf. eq. (2.5))

$$F_0^*(\theta) = \sum_{i=0}^f f C_i (\gamma^*)^i (1-\gamma^*)^k \theta^i = (1 - \gamma^* + \gamma^* \theta)^f \quad (3.17)$$

Equation (3.15) will be generalized below (eq. (4.3)) to cover the presence of intra-molecular reactions. Here it is emphasized that nothing is changed in the derivation of the $(f-1)$ substitution parameters of eq. (3.13) if the system contains cyclic species owing to intra-molecular condensation steps.

The linear FSSE is given by

$$\gamma(i) = Ki \quad (3.18)$$

and serves as the first approximation to the general FSSE and is found in section (6.2) to fit the equilibrium system $\text{POCl}_3/\text{P}_2\text{O}_5$.

From eq. (3.13)

$$\phi(i) = \exp - \frac{Ki(i-1)}{2RT} \quad (3.19)$$

Using the abbreviation

$$N = \exp - K/2RT \quad (3.20)$$

eq. (3.19) becomes

$$\phi(i) = N^{i(i-1)} \quad (3.21)$$

Substituting this in eq. (3.15) leads to

$$F_0(\theta) = N_0 \sum_{i=0}^f f C_i \gamma^i (1-\gamma)^k N^{i(i-1)} \theta^i \quad (3.22)$$

The equilibrium constant K^* for the random bond-forming reaction between two units A and B bearing already i_1 and i_2 links respectively (fig. (3.1)) acquires a factor $N^{2(i_1+i_2)}$ in presence of the FSSE to yield the new equilibrium constant:

$$K = K^* N^{2(i_1+i_2)} \quad (3.23)$$

This follows by considering the changes in the equilibrium concentrations of the reactants and products when changing the values of the appropriate coefficients in eq. (3.22) from unity (random case) to N (for the FSSE), and noting that

$$\frac{N^{(i_1+1)i_1} N^{(i_2+1)i_2}}{N^{(i_1-1)i_1} N^{(i_2-1)i_2}} = N^{2(i_1+i_2)} \quad (3.24)$$

The linear FSSE treatment is analogous to the theory by Bjerrum (1957) for polyvalent inorganic complexes, where the place of the parameter N

is taken by the reciprocal of the "spreading coefficient" x .

If the FSSE factor $N^{2(l_1 + l_2)}$ in the equilibrium constant is to be divided equally between the forward and backward rate constants k^* and $k^{*'} respectively we have simply$

$$k = k^* N^{l_1 + l_2} \quad (3.25)$$

$$k' = k^{*'} N^{-l_1 - l_2} \quad (3.26)$$

This principle remains essentially unchanged in presence of a cyclization component to the polycondensation reaction; it is used in section (4.7).

3.4 Statistical Parameters of Equilibrium Systems with FSSE

The $\lg f$ for systems with FSSE (eq. (3.15)) has been derived in terms of the parameter γ , this is used to generate different degrees of conversion α according to equation (2.9):

$$\begin{aligned} \alpha &= F_0'(1)/f \\ &= N_0 \left(\sum_{i=0}^{\infty} f C_i \gamma^i (1-\gamma)^K \phi(i) i \right) / f \end{aligned} \quad (3.27)$$

In principle, γ can be eliminated from all formulae in favour of α using eq. (3.27); in practice it is convenient to calculate all other statistical parameters in terms of γ and then plot these against α , calculated from eq. (3.27).

The gel point condition (see eq. (2.25))

$$F_1'(1) = 1 \quad (3.28)$$

becomes, in terms of γ , using eq. (3.15), (3.1)

$$\sum_{i=0}^f f C_i \gamma_c^i (1 - \gamma_c)^k \phi(i) i(i-1) = \sum_{i=0}^f f C_i \gamma_c^i (1 - \gamma_c)^k \phi(i) i \quad (3.29)$$

and for a linear FSSE (eq. (3.22))

$$\begin{aligned} \sum_{i=0}^f f C_i \gamma_c^i (1 - \gamma_c)^k N^{i(i-1)} i(i-1) \\ = \sum_{i=0}^f f C_i \gamma_c^i (1 - \gamma_c)^k N^{i(i-1)} i \end{aligned} \quad (3.30)$$

Equation (3.30) has been solved for various values of f and N and the results are plotted as graphs of α_c against N in figure (3.2). This figure (3.2) illustrates that gelation is delayed from the random value (eq. (2.31)) in a f -functional polycondensation if the value of the linear FSSE parameter N is less than unity (its random value). This case ($N < 1$) corresponds with an equilibrium in which branched molecules are relatively less favoured than unbranched molecules and hence the overall conversion in this equilibrium mixture must be larger than that of a random equilibrium mixture for gelation to occur. It can be seen (fig. (3.2)) that for a f -functional monomer a gel point at $\alpha_c = 0.30$ corresponds to a value of $N = 1.1$ (the random value $N = 1.0$ corresponds to $\alpha_c = \frac{1}{3}$). Substituting this value into eq. (3.20) gives the equilibrium constant K a value of -115 cal./mole at 300°K , and eq. (3.18), (3.12) show that this corresponds to a decrease of 115 cal./mole in the free energy of the reaction between a monomer and a unit with one link in comparison with the free energy of a random reaction between

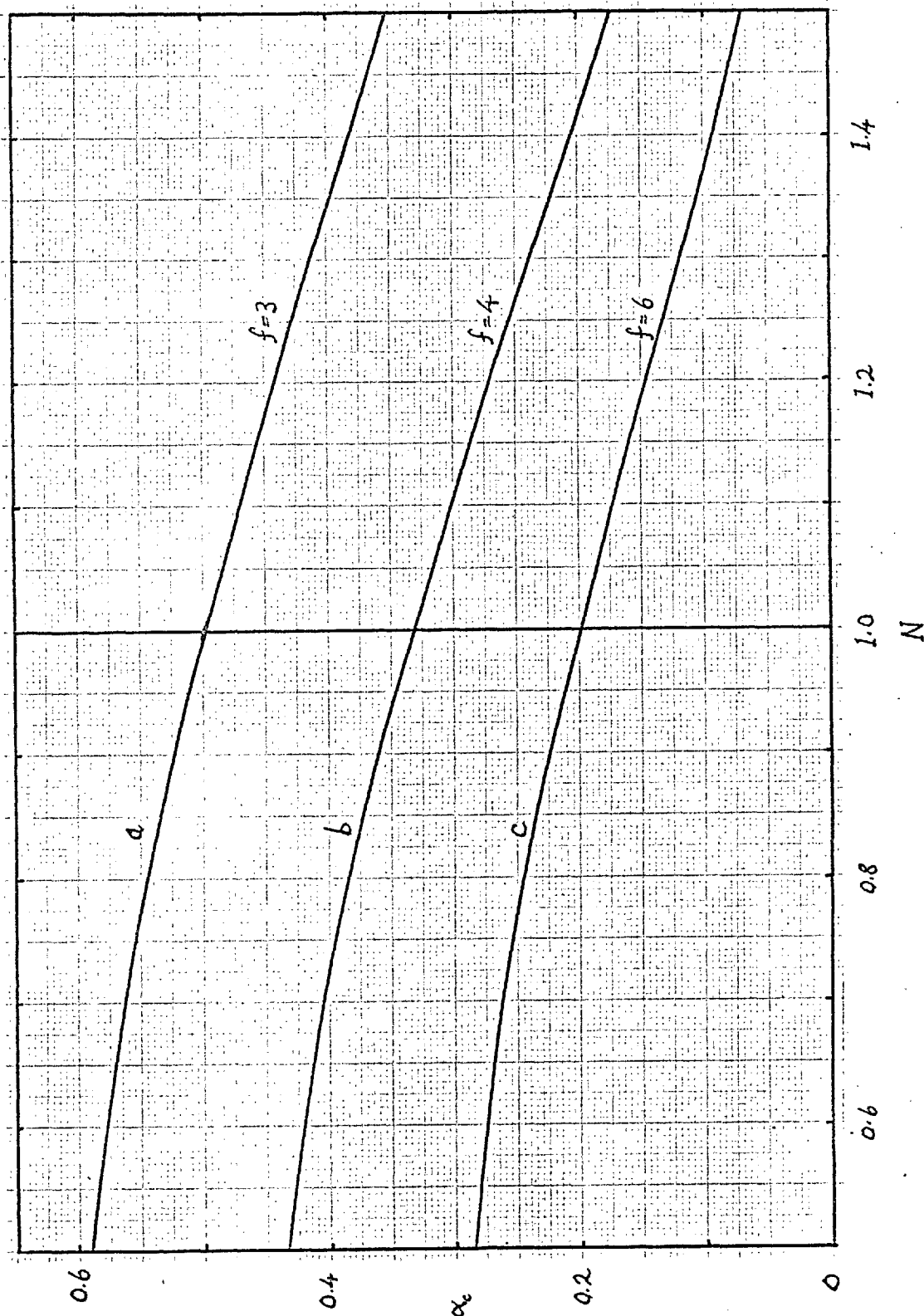


Fig. 3.2 α_c against N for thermodynamically controlled linear substitution effect.

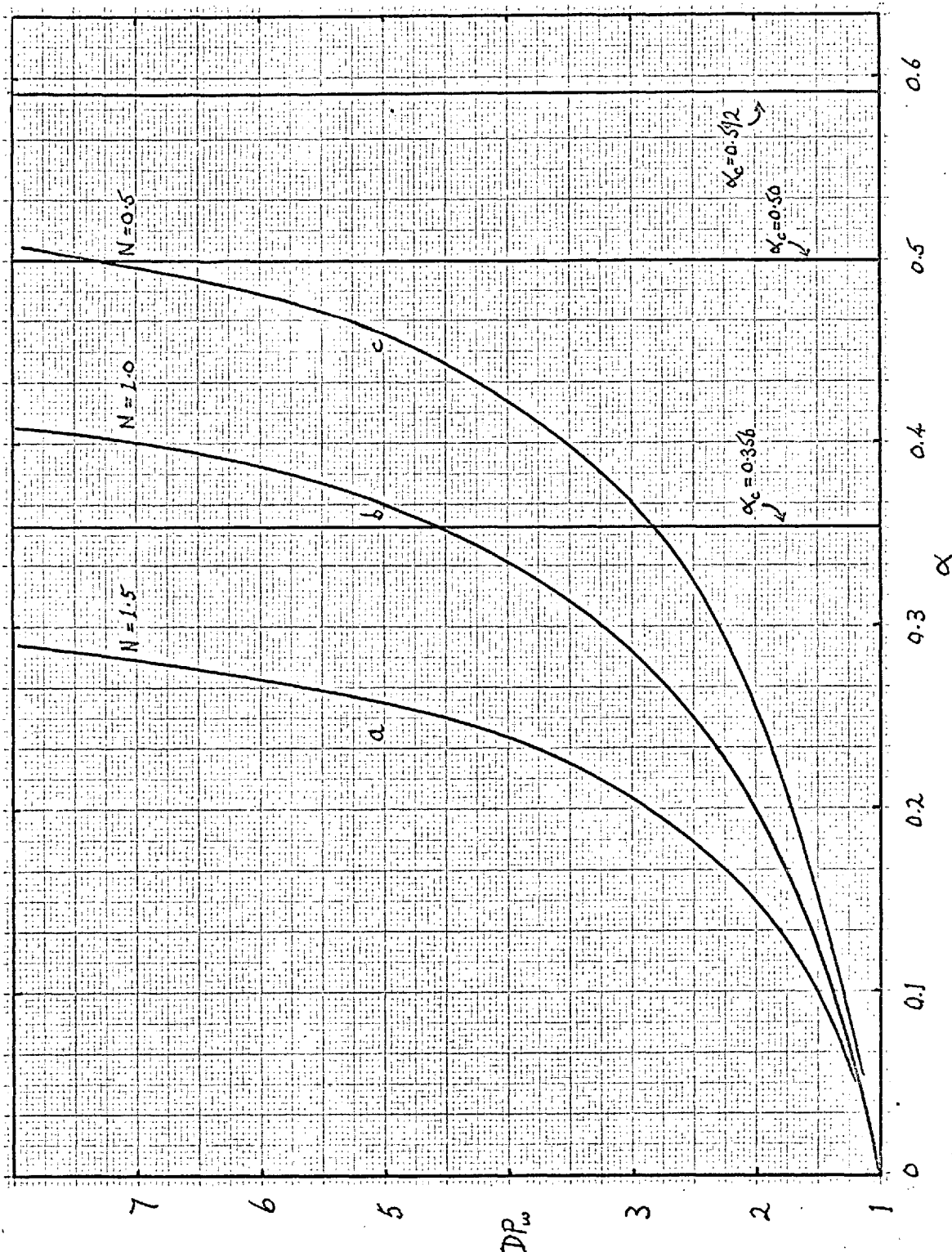


Fig. 3.3 DP_w against α for thermodynamically controlled linear substitution effect; $f = 3$.

these two molecules. It is apparent that a relatively small (in the order of a few hundred cal./mole) non-random free energy contribution can make a large deviation to the gelation of polycondensing systems. Fig. (3.2) can, of course, be used to compute the value of α_c knowing the value of N and this value can then be checked experimentally.

Similarly the DP_w of f -functional systems containing a FSSE can be calculated using eq. (2.29), (3.15). Figure (3.3) shows such a calculation for a tri-functional system, the DP is plotted against α for values of $N = 0.5, 1.0$ (random), and 1.5 .

3.5 Statistics of the Kinetically Controlled Linear FSSE

In the kinetically controlled linear substitution effect, a term (cf. eq. (3.12), (3.18), (3.25))

$$\Delta G^\ddagger = K(i_1 + i_2)/2 \quad (3.31)$$

is added to the free energy of activation of forming a bond between units with i_1 and i_2 links respectively, in addition to the free energy of activation for the random reaction. The corresponding rate constant is then

$$k = k^* \exp(-K/2RT) = k^* N^i \quad (3.32)$$

with

$$i_1 + i_2 = i \quad (3.33)$$

and where k^* is the rate constant for the random reaction, and N is defined as $\exp(-K/2RT)$, (eq. (3.20)).

To calculate $F_i(\theta)$, it is simpler to operate with the probabilities P_i of eq. (2.6) than with $\phi(i)$ of form (3.15). In place of γ , P_i is

then the convenient parameter for generating different degrees of conversion, etc. From the law of mass action, the kinetic second order rate equations take the form:

$$-dP_i/dt = k^* [N^i (f-i)P_i - N^{i-1} (f-i+1) P_{i-1}] \times \sum_{i=0}^f N^i (f-i)P_i \quad (3.34)$$

where $0 \leq i \leq f$ and $P_{-1} = 0$.

Eliminating the time,

$$dP_i/dP_0 = N^{i-1} [N(f-i)P_i - (f-i+1)P_{i-1}] / P_0 f \quad (3.35)$$

The solution which is obtained by the use of the Laplace transform is outlined in section (3.6), reads (eq. (3.53)):

$$P_i = \frac{N^{i(i-1)/2} f!}{(f-i)!} \sum_{j=0}^i \frac{P_0 N^{j(f-j)/f}}{\prod_{m=0}^{j-1} [(f-m)N^m - (f-j)N^j]} \quad (3.36)$$

where the prime in $\prod$ denotes omission of the zero term arising from $m = j$. The solution is not valid at the singular points

$$N = [(f-j)/(f-m)]^{j-m} \quad (3.37)$$

Care is required in computation because there are $f(f-1)/2$ such terms. Eq. (3.37) checks against the normalization condition $\sum P_i = 1$.

We have the following relations from eq. (2.6), (3.1):

$$F_0(\theta) = \sum_{i=0}^f P_i \theta^i \quad (3.38)$$

$$F_1(\theta) = \sum_{i=0}^f i P_i \theta^i / \sum_{i=0}^f i P_i \quad (3.39)$$

$$F_1'(1) = \sum_{i=0}^f i(i-1)P_i / \sum_{i=0}^f i P_i \quad (3.40)$$

The gel point condition (eq. (3.28)) is then found by equating the r.h.s. of eq. (3.40) to unity. The evaluation of the P_i according to eq. (3.36) was performed on a computer for appropriate values of f and N , as was the processing of the $F_s(\theta)$ thus determined (eq. (3.38)) to yield the statistical parameters as described in Chapter 2. The critical values at the gel point are presented in terms of plots of α_c against $N^{1/2}$ in figure (3.4), together with a DP_w plot (fig. (3.5)) for a trifunctional condensation, in a form suitable for comparison with the thermodynamically controlled case (fig. (3.2), (3.3)). The substitution effect on the free energy is postulated (eq. (3.25), (3.26)) to be equally split between the activation energies of the forward and backward reactions. A value of $N^{1/2}$ in a kinetically controlled reaction is therefore best compared with a value of N under equilibrium conditions.

3.6 Laplace Transform Solution of the Kinetic Rate Equation (3.35)

The kinetic second order rate equations for a system that has a kinetically controlled linear FSSE are summarized (eq. (3.35)):

$$dP_i/dP_0 = N^{i-1} [N(f-i)P_i - (f-i+1)P_{i-1}] / P_0 f \quad (3.41)$$

Let

$$\log P_0 = s \quad ; \quad P_0 = \exp - s \quad (3.42)$$

Then eq. (3.41) becomes

$$-dP_i/ds = N^{i-1} [N(f-i)P_i - (f-i+1)P_{i-1}] / f \quad (3.43)$$

Defining the Laplace Transform of $P_i(s)$ by

$$q_i(z) = \int_0^\infty \exp(-zs)P_i(s) ds \quad (3.44)$$

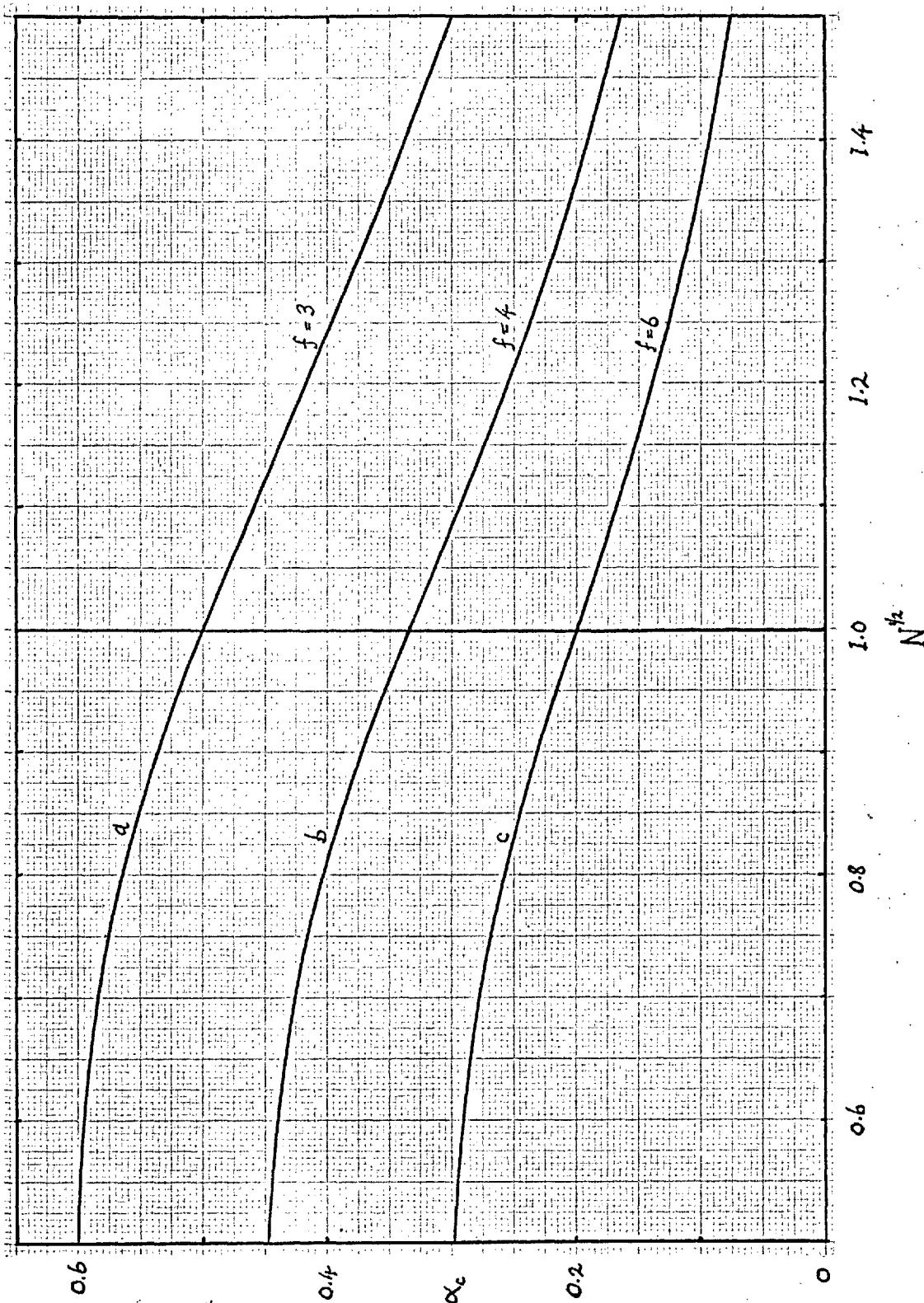


Fig. 3.4 α_c against $N^{1/2}$ for kinetically controlled linear substitution effect.

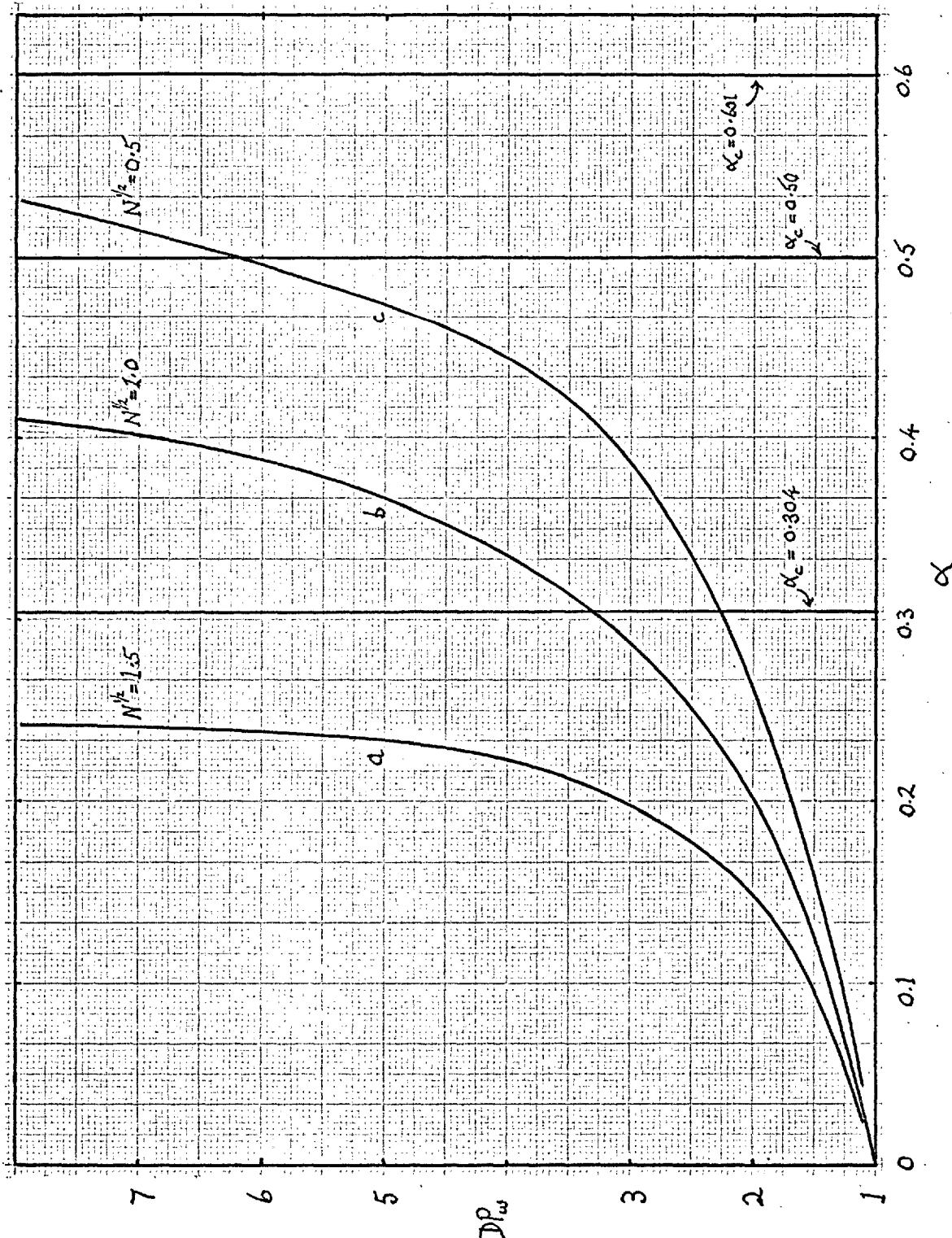


Fig. 3.5 DP_w against α for kinetically controlled linear substitution effect; $f = 3$.

eq. (3.43) can be written

$$z q_i(z) = N^{i-1} [(f - i + 1) q_{i-1}(z) - N(f - i) q_i(z)] / f \quad (3.45)$$

since $P_{i(i \neq 0)} = 0$ at $s = 0$. The difference equation (3.45) may be rearranged to give

$$[z + (f - i)N/f] q_i(z) = N^{i-1} (f - i + 1) q_{i-1}(z) / f \quad (3.46)$$

From eq. (3.45) one obtains by successive iterations

$$q_i(z) = \frac{N^{i(i-1)/2}}{f^i} \left\{ \frac{(f - i + 1)}{[z + (f - i)N/f]} x \right. \\ \left. \frac{(f - i + 2)}{[z + (f - i + 1)N^{i-1}/f]} x \dots x \right. \\ \left. \frac{f}{[z + (f - 1)N/f]} x \frac{1}{z + 1} \right\} \quad (3.47)$$

or

$$q_i(z) = \frac{N^{i(i-1)/2}}{f^i (f - i)!} \prod_{j=0}^i [z + N^j (f - j)/f]^{-1} \quad (3.48)$$

since we know that

$$q_0(z) = (z + 1)^{-1} \quad (3.49)$$

the product term in eq. (3.48) can be decomposed into partial fractions:

$$\prod_{j=0}^i [z + N^j (f - j)/f]^{-1} = \sum_{j=0}^i A_j [z + N^j (f - j)/f]^{-1} \quad (3.50)$$

where

$$1/A_j = \prod_{m=0}^i [N^m (f - m)/f - N^j (f - j)/f] \quad (3.51)$$

(the prime in π' denotes omission of the zero term arising from $m = j$). By virtue of eq. (3.50) and eq. (3.51), it follows that the inverse transform of eq. (3.48) can be written in the form

$$P_i = \frac{N^{i(i-1)/2} f!}{f^i (f-i)!} \sum_{j=0}^i \frac{\exp(-sN^j(f-j)/f)}{\pi'_{m=0} [N^m(f-m)/f - N^j(f-j)/f]} \quad (3.52)$$

or using eq. (3.42):

$$P_i = \frac{N^{i(i-1)/2} f!}{(f-i)!} \sum_{j=0}^i \frac{P_j N^j(f-j)/f}{\pi'_{m=0} [N^m(f-m) - N^j(f-j)]} \quad (3.53)$$

which is the required result.

CHAPTER 4

INTRAMOLECULAR CONDENSATION

4.1 Introduction

Early theories of the distribution of molecular species in condensation polymers (Flory 1953) were severely limited by failure to account for cyclic structures formed by intramolecular reactions. The first step towards inclusion of these non-random reactions into a kinetic scheme was taken by Jacobson and Stockmayer (1950), who considered the theory of linear systems at equilibrium. Their approach to the evaluation of the probability of ring closure was to assume a Gaussian distribution of end-to-end distances. A similar treatment of equilibrium bifunctional cyclic distributions has recently been published by Carmichael and Kinsinger (1964) in which the probability of ring closure was calculated from a detailed structural model for the chain, with fixed bond lengths, fixed bond angles, and fixed rotational states; ring closure being assumed to occur when the end-to-end distance is less than one bond length.

These theories have been tested (Carmichael and Winger 1965) against experimentally observed cyclic distributions in dimethylsiloxanes. It is concluded that both models qualitatively predict the distribution of cyclic species in this system, but neither account quantitatively for the experimental results.

The ring-chain equilibrium in polydecamethylene adipate has been

studied by Beckmann, Jacobson and Stockmayer (1950) and the results they obtain are in good agreement with the equilibrium theory of Jacobson and Stockmayer (1950). The chief advantage of the Jacobson-Stockmayer formulation is that the ring-chain equilibrium constant is predicted as a function of ring size. In the discrete state model of Carmichael and Kinsinger (1964) the ring closure probability must be evaluated for each cyclic species. This model also arbitrarily assumes that ring closure occurs when the end-to-end distance is less than one bond length. Furthermore, an additional parameter, the volume occupied by a chain atom, must be calculated and this adds much uncertainty to the method.

In polyfunctional polycondensation ($f > 2$) the combinatorial problem of evaluating the probability of ring closure presents much greater difficulty. Harris (1955) tackled the problem of f -functional polycondensation assuming that spatial restrictions allow a chain end to be available for ring closure only to ends within a fixed distance. However his equations do not reduce to those of Jacobson and Stockmayer (1950) or Carmichael and Kinsinger (1964) when f is set to 2. Flory's method for the calculation of the extent of reaction at gelation of polymer systems is extended by Kilb (1958) in an approximate manner to include ring formation. All these models predict that the gel point is dependent upon the dilution of the system, so that at higher dilutions gelation occurs at higher extents of reaction. This concentration dependence of the gel point was first predicted by Stockmayer (1945) for systems which can undergo intra-

molecular condensation. To investigate this prediction Stockmayer (1945) measured the gel points for the pentaerythritol/adipic acid system in the presence of various quantities of an inert solvent. Since ring-formation should be more prevalent at higher dilutions because of its lower kinetic order compared with intermolecular condensation (see section (4.7)), he extrapolated the results to a fictitious infinite concentration (zero volume) to eliminate the effect of rings and afford a valid comparison with the random value. The result of this extrapolation was in excellent agreement with the predicted random value. This extrapolation technique is used in chapter 7 to explore the behaviour of this polyester system more fully.

The theory of branching processes provides the proper framework for the combinatorial problems that arise in considering ring closure. The model with FSSE (chapter 3) is now developed to include cyclization and later specialized to include a detailed regime of cyclization. The extension of the scheme to system with cyclization and at most FSSE is discussed in detail from a thermodynamic approach, the extension to kinetically controlled systems (section (4.9)) follows similar lines.

The statistical thermodynamic approach, though expressed in terms of the balance of forward and backward reaction rather than partition functions, remains basically the same as Jacobson and Stockmayer's (1950) treatment for bifunctional systems, to which it exactly degenerates for $f = 2$ (see section (4.7)). But while their

solution depended on feeding into the system of equations known statistical results concerning the molecular weight distribution (ibid. p.1604, eq. (11)), we feed in the much simpler link probability distribution. Convenience generally favours the calculation of statistical averages via the lpd rather than via the molecular weight distribution (Gordon 1962); in presence of the approximations necessary when treating cyclization, the advantage of the lpd is decisive. Thus excellent estimates of averages can be obtained while the weight fractions of individual species cannot be calculated reliably except possibly for the simplest structures such as the dimeric pyrophosphoryl dichloride (see section (6.3)).

The nature of the problem when the lpd is used stands out clearly. The treatment of branching processes by generating functions (F_0 , F_1 , etc.) referring to successive generations discounts any correlation effects between non-adjacent generations such as are clearly involved in the formation of rings, between pairs of functionalities belonging to units on non-adjacent generations. (Similar correlation difficulties would arise with systems involving a second shell or higher substitution effect.) However, most of the statistical average parameters which can be measured are independent of the nature of these long-range correlations because they can be calculated from the lpgf of the members of the zeroth generation alone without involving the other generations. (This is true of the parameters α , σ , DP_n , v_0 , v_1 , v_2 , v_3 defined later). Other parameters like the gel point, or more generally DP_w , are affected by long-range

correlations; the treatment then becomes approximate, but it is always asymptotically correct as the degree of cyclization goes to zero. The experimental gel point in the equilibrium system $\text{POCl}_3/\text{P}_2\text{O}_5$ is found (section (6.3)) to be in good accord with the approximate theory, which is expected to be serviceable quite generally.

4.2 Derivation of link probability generating function

In presence of ring-formation, there now occurs a fraction of the functionalities which have become engaged pairwise in ring-forming links; and

$$\omega + \alpha + \sigma = 1 \quad (4.1)$$

The symbols ω , α , and σ will be used as subscripts to indicate whether various quantities refer to free functionalities, those involved in cross-links, or ring-forming links, respectively. In a ring involving x (repeat) units, there is exactly one σ -type link formed intramolecularly and $(x - 1)$ α -type links formed intermolecularly. Once the ring is formed, the distinction is somewhat artificial because the σ -type link bears no special label; the artifice is used because it simplifies the theory.

The ensemble M is now constructed precisely as before by using each unit as the root of one graph. To convert all these graphs to trees (free from rings), the additional step is taken to split mentally all the ring forming (σ -type) links, as is shown in fig. (4.1b) and (4.1c). For graphs with more than one ring, this reduction to tree-form cannot be unambiguously reversed; it is

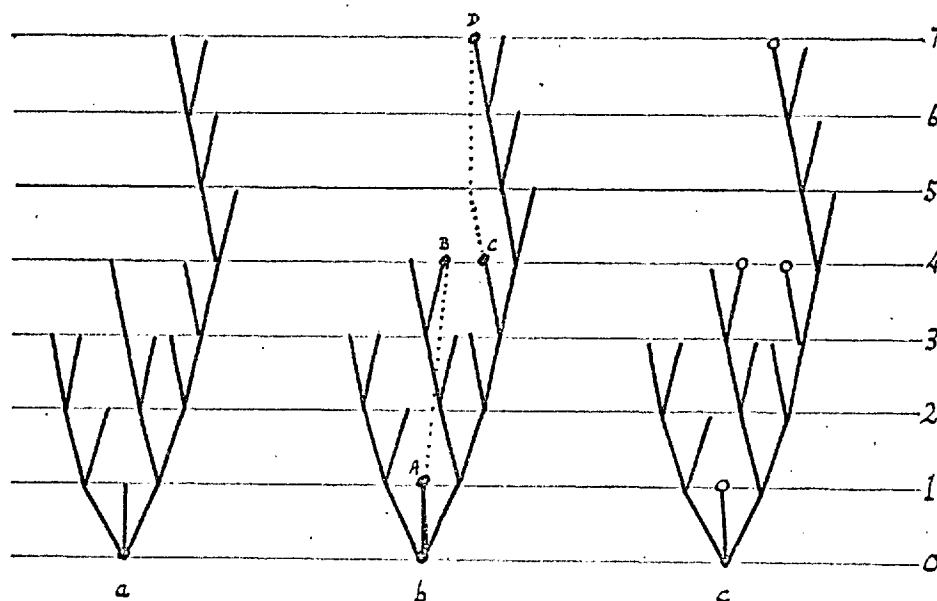


Fig. 4.1 Typical molecular tree from trifunctional monomer with conventional numbering of generations on the right. (a) absence of rings; (b) ring-closing links formally stretched, shown in dotted lines A-B and C-D; (c) ring-closing links formally split: ring-closing functionalities shown as circles

not deducible from fig. (4.1c) how the four σ -type functionalities were paired in the original molecule in fig. (4.1b) (actually AB, CD; but it might have been AC, BD, etc.). This ambiguity is of no consequence to the theory.

All statistical parameters for the molecular system are again calculated in terms of the lpgf; this is now written in more general terms, using three dummy variables θ_w , θ_α , θ_σ , so that the coefficient of $\theta_\alpha^i \theta_\sigma^j \theta_w^k$ is the chance of finding i cross-linked,

j ring-closing, and k free functionalities on a randomly chosen unit; and

$$i + j + k = f \quad (4.2)$$

In the vector notation, $\theta = (\theta_x, \theta_r, \theta_w)$ and $\theta = \mathbf{1}$ means

$\theta_x = \theta_r = \theta_w = 1$. For f-functional polycondensation systems in equilibrium, ignoring minor correlation effects (discussed in section 4.3) which arise from a small fraction of the fused-ring systems present, the lpgf can be written down exactly:

$$F_o(\theta) = N_o \sum_{i=0}^f \sum_{j=0}^{f-1} \frac{f!}{i!j!k!} \gamma^i (i\tau)^j (1-\gamma)^k \rho(i+j) \theta_x^i \theta_r^j \theta_w^k \quad (4.3)$$

with the normalizer

$$N_o = 1 / \sum_{i=0}^f \sum_{j=0}^{f-1} \frac{f!}{i!j!k!} \gamma^i (i\tau)^j (1-\gamma)^k \rho(i+j) \quad (4.4)$$

To remove an indeterminacy one defines

$$(i\tau)^j = 1, \quad \text{when } i = j = 0 \quad (4.5)$$

By factorising out the combinatory term $f!/i!j!k!$, one may restrict the proof of (4.3) to showing that the chance of finding that i specified functionalities of a unit belong to cross-links, j specified functionalities to ring-closing links and that k specified functionalities are free, is correctly given by $N_o \gamma^i (i\tau)^j (1-\gamma)^k \rho(i+j)$ when the parameters γ , τ , $\rho(i+j)$ and N_o are properly defined. Now N_o is merely the normalizer. The

probabilities for the occurrence of units without ring-closing links ($j = 0$) are correctly given by eq. (4.3) by definition of the substitution parameters $\phi(i)$. In particular, since $\phi(0) = \phi(1) = 0$, γ is just the conditional probability that a specified functionality belongs to a cross-link, given that the other $(f - 1)$ functionalities on the same unit are known to be free. Next τ is defined so that the coefficient of $\theta_\alpha \theta_\sigma \theta_\omega^{f-2}$ is correct. The conditional probability of finding a specified functionality to belong to a ring-forming link, given that one other specified functionality on the same unit is known to belong to a cross-link, while the other $(f - 2)$ are free, then turns out to be $\tau\phi(2)/[(\gamma + \tau)\phi(2) + 1 - \gamma]$. The parameter τ thus generally increases with the degree of cyclization. It remains to show that eq. (4.3) gives correctly the ratios of probabilities p_r/p_w of a specified functionality being ring-closing or free for arbitrary states of the other $f - 1$ functionalities on the same unit. Eq. (4.3) gives

$$p_r/p_w = \frac{\tau}{1 - \gamma} \frac{\phi(i + j)}{\phi(i + j - 1)} \quad i \quad (4.6)$$

The constant factor $\tau/(1 - \gamma)$ on the right is trivial as long as eq. (4.3) refers to a normalized distribution. The factor $\phi(i + j)/\phi(i + j - 1)$ reflects correctly the assumption that a ring-closing link exerts the same substitution effect as a cross-link. The absence of further dependence of p_r/p_w on j reflects the neglect of correlations which are normally quite small and unknown even as regards the direction in which they operate. This neglect is further

discussed in section (4.3).

The remaining factor i expresses exactly the remaining dependence of p_c/p_u on i . Certainly this factor is correct when $i = 0$, because there is no chance of a ring-closure on a unit free from cross-links; at least one cross-link is required for the cyclic path to return to the unit. More generally, the factor i is correct, because the cyclic path closed by the ring-closure

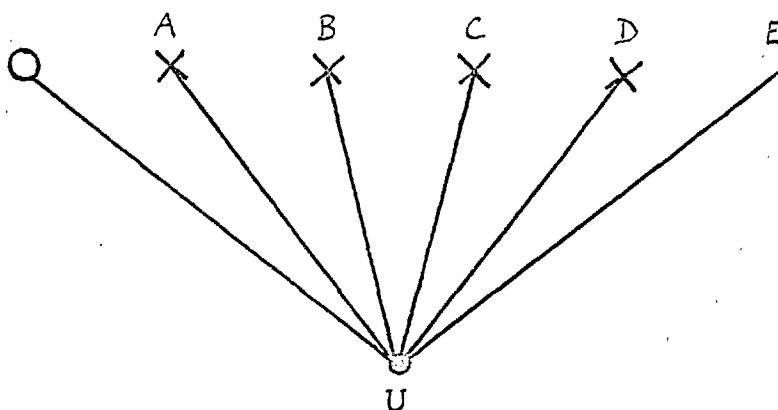


Fig. 4.2 Schematic view of a hexafunctional unit U on generation zero. The circle denotes a ring-closing functionality (cf. fig. (4.1c)), the crosses denote cross-links to units A , B , C , D on generation one, and E is a free functionality. The ring closure (whose formal splitting produced the ring-closing functionality shown) goes with equal probabilities to one of the sub-trees (not shown) rooted on A , B , C , or D .

returns to the same unit with equal chances along any cross-link

connecting the unit U to children A, B ... (fig. 4.2) in the first generation. The equality of these chances follows because under the regime of the FSSE no correlation exists between the distribution of the total progeny of a given child (say A) and the number of brothers (B, C, D, ...) which it happens to have. Two brothers (say A and B) are separated by two links (AU and UB). Accordingly, it would require at least a second shell substitution effect to generate correlation effects between their progeny which could invalidate the factor i in (4.6).

4.3 Neglect of minor correlations

The absence of any function of j on the right of (4.6) (beside the substitution parameters $\phi(i, j)$) implies that the relative chances p_r and p_f of a given functionality being ring-closing or free are independent (apart from the FSSE) of the number of ring-closures already borne by the unit. In the ensemble M derived from the actual molecular system there would, however, occasionally be correlations which are thus neglected. These correlations affect only such units as bear at least two ring-closing links whose two cyclic paths lead back to the same unit via the same cross-link. This situation arises only in fused ring structures, and then generally only rarely, namely when the ring-closing links of two or more fused rings occur on the same unit.

As an example consider the carbon skeleton of naphthalene with the carbon atoms as units. If the links between these C atoms are made in random sequence, only six out of thirty-five molecules

synthesised would have one C atom (out of ten) which bears two ring-closing links. Thus the neglected correlations would affect only one kind of member of the zeroth generation, whose proportion in the absence of the neglected correlation is 6/350.

The nature of these correlations would depend on the detailed regime governing the thermodynamics of forming fused rings of various sizes. The correlations would be dominated by configurational effects. The opportunities for a second ring-closure involving a given unit could increase or decrease owing to the change in configuration imposed on the molecule by a pre-existing ring closure on the same unit.

We conclude from this discussion that even in systems containing a fair proportion of fused-ring structures, the lpgf (eq. (4.3)) should be an excellent approximation to the truth. Without further approximation, $F_1(\theta)$ is found from eq. (4.3) (using eq. (3.1)):

$$F_1(\theta) = N_1 \sum_{i=1}^f \sum_{j=0}^{f-1} \frac{f!}{(i-1)!j!k!} \gamma^i (i\tau)^j (1-\gamma)^k \rho(1+j) \theta_x^{i-1} \theta_\tau^j \theta_\omega^k \quad (4.7)$$

Here the normalizer is given by

$$N_1 = 1 / \sum_{i=1}^f \sum_{j=0}^{f-1} \frac{f!}{(i-1)!j!k!} \gamma^i (i\tau)^j (1-\gamma)^k \rho(1+j) \quad (4.8)$$

Statistical parameters of interest in the application to $\text{POCl}_3/\text{P}_2\text{O}_5$ (see section (6.2)) can, for the most part, be obtained from F_0 and F_1 alone, and thus are found again without further approximation.

But the gel point, and more generally DP_w , used in the study of polyesterification (chapters 7, 8), require knowledge of the lpgf of all higher generations ($F_2(0)$, $F_3(0)$ etc.). To this end we introduce one approximation,

$$F_1(0) = F_x(0) \quad (x = 2, 3, 4 \dots) \quad (4.9)$$

This has been shown to be exactly true for systems with at most FSSE (section 3.2) and thus is exactly true for systems with cyclization in the limit $\tau \rightarrow 0$, i.e. as cyclization is eliminated eq. (4.3) then returns to eq. (3.15).

4.4 Summary of the proposed model

The model adopted for f-functional polycondensation with FSSE and cyclization is contained completely in eq. (4.3), (4.7) and (4.9). This model is specialised below in two respects: the detailed regime of cyclization, not so far specified, is particularized to the random-flight scheme first derived by Kuhn (1934), and the FSSE is specialized to the linear case (of eq. (3.18)). All the approximations used arise from neglect of correlations, already partly expounded above, and further discussed in section (4.5). As a result of this neglect, the model works with an ensemble G (defined by eq. (4.3), (4.7) and (4.9)) which is not exactly the same as the true molecular ensemble M of trees. It is emphasised that there is no further need for mathematical approximations in calculating statistical parameters of the model ensemble G, and that the differences between G and M disappear asymptotically when the degree of cyclization σ goes to zero. This asymptotic behaviour can be explored experimentally by using the extrapolation procedure to infinite concentration first applied for

the special case of gel points by Stockmayer (1945) (see section 4.1). The statistical parameters of G are derived by standard methods in section (4.5) and introduced in section (4.7) into the rate equations which are thereby solved. Before this, the differences between the ensembles G and M are further clarified in section (4.5). These differences may be considered as being of two types: approximations arising in the assumption that $\mathbb{F}_g(0)$ is independent of g ($g \geq 1$) (eq. (4.9)) due to the neglect of knowledge about the forbears of a given unit; and general correlations arising from ring-closing links on a given tree.

4.5 Neglect of other correlations

A unit X on generation x is known to have a line of x forbears linking it through its father on generation $(x - 1)$, its grand-father on $(x - 2)$, back to the zeroth generation (root) of its tree (cf. fig (4.1)). This knowledge is neglected by eq. (4.9) which assigns equal probability distributions to the fates of functionalities on units belonging to any generation except the zeroth. In reality the $(x - 1)$ functionalities on X which point upwards are more likely to be found engaged in ring-forming links, the larger the value of x . This is because the x forbears being known to exist, there are increased probabilities of finding rings to exist which include some or all of these x units. This increasing chance for finding σ -type links, and more generally the coefficients of $\mathbb{F}_x(0)$, in any case, converge for large x . This is because the rate of forming a ring of size x between a given pair of functionalities goes to zero

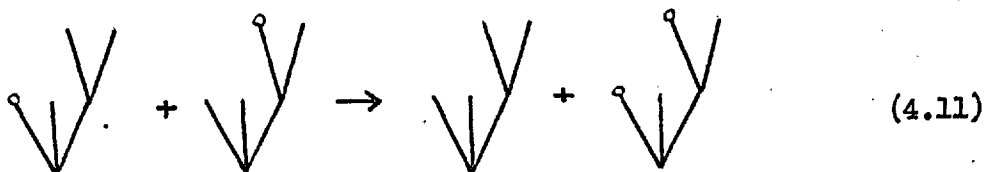
strongly as x increases; for the random-flight model, this rate is $O(x^{-3/2})$. Accordingly there is some x so large that rings of size $> x$ can be neglected altogether: to this approximation

$$\bar{F}_x(\theta) \approx \bar{F}_{x+1}(\theta) \approx \bar{F}_{x+2}(\theta) \dots \text{etc.} \quad (4.10)$$

In effect, our model approximates to the true gel point condition $(\partial \bar{F}_x(\theta)/\partial \theta_x)_{\theta=1} = 1$ by using $(\partial \bar{F}_1(\theta)/\partial \theta_x)_{\theta=1} = 1$ as in absence of cyclization (eq. (3.28)).

The purpose of the model is to give reliable estimates of statistical parameters (average quantities) for any f at the highest degrees of cyclization expected in practice, even in the presence of a reasonable amount of fused ring structures. The model is not designed to calculate weight fractions of individual species, because the neglect in the theory of branching processes of correlations, affecting pairs of distant generations, then becomes more serious. For instance, as each ring contains two ring-closing functionalities, each tree in the molecular ensemble M must contain an even number of such functionalities. However, the ensemble of trees G generated by the model (eq. (4.3), (4.7), (4.9)) contain a proportion which have an odd number of ring-closing functionalities. Such aesthetic faults do not seriously affect the statistical parameters, as shown by the following argument. The ensemble G could be corrected to correspond much more closely to the molecular ensemble M by a treatment which leaves all averages invariant but produces the desired correlations. Thus let a subtree be defined as a unit on generation $g > 1$, together with all its progeny. The

treatment consists in exchanging pairs of subtrees belonging to different trees but belonging to the same g . This process is illustrated in (4.11) for the complete removal of the simplest kinds of trees with an odd number of ring-closing functionalities (i.e. converting two 'ones' to a 'zero' and a 'two').



Clearly such processes of interchange cannot alter the mean size DP_w of the trees in G ; nor, therefore, the gel point. The process leaves invariant the $lpgf$, and none of the other statistical average quantities defined below in terms of the $lpgf$ are affected either. This exchange process is not proposed for practical use, nor, therefore, are detailed rules given for carrying it out. The argument is presented merely to give confidence in the calculation of average quantities from an ensemble which has such obvious faults. Moreover, the weight fractions of small species, such as the dimeric pyrophosphoryl dichloride (see section (6.3)), which are generated without appeal to long-range correlations between units on distant generations, may still be calculated from G with reasonable confidence, bearing in mind that G is exact in the limit of zero degree of cyclization.

4.6 Calculation of statistical parameters

The following standard manipulations extract the required statistical parameters from the system of equation (4.3), (4.7) and (4.9); these parameters will be fed into the system of rate equations in the next section and lead to their solution.

The fraction of functionalities engaged in cross-links is

$$\alpha = \left[\frac{\partial F_c(\theta)}{\partial \theta_\alpha} \right]_{\theta=1} / f \quad (4.12)$$

and the fraction engaged in ring-closing bonds is

$$\sigma = \left[\frac{\partial F_c(\theta)}{\partial \theta_\sigma} \right]_{\theta=1} / f \quad (4.13)$$

The mean number of cross-links leading from a unit on generation g to units on $g + 1$, when $g > 0$, is

$$a = \left[\frac{\partial F_1(\theta)}{\partial \theta_\alpha} \right]_{\theta=1} \quad (4.14)$$

The critical value at the gel point is given by

$$a_c = 1 \quad (4.15)$$

The mean number of free functionalities borne by a unit on any generation $g > 0$ is

$$n = \left[\frac{\partial F_1(\theta)}{\partial \theta_\omega} \right]_{\theta=1} \quad (4.16)$$

The mean number of cross-links borne by a unit known to have at least one free functionality is

$$A = \left[\frac{\partial^2 F_0(\theta)}{\partial \theta_\alpha \partial \theta_\omega} / \frac{\partial F_0(\theta)}{\partial \theta_\omega} \right]_{\theta=1} \quad (4.17)$$

Finally, if a free functionality is chosen at random from those borne by units of the zeroth generation, the mean total number of free functionalities borne by all units of the $(i - 1)$ th generation of the corresponding tree is

$$n_i = A a^{i-2} n \quad i = 2, 3, \dots \quad (4.18)$$

Clearly, within the approximation of the model used, n_i is the mean number of reaction partners available for a free functionality chosen at random in the molecular system to produce rings of the size which involves i units. It is postulated that $i \neq 1$, i.e. two functionalities borne by the same unit do not close a ring together. (In the system $\text{POCl}_3/\text{P}_2\text{O}_5$ examined in chapter 6, this postulate correctly forbids the formation of 2-membered rings, i.e. $P = 0$ double bonds). The model can readily be adapted to include the term $i = 1$ where appropriate.

Though the general case is no more difficult, it is often appropriate, e.g. in fitting the data on $\text{POCl}_3/\text{P}_2\text{O}_5$ in section (6.3), to specialize the treatment to the linear case of the FSSE. The argument which led from eq. (3.15) to (3.22) in absence of cyclization, equally transforms the more general equation (4.3), thus:

$$F_0(\theta) = N_0 \sum_{i=0}^f \sum_{j=0}^{f-1} \frac{f!}{i!j!k!} \gamma^i (1-\gamma)^j (1-\gamma)^k N^{(i+j)(i+j-1)} \theta_\alpha^i \theta_\sigma^j \theta_\omega^k \quad (4.19)$$

Similarly (4.7) reduces to

$$F_1(\theta) = N_1 \sum_{l=1}^f \sum_{j=0}^{f-1} \frac{f!}{(l-1)!j!k!} \gamma^l (1-\gamma)^j (1-\gamma)^k N^{(l+j)(l+j-1)} \theta_\alpha^{l-1} \theta_\sigma^j \theta_\omega^k \quad (4.20)$$

The statistical parameters defined by the equations for a linear FSSE ((4.19), (4.20), (4.12), (4.13), (4.14), (4.16), (4.17)) for the cases $f = 3, 4, 6$ are summarized in Appendix A in terms of γ and τ . Use of these equations will be made when treated the $\text{POCl}_3/\text{P}_2\text{O}_5$ system (chapter 6) and in evaluating the critical gel parameters for f -functional polycondensation equilibrium systems with cyclization and FSSE (section (4.7)).

4.7 Equilibrium Concentrations of Cross-Links and Ring-Closing Links, using Random-Flight Statistics

At equilibrium, rates of cross-link formation and breakage are equated; assuming cross-linking to be a second order reaction this yields

$$k_\alpha S_\alpha (1 - \alpha - \sigma)^2 C_0 = k^1 S_\alpha^1 \alpha + k^1 S_\alpha^1 \sum_{i=1}^{\infty} (i-1) \sigma_i \quad (4.21)$$

where C_0 is the initial concentration of functionalities. k_α and k^1 are the rate constants (in absence of FSSE) for cross-linking and for breaking cross-links. S_α and S_α^1 are factors, discussed below,

modifying the rate constants to allow for the FSSE. The fraction of all functionalities which are engaged in links closing rings of size i units is denoted by σ_i . This set of parameters, infinite in number, is later cancelled from the treatment. It will be assumed that the ring size i can vary from 2 to infinity. In the polyphosphoryl chloride system the existence of rings involving two units is doubtful; such rings would involve only four atoms (alternately P and O). For this reason, a special calculation will be presented (see table (6.3) and fig (6.2)) assuming that $i \geq 3$. Whatever the smallest ring size i_0 which is admitted, we have

$$\sum_{i=i_0}^{\infty} \sigma_i = \sigma \quad (4.22)$$

The last term in (4.21) arises from the breakage of all links (lying in rings) which were formed bimolecularly (i.e. as cross-links). Their formation preceded that of the corresponding ring-closing link. The use of the same rate constant k' for breaking all links, whether they lie in rings or not, means that the entropy contribution to the free energy of forming a bond in a ring (rather than a cross-link) is allocated entirely to the entropy of activation of the forward (ring-closing) reaction, leaving the entropy of activation of a ring-splitting reaction equal to that for splitting a true cross-link with production of two molecules. This treatment seems physically reasonable. Accordingly we also equate the rates

of ring-closures and splittings in the form:

$$k_r S_r (1 - \alpha - \sigma) n_i (i\nu)^{-3/2} = k' S'_\alpha \sigma_i (i - 1) + k' S'_r \sigma_i \quad (4.23)$$

The number of ring atoms per repeat unit in a ring is denoted by ν in the notation of Jacobson and Stockmayer (1950), who also use the random-flight regime for cyclization embodied in the factor $(i\nu)^{-3/2}$

The substitution effect parameters S_α and S_r for bond-forming reactions, and S'_α and S'_r for bond-splitting will now be derived for the linear ESSE. Here it is appropriate to consider the free energy contributions of the substitution effect equally split between the activation energies of bond forming and bond splitting reactions. By applying (3.25), the correct substitution parameter S_α multiplying the cross-linking rate constant k_α is then seen to be the weighted mean of $N^{i_1 + i_2 + j_1 + j_2}$, where the weightings are provided by the probabilities that two units, known to have at least one free functionality each (so that they are able to become cross-linked together), should have in addition i_1 and i_2 cross-links respectively and j_1 and j_2 ring-forming links respectively. (It is recalled that both types of links exert equal substitution effects). This weighted mean is very simply expressed in terms of the lgpf:

$$S_\alpha = \left\{ \left[\left(\partial F / \partial \theta_\alpha \right)_{\theta_\alpha=1, \theta_r=\theta_\alpha=N} \right] / \left[\left(\partial F / \partial \theta_\alpha \right)_{\theta=1} \right] \right\}^2 \quad (4.24)$$

Using (3.26), we find on the same principles that the substitution parameter S'_α multiplying the rate constant for bond splitting is:

$$S'_\alpha = \left\{ \left[(\partial F_0 / \partial \theta_\alpha)_{\theta_\omega=1, \theta_\alpha=\theta_\sigma=N^{-1}} \right] / \left[(\partial F_0 / \partial \theta_\omega)_{\theta=1} \right] \right\}^2$$

$$= \left\{ F_1(1, N^{-1}, N^{-1}) \right\}^2 \quad (4.25)$$

Similar principles also lead to S_σ and S'_σ

$$S_\sigma = \left\{ \left[N(\partial F_1 / \partial \theta_\omega)_{\theta_\omega=1, \theta_\alpha=\theta_\sigma=N} \right] / \left[(\partial F_1 / \partial \theta_\omega)_{\theta=1} \right] \right\}^2 \quad (4.26)$$

$$S'_\sigma = \left\{ \left[(\partial F_0 / \partial \theta_\sigma)_{\theta_\omega=1, \theta_\alpha=\theta_\sigma=N^{-1}} \right] / \left[(\partial F_0 / \partial \theta_\sigma)_{\theta=1} \right] \right\}^2 \quad (4.27)$$

Eq. (4.23) is divided by i to yield the approximate equation (which is exact in the absence of a FSSE):

$$k_\sigma S_\sigma (1 - \alpha - \sigma) n_i i^{-3/2} \approx k'_\sigma S'_\sigma S'_\alpha \quad (4.28)$$

The omitted term $k'_\sigma \sigma_i (S'_\sigma - S'_\alpha)/i$ is practically negligible with respect to $k'_\sigma S'_\sigma S'_\alpha$, partly because of the factor $1/i$, but particularly because of S'_α and S'_σ differ only very slightly for a moderate FSSE (see table (6.2)). The neglect of this term makes it possible to eliminate S'_α , S'_σ , and k' from what follows. Thus (4.28) immediately leads to the simple ring-size distribution

$$\sigma_i = \frac{\sigma n_i i^{-5/2}}{\sum n_i i^{-5/2}} \quad (4.29)$$

by the use of eq. (4.22). In particular, the mean number of units belonging to a ring is

$$\bar{r} = \frac{\sum \sigma_i i}{\sigma} = \frac{\sum_{i=i_0}^{\infty} n_i i^{-3/2}}{\sum_{i=i_0}^{\infty} n_i i^{-5/2}} \quad (4.30)$$

This equation agrees exactly with the calculation by Jacobson and Stockmayer (1950) of this quantity (their eq. (9), their symbol D_r) for bifunctional systems, and generalizes it to f-functional polycondensation with a moderate FSSE. The evaluation of the summations in eq. (4.30) is discussed in Appendix F. A dimensionless quantity λ , evaluated later from random flight statistics (section (4.8)), is defined thus:

$$\lambda = k_c/k_x \nu^{3/2} C_0 \quad (4.31)$$

Eq. (4.28) is summed over all i and the result divided into eq. (4.21). By means of (4.30) and (4.31) this leads to

$$\lambda = \sigma(1 - \alpha - \sigma) S_x / S_c \left[(\alpha + \sigma) \left(\sum_{i=i_0}^{\infty} n_i i^{-5/2} \right) - \sigma \sum_{i=i_0}^{\infty} n_i i^{-3/2} \right] \quad (4.32)$$

At the gel point (denoted by a subscript c) eq. (4.33) simplifies further. Since at the gel point $a_c = 1$ (eq. (4.15)), eq. (4.18) shows that n_{ic} becomes a constant irrespective of i :

$$n_{ic} = n_c A_c \quad (4.33)$$

Thus at the gel point eq. (4.30) simplifies to:

$$\bar{r} = \frac{\sum_{i=i_0}^{\infty} i^{-3/2}}{\sum_{i=i_0}^{\infty} i^{-5/2}} \quad (4.34)$$

Accordingly, the summations in (4.32) reduce to numerical values of the Riemann zeta function which are found from tables, so that, e.g., for $i_0 = 2$

$$\lambda = \frac{\sigma_c (1 - \alpha_c - \sigma_c) S_x}{A_c n_c S_\sigma [0.341 \alpha_c - 1.271 \sigma_c]} \quad (4.35)$$

All the quantities on the right of this equation are defined in terms of the lpgf $\bar{F}_c(\theta)$ of eq. (4.19) and thus depend only on f , N , τ_c and γ_c . Of these τ_c may be eliminated by using the gel point condition (4.15) in the explicit form

$$\begin{aligned} & \sum_{i=2}^f \sum_{j=0}^{f-1} \frac{f!}{(i-2)!j!k!} \gamma_c^i (i\tau_c)^j (1-\gamma_c)^k N^{(i+j)(i+j-1)} \\ &= \sum_{i=1}^f \sum_{j=0}^{f-1} \frac{f!}{(i-1)!j!k!} \gamma_c^i (i\tau_c)^j (1-\gamma_c)^k N^{(i+j)(i+j-1)} \end{aligned} \quad (4.36)$$

obtained from eq. (4.14). Thus for fixed f and N , all the variables on the right of (4.35) can be evaluated in terms of γ_c ; and γ_c can then be eliminated between α_c and σ_c .

This procedure was used to construct figures in Appendix C for $f = 3, 4, 6$ using the equations set out in Appendix A. It is confidently suggested that these figures can be used to predict the extent of cyclization in equilibrium f -functional polycondensations. The α_c axes of these figures (C1, C2, C3) correspond to ring-free systems and the function $N(\alpha_c)$ there agrees with the treatment given in section (3.4) and the graph (3.2).

4.8 Evaluation of λ from random-flight (Gaussian chain) statistics

According to the model, which goes back to Kuhn (1934), the ratio k_p/k_x (here equal to $\lambda C_0 \nu^{-3/2}$) of the rate constant for cyclization to that for cross-linking is obtained from the ratio of the probabilities of finding suitable reaction partners for a randomly chosen free functionality within a small volume surrounding it. The chance p_x that a functionality belonging to a foreign unit falls within a small cube $dx dy dz$ surrounding a functionality is proportional to the mean volume associated with a functionality.

$$p_x dx dy dz = fN_d \cdot dx dy dz / M \quad (4.37)$$

where M and d are the molecular weight and density respectively of the monomer, and N is Avogadro's number. Thus

$$k_x dx dy dz = KfN_d \cdot dx dy dz / (MC_0) \quad (4.38)$$

where K is the reciprocal mean life time of functionality remaining unreacted when it is inside the cube $dx dy dz$. Similarly the chance p_p that the end of a random walk falls within this cube is given for a freely jointed chain by

$$p_p dx dy dz = dx dy dz (2\pi\nu l^2/3)^{-3/2} \quad (4.39)$$

where l is the mean length of the bonds in the walk. Hence

$$k_p(1\nu)^{-3/2} dx dy dz = K dx dy dz (2\pi\nu l^2/3)^{-3/2} \quad (4.40)$$

assuming the reciprocal life time K to be the same as for the cross-linking reaction. Combining eq. (4.38), (4.40):

$$k_p/k_x = MC_0 (2\pi l^2/3)^{-3/2} / (fN_d) \quad (4.41)$$

or substituting for λ (eq. (4.31)),

$$\lambda = \left[\frac{3}{2\pi\nu} \right]^{3/2} \frac{M}{f N d l^3} \quad (4.42)$$

Using a random walk which preserves the value β of all the valence angles one arrives at

$$\lambda = \left[\frac{3(1 + \cos \beta)}{2\pi\nu(1 - \cos \beta)} \right]^{3/2} \frac{M}{f N d l^3} \quad (4.43)$$

By calculating the value of λ from eq. (4.43) for an equilibrium f -functional polycondensation and using the observed gel point $(\alpha_c + \sigma_c)$, one can use the graphs (C1, C2, C3) to evaluate the substitution parameter N . Alternatively knowing any two of the three parameters $\lambda, N, (\alpha_c + \sigma_c)$ either by experiment or calculation, these graphs enable the remaining one to be fixed and thus an estimate to be made of the FSSE or amount of cyclization (σ_c) present in the equilibrium system at the gel point.

4.9 Kinetically Controlled Systems

The treatment is now extended to the more difficult case of kinetic control (i.e. zero rate of back reaction). As in section (3.5) the FSSE will be restricted to the linear case, in which the free energy of activation of forming a link is proportional to the total number of links already borne by the two units to be bonded. (In this respect, again no distinction is made between ring-closing links and intermolecular cross-links). Thus to the free energy of

activation of forming a bond in the random reaction, a term (cf. eq. (3.31))

$$\Delta G^\ddagger = K(v_1 + v_2)/2 \quad (4.44)$$

is added when forming a bond between units with v_1 and v_2 links respectively. The corresponding rate constant is then

$$\begin{aligned} k &= k^* \exp(-K(v_1 + v_2)/2RT) \\ &= k N^{(v_1 + v_2)} \end{aligned} \quad (4.45)$$

where k^* is the rate constant for the random reaction, and N is defined as $\exp - K/2RT$, (eq. (3.20)). Subscripts α and σ are given to k^* as follows: k_α^* refers to the random cross-linking reaction, and k_σ^* to intramolecular reaction in the absence of a substitution effect. The lpgf is written in terms of the normalized probabilities $P_{i,j}$ that a unit chosen at random has i cross-links and j ring-closing bonds:-

$$F_0(\theta) = \sum_{i=0}^f \sum_{j=0}^{f-i} P_{i,j} \theta_\alpha^i \theta_\sigma^j \theta_w^k \quad (4.46)$$

where θ is the vector $(\theta_\alpha, \theta_\sigma, \theta_w)$, and

$$i + j + k = f \quad (4.47)$$

The following notation is used for average quantities

$$\langle f(i, j, k) \rangle = \sum_{i=0}^f \sum_{j=0}^{f-i} P_{i,j} f(i, j, k) \quad (4.48)$$

and the standard manipulations (eq. (4.12) to (4.16)) extract the

required statistical parameters from the lpgf.

The fraction of functionalities engaged in cross-links is

$$\alpha = \left[\frac{\partial F_0(\theta)}{\partial \theta_x} \right]_{\theta=1} / f = \langle i \rangle / f \quad (4.49)$$

where $\mathbf{1}$ is the vector (1, 1, 1); and the fraction engaged in ring-closing bonds is

$$\sigma = \left[\frac{\partial F_0(\theta)}{\partial \theta_r} \right]_{\theta=1} / f = \langle j \rangle / f \quad (4.50)$$

The mean number of cross-links leading from a unit on generation g to units on $(g + 1)$, when $g > 0$, is

$$a = \left[\frac{\partial F_1(\theta)}{\partial \theta_x} \right]_{\theta=1} = \langle i(i - 1) \rangle / \langle i \rangle \quad (4.51)$$

and the critical value at the gel point is given by

$$a_c = 1 \quad (4.52)$$

The mean number of free functionalities borne by a unit on any generation $g > 0$ is

$$n = \left[\frac{\partial F_1(\theta)}{\partial \theta_w} \right]_{\theta=1} = \langle ik \rangle / \langle i \rangle \quad (4.53)$$

Let a unit be known to have i cross-links and k free functionalities. Then the mean number of functionalities available to it for forming a ring of x units is ikm_x , where

$$m_x = n a^{x-2} \quad (4.54)$$

The smallest ring size, x_0 , is postulated to be two units, although the model can readily be adapted to include the term $x = 1$ where appropriate.

It is postulated that the rate at which a given functionality closes a ring is proportional to the number i of cross-links borne by the unit to which the functionality belongs. The kinetic rate equations may be written in terms of the rate constant of cross-linking and cyclization for a second order reaction:

$$-\frac{dP_{i,j}}{dt} = k_{\alpha}^* C_0 \left[k N^{(i+j)} P_{i,j} - (k+1) N^{(i+j-1)} P_{i-1,j} \right] \langle k N^{i+j} \rangle + \left\{ i k_{\gamma}^* \left[k N^{(i+j)} P_{i,j} - (k+1) N^{(i+j-1)} P_{i,j-1} \right] \frac{\langle i k N^{(i+j)} \rangle}{\langle i k \rangle} \sum_{x=x_0}^{\infty} m_x (x\nu)^{-3/2} \right\} \quad (4.55)$$

(For economy of notation, i and j feature as summation indices in the averages (cf. eq. (4.48)) and as free indices elsewhere in eq. (4.55)). C_0 is the initial concentration of functionalities and ν is number of ring atoms per repeat unit. There are $\frac{f(f+1)}{2} + 1$ of these equations (4.55), because $0 \leq i \leq f$ and $0 \leq j \leq (f-i)(1-\delta_0^i)$ where δ_j^x is the Kronecker delta. The initial conditions are

$$P_{0,0} = 1; \quad P_{i,j} = 0 \text{ for } i > 0 \quad (4.56)$$

A computer programme to solve this system of differential equations (4.55) has been written and details are given in Appendix F. The dimensionless quantity λ which has been defined as

$$\lambda = k_{\gamma}^* / (k_{\alpha}^* \nu^{-3/2} C_0) \quad (4.57)$$

in eq. (4.31) can once again be used as a cyclization parameter and is related to the molecular parameters of the system by eq. (4.43). Using the gel point condition (eq. (4.52)) α_c and σ_c have been evaluated, by solving the differential equation and using eq. (4.49), (4.50), as a function of λ and $N^{1/2}$ for the cases $f = 3, 4, 6$. These plots are shown in Appendix C (fig. C4, C5, C6) in a form suitable for comparison with similar plots (fig. C1, C2, C3) from the thermodynamic treatment. The reason for using $N^{1/2}$ as a parameter in the kinetic control cases was explained in section (3.5). The α_c axes of these figures (C4, C5, C6) correspond to the ring-free systems and the function $N(\alpha_c)$ there agrees with the solution of the differential rate equations (4.55) by Laplace Transforms given in section (3.6) and with fig (3.4). This gives confidence to the method of solving these differential equations (4.55) when $k_{\sigma}^* \neq 0$ as outlined in Appendix F.

It is shown in Appendix B that the rate equations (4.55) are consistent with the differential equations for α and σ given for the equilibrium treatment (eq. (4.21), (4.23)), when the backward rate constant (k') is equated to zero. Thus by differentiating eq. (4.49) it is shown that

$$d\alpha/dt = k_{\alpha}^* f (1 - \alpha - \sigma)^2 C_0 S_{\alpha} \quad (4.58)$$

where

$$S_{\alpha} = \left[\frac{\langle k N^{(i,j)} \rangle}{\langle k \rangle} \right]^2 \quad (4.59)$$

is the substitution parameter for cross-linking (eq. (4.24)).

Similarly one shows that

$$d\sigma/dt = k_{\sigma}^*(1 - \alpha - \sigma) A S_{\sigma} \sum_{x=x_0}^{\infty} m_x(x)^{-3/2} \quad (4.60)$$

where

$$A = \langle ki \rangle / \langle k \rangle \quad (4.61)$$

is the mean number of cross-links borne by a unit known to have at least one free functionality (eq. (4.17)), and the substitution parameter for ring-formation (eq. (4.26)) is

$$S_{\sigma} = \left[\langle ikN^{(i+i)} \rangle / \langle ik \rangle \right]^2 \quad (4.62)$$

The consistency with the equilibrium case follows by comparing eq. (4.58) with eq. (4.21) and eq. (4.60) with eq. (4.23).

Like the equilibrium treatment, the kinetic equations (4.55) are asymptotically correct as the degree of cyclization goes to zero. (At least this is so if, for small enough degrees of cyclization, molecules with more than one ring can be neglected in comparison with those which have one). The approximations in the kinetic and equilibrium cases are quite analogous. However, the neglect of correlations arising from the formation of more than one ring-closing link on a given unit is somewhat more serious in the kinetic case. The reason for this is as follows. The treatment sets the chance of a given functionality engaging in a ring-closure proportional to the number of cross-links borne by its unit. This reflects correctly the equality of the chances of this ring-closure involving a

functionality on any one of the subtrees connected to these cross-links. If the unit also bears other ring-closures already, this may indicate that these subtrees are of a favourable size and shape for further ring-closures to be formed, a bias which is neglected in the treatment. This bias is less serious in the equilibrium case, because the bond-splitting reactions will then tend to randomise the size and shape of subtrees.

CHAPTER 5

GENERALIZATION TO INCLUDE POST-GEL PARAMETERS

5.1 Introduction

The work of Gordon (1962) has been extended by Good (1963) to obtain formulae for the weight average and higher average degrees of polymerization of the sol fraction. A convenient general method of obtaining all statistical parameters in a form which applies to the sol fraction after gelation and to the whole system before the gel point has been published by Dobson and Gordon (1964). This general method will be briefly discussed and then used (section (5.2)) to construct a model for kinetically controlled reactions after the gel point.

Using the random case of f-functional polycondensation it has been shown (section (2.1)) that the lpgf ($F_g(\theta)$) for the offsprings of a unit in the g^{th} generation is independent of g for $g \geq 1$, and is thus the same function as $F_1(\theta)$. Starting with an individual in the first generation, the pgf for the total number of individuals in the first, second, ... $(g + 1)$ generations is

$$\theta F_1(\theta F_2(\theta F_3(\dots \theta F_g(\theta)))) \quad (5.1)$$

(see for example Good 1949).

Since $F_g(\theta) < 1$ when $\theta < 1$, it follows that the expression (5.1) is a decreasing function of g , for each θ ($0 \leq \theta \leq 1$), and therefore tends to a limit as $g \rightarrow \infty$. This limit is taken to be the definition

of the function $u(\theta)$ which was shown in section (2.3) to be the pgf for the whole tree, starting from one individual in the first generation. Thus as before (eq. (2.22)):

$$\begin{aligned} u(\theta) &= \theta F_1(\theta F_1(\theta F_1(\dots))) \\ &= \theta F_1(u(\theta)) \end{aligned} \quad (5.2)$$

Good (1963) has shown that this functional equation (5.2) has a unique solution when $\theta = 1$ only if $F_1'(1) \leq 1$ (in which case the solution is $u(1) = 1$), whereas if $F_1'(1) > 1$, then there are two solutions. It should be noted that $F_1'(1) = 1$ is the gel point condition. One of these solutions is trivial and equal to unity, whilst the notation v is reserved for the other one. Thus the solution of

$$u(1) = F_1(u(1)) \quad (5.3)$$

always has unity as one root, but after the gel point the equation has another positive root, less than unity. The lowest positive root (v) is the probability of extinction starting from an individual in the first or later generations, where extinction means that the sub-tree rooted on that individual is of finite size, i.e. V is the chance that all the successors carried on one end of a randomly chosen link finally become extinct. The probability of extinction starting from an individual in the zeroth generation is $F_0(v)$, which is the sol fraction S . In any individual instance, v has to be found by solving $v = F_1(v)$ (eq. (5.3)).

For systems with at most a FSSE the lpgf $F_*(\theta)$ can be generalized

(Dobson and Gordon 1964) so as to apply the sol fraction after gelation and to the whole system before the gel point; all functions and parameters thus generalized ^{are} ~~as~~ given a circumflex ($\wedge$). Mathematically the required generalization consists in making the weight fraction gf for the sizes of a tree conditional on the tree being finite, and is

$$\hat{F}_0(\theta) = F_0(v\theta)/F_0(v) \quad (5.4)$$

for the coefficient p_i of θ^i in $F_0(v\theta)/F_0(v)$ is proportional to the coefficient of θ^i in $F_0(\theta)$ and also to v^i . But p_i is the chance that a randomly chosen unit has i off-springs, and v^i is the chance that the i children are all roots of finite proper sub-trees. Thus $\hat{F}_0(\theta)$ is the pgf of the number of children of all units in the sol fraction of the original system taken as roots of an ensemble of trees. Using the standard formulae (section (2.4)), all other statistical functions and parameters can be generalized by using $\hat{F}_0(\theta)$ in place of $F_0(\theta)$.

5.2 Post-gel Model for Kinetically Controlled Systems

It is apparent that the model for kinetically controlled polycondensation with cyclization (section (4.9)) is of no use after the gel point. It can be seen from the kinetic rate equation (4.55) that the rate of cyclization is infinite after the gel point, since the summation of available reaction partners (n_x) diverges when the mean number of functionalities (a) on generations higher than the zeroth is greater than unity. Experimental data (see section (7.6)) shows that the polyesterification reaction proceeds smoothly through

the gel point. In order to fit this observation we propose a model for kinetically controlled systems in which the number of reaction partners available to a free functionality is restricted. Firstly the physical basis of the model is briefly discussed.

After gelation, the path linking two functionalities in a molecule contains certain links whose successors in one direction never become extinct, such links are called ties, see fig. (5.1).

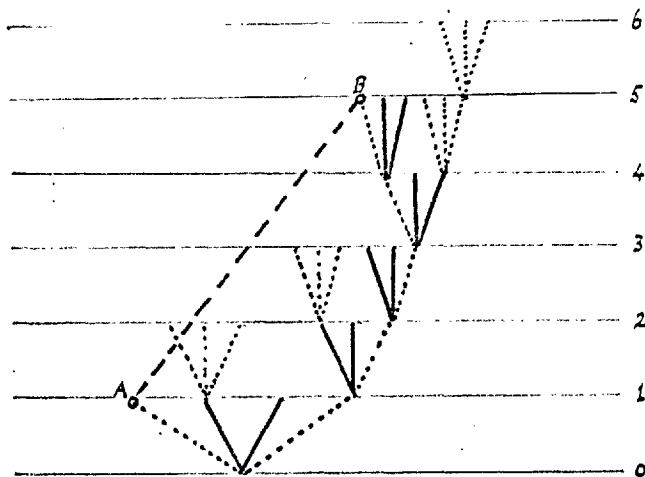


Fig. 5.1 A typical tree showing the 10 links radiating from the path linking the two functionalities A and B that form a ring - closing bond. The remaining links are shown as dotted lines

A path which radiates t ties contains at least $(t - 2)/(f - 1)$ network junction points as defined in rubber elasticity theory (Dobson and Gordon 1965). A pair of adjacent network junction points have an end-to-end vector which does not have a Gaussian length distribution. Instead each such network junction point

performs Gaussian fluctuations about a fixed point (James, 1947).

Thus the points A and B in fig. (5.1) are broadly speaking the more seriously impeded, as regards colliding to form a ring, the more network function points the path A-B contains.

The model postulates that cyclization between a pair of functionalities is prohibited when there are ^{more than} at least m ties radiating from the path linking them. For a f -functional polycondensation there are $(f - 2)(g + 1)$ radiating functionalities available for the formation ^{of a bond} between a functionality on the zeroth and one of the g^{th} generation. Each such radiating functionality has an independent chance $(1 - v)$ of being a tie if it is a cross-link, where v is the extinction probability (section (5.1)). Thus the mean number of expected ties (t_m) on a path of $(g + 1)$ links is

$$t_m = (f - 2)(g + 1)(1 - v) \propto \quad (5.5)$$

A tie generating function $T(\theta)$ is now constructed

$$T(\theta) = (1 - t + t\theta)^{(f-2)(g+1)} \quad (5.6)$$

where

$$t = (1 - v) \propto \quad (5.7)$$

The chance of finding m ties is merely the coefficient of θ^m in $T(\theta)$, i.e.

$$\binom{(f-2)(g+1)}{m} t^m (1 - t)^{(f-2)(g+1) - m} \quad (5.8)$$

where $\binom{x}{y}$ is the binomial coefficient $x!/(y!(x - y)!)$.

Incorporating this model into the kinetic rate equation (4.55), we have:

$$\begin{aligned}
-\frac{d P_{i,j}}{dt} &= k_{\alpha}^* C_0 \left[k N^{i+j} P_{i,j} - (k+1) N^{i+j-1} P_{i-1,j} \right] \langle k N^{i+j} \rangle \\
&+ i k_{\sigma}^* \left[k N^{i+j} P_{i,j} - (k+1) N^{i+j-1} P_{i,j-1} \right] \langle i k N^{i+j} \rangle \\
&\times \sum_{x=x_0}^{\infty} \left[m_x (xv)^{-3/2} \sum_{l=0}^m t(x, l) \right] / \langle i k \rangle
\end{aligned}
\tag{5.9}$$

where

$$t(x, l) = \binom{(f-2)(x+1)}{l} t^l (1-t)^{(f-2)(x+1)-l}
\tag{5.10}$$

The inclusion of the term $t(x, l)$ removes the discontinuity in the previous equation (4.55) at the gel point when the function m_x is unity. The summation in eq. (5.9) is discussed and calculated in Appendix F. This model (eq. (5.9)) is used in the following section (5.3) to investigate the change in the amount of cyclization (σ) as m — the maximum number of ties allowed in the path between two functionalities before cyclization is prohibited, is increased.

5.3 Application to a Copolymer System

To illustrate the use of this post-gel model, we shall consider the polyesterification of pentaerythritol and adipic acid. With reference to section (2.5) we may write down the lpgf in terms of ${}_s P_{i,j}$, the chance that a unit of type s chosen at random in a copolymer system has i cross-links and j ring-closing bonds (eq. (2.32), (4.46)):

$$F_s(\theta) = \sum_{i=0}^{f_s} \sum_{j=0}^{f_s-1} {}_s P_{i,j} \theta_{\alpha}^i \theta_{\sigma}^j \theta_{\omega}^{k_s}
\tag{5.11}$$

Following eq. (5.9) we can immediately write down the corresponding second order rate equations for a two component system in which the subscript s refers to quantities pertinent to units of type s:

$$\begin{aligned}
 - \frac{d {}_1P_{i,j}}{dt} = & k_{\alpha}^* {}_2C^{\circ} \left[k_1 N_1^{i+j} {}_1P_{i,j} - (k_1+1) N_1^{i+j} {}_1P_{i-1,j} \right] \langle k_2 N_2^{i+j} \rangle \\
 & + i k_{\sigma}^* \left[k_1 N_1^{i+j} {}_1P_{i,j} - (k_1+1) N_1^{i+j} {}_1P_{i,j-1} \right] \langle i k_2 N_2^{i+j} \rangle \\
 & \times \sum_{x=1}^{\infty} \left[{}_2m_x (x)^{-3/2} \sum_{l=0}^m t(x,l) \right] / \langle i k_2 \rangle \quad (5.12)
 \end{aligned}$$

where

$${}_2m_x = \frac{\langle i k_2 \rangle}{\langle i {}_2P_{i,j} \rangle} \left[\frac{\langle i(i-1) {}_1P_{i,j} \rangle \langle i(i-1) {}_2P_{i,j} \rangle}{\langle i {}_1P_{i,j} \rangle \langle i {}_2P_{i,j} \rangle} \right]^{x-2} \quad (5.13)$$

and $t(x,l)$ is the coefficient of θ^l in $T(\theta)$, where (cf. eq. (5.6))

$$T(\theta) = (1 - t_1 + t_1 \theta)^{(f_1-2)x} (1 - t_2 + t_2 \theta)^{(f_2-2)x} \quad (5.14)$$

and

$$t_s = (1 - V_s) \alpha_s \quad (5.15)$$

A similar expression to eq. (5.12) holds for $-d({}_2P_{i,j})/dt$ in which the subscripts 1 and 2 are interchanged. There are of course two linear substitution parameters, (N_1 and N_2), one for each component.

For the pentaerythritol/adipic acid system $f_1 = 4$, $f_2 = 2$ and thus (eq. (5.14))

$$t(x,l) = \binom{2x}{l} t_1^l (1 - t_1)^{2x-l} \quad (5.16)$$

By integrating (see Appendix F) eq. (5.12) and the corresponding rate equation for $-d({}_2P_{i,j})/dt$ and using the relations (eq. (4.49), (4.50)) σ may be computed as a function of α for different values of

the post-gel cyclization parameter (m) - the maximum number of ties allowed to radiate from the path between two functionalities if cyclization is to be allowed. Such a plot for the pentaerythritol/adipic acid system is shown in fig. (5.2). This figure shows that an infinite range in the value of $\frac{1}{\alpha}$ can be obtained after the gel point by varying m from 1 to ∞ . It is shown (section (7.6)) that the polyesterification reaction proceeds smoothly through the gel point and thus a value of m between 3 and 12 can be chosen as a typical post-gel cyclization parameter on the basis of this observation.

This post-gel model can be used to remove the discontinuity present in the previous model at the gel point. Of course it cannot be taken too far beyond the gel point since other effects which influence the cyclization regime soon become important. For example, Matula, Groenweghe and Van Wazer (1964) discuss the fact that after gelation the molecule cannot be accommodated in space and hence ring closure is imposed by physical crowding.

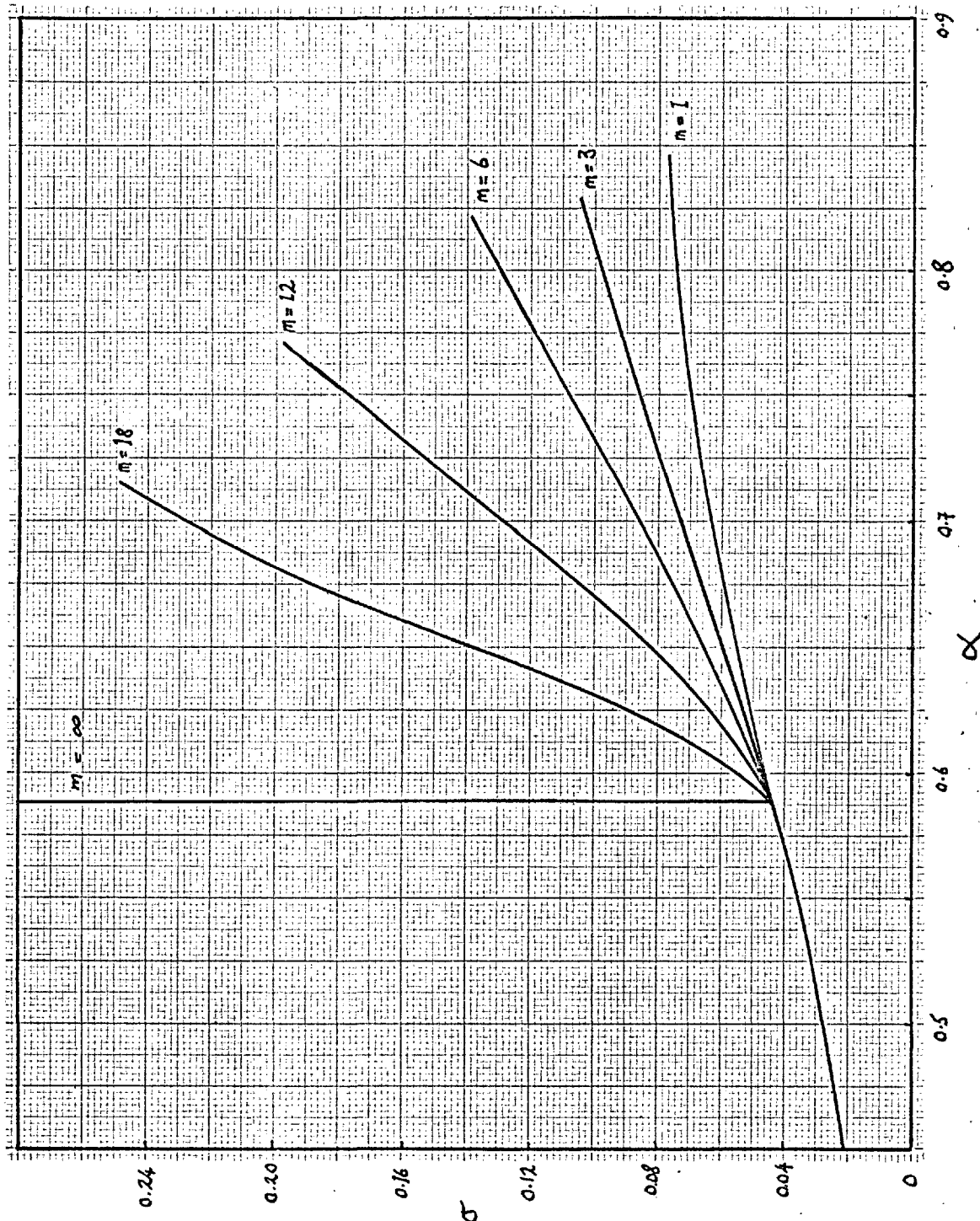


Fig. 5.2 σ against α for kinetically controlled second order reaction (two component system) as a function of the post-gel cyclization parameter m . $f_1 = 4$, $f_2 = 2$, $N_1 = N_2 = 1$, $\lambda = 0.366$.

system is identical with that of a simple (albeit hypothetical) trifunctional polycondensation reaction. Accordingly this state will now be treated in terms of polycondensation theory and nomenclature; in particular the reorganization heat order of the scrambling reaction is just the substitution effect of the polycondensation.

6.2 The link probability generation function

The appropriate case ($f = 3$) of eq. (4.3) is

$$\begin{aligned} F_0(\theta) = N_0 [& ((1 - \gamma)\theta_\omega)^3 + 3\gamma\theta_\alpha((1 - \gamma)\theta_\omega)^2 + 3\beta(2)\gamma\theta_\alpha(1 - \gamma)\theta_\omega \\ & \cdot (\gamma\theta_\alpha + 2\tau\theta_\sigma) + \beta(3)\gamma\theta_\alpha((\gamma\theta_\alpha)^2 + 3\tau\theta_\sigma(2\gamma\theta_\alpha + \tau\theta_\sigma))] \quad (6.2) \end{aligned}$$

is seen to have the four independent parameters γ , τ , $\beta(2)$ and $\beta(3)$, in terms of which the whole equilibrium system is defined. It turns out that the data can be fitted as closely as is reasonable with the linear FSSE theory of eq. (4.19), which here involves only three parameters γ , τ , and N , (see Appendix A):

$$\begin{aligned} F_0(\theta) = N_0 [& ((1 - \gamma)\theta_\omega)^3 + 3\gamma\theta_\alpha((1 - \gamma)\theta_\omega)^2 + 3N^2\gamma\theta_\alpha(1 - \gamma)\theta_\omega \\ & \cdot (\gamma\theta_\alpha + 2\tau\theta_\sigma) + N^3\gamma\theta_\alpha((\gamma\theta_\alpha)^2 + 3\tau\theta_\sigma(2\gamma\theta_\alpha + \tau\theta_\sigma))] \quad (6.3) \end{aligned}$$

The parameters α and σ are derived therefrom using eq. (4.12) and (4.13). Experimentally, the mechanism for reaching the equilibrium described above allows values of $\alpha + \sigma$ to be pre-selected; the stoichiometry demands:

$$R = 3(1 - \alpha - \sigma) \quad (6.4)$$

The kinetic process of attaining the equilibrium state is of no further interest. The lpgf of eq. (6.3) will now be compared with

measurements by Groenweghe, Payne and Van Wazer (1960) at six values of R lying between the gel point, which occurs in the range $R = 1.1$ to 1.2 , and a maximum of $R = 2$. (At higher values of R the concentration of triply linked P , to which these calculations are sensitive, becomes too low to be reliably measured). These measurements determine the four concentrations of P atoms with zero, one, two, or three links respectively, without, however, distinguishing ring-closing links from cross-links as defined here. It is therefore appropriate to simplify eq. (6.3) by considering the special case obtained by setting $\theta_\omega = \theta_\sigma = 1$:

$$F_0(\theta_\omega, 1, 1) = \sum_{q=0}^3 v_q \theta_\omega^q \quad (6.5)$$

Thus the seven distinct terms in eq. (6.3) are now reduced to the four required, as set out in fig. (6.1) in terms of the nomenclature used by the original authors. The measurements of the v_q (defined by eq. (6.5) at the six values of R as provided by Van Wazer

Notation

Van Wazer:	ortho	end	middle	branch
This work:	v_3	v_2	v_1	v_0

Fig. 6.1 Comparison of notations for the states of P -atoms in the system $POCl_3/P_2O_5$. Circles denote ring-closing functionalities; crosses denote cross links.

are shown in table (6.1), together with the two available checks

TABLE 6.1

Nmr data for $\text{POCl}_3/\text{P}_2\text{O}_5$ and parameters deduced

Mole ratio R (from ingredients)	1.992	1.660	1.492	1.332	1.241	1.200	Mean	Standard Deviation
Proportions of repeat units (fig. 6.1) from nmr								
v_0	0.085	0.155	0.196	0.218	0.232	0.198	-	-
v_1	0.239	0.335	0.354	0.377	0.379	0.389	-	-
v_2	0.308	0.302	0.297	0.277	0.282	0.296	-	-
v_3	0.369	0.209	0.153	0.129	0.108	0.117	-	-
$\sum v_i$ (eq. 6.6)	1.001	1.001	1.000	1.001	1.001	1.000	-	-
$\sum v_i q$ (eq. 6.7)	1.962	1.566	1.407	1.318	1.267	1.332	-	-
K_1 (eq. 6.8)	0.458	0.417	0.465	0.425	0.455	0.387	0.435	6.9%
K_2 (eq. 6.9)	0.930	0.768	0.614	0.634	0.515	0.519	0.663	24.1%
N (eq. 6.10)	1.088	1.031	1.078	1.031	1.081	1.984	1.049	3.86%
γ (eq. 6.8, 6.9)	0.218	0.325	0.393	0.417	0.465	0.457	-	-
τ (eq. 6.8, 6.9)	0.148	0.189	0.115	0.164	0.075	0.139	-	-
α (eq. 4.12, 6.3)	0.271	0.367	0.438	0.443	0.505	0.456	-	-
σ (eq. 4.13, 6.3)	0.076	0.112	0.093	0.118	0.073	0.100	-	-

arising from normalization

$$\sum_{q=0}^3 v_q = 1 \quad (6.6)$$

and stoichiometry

$$\sum_{q=1}^3 v_q q = R \quad (6.7)$$

Eq. (6.6) checks well against the data in table (6.1). Eq. (6.7) checks less well but is more sensitive to errors. Taking into account the normalization condition, there are just three independent measurements of the v_q at each R - value to determine the three unknown parameters γ , τ , and N by comparing coefficients of (6.3) and (6.5). The results are also shown in table (6.1). The calculation was simplified by constructing the homogeneous functions:

$$K_1 = v_0 v_2 / v_1^2 = N^2 (\gamma^2 + 6\gamma\tau + 3\tau^2) / 3(\gamma + 2\tau)^2 \quad (6.8)$$

and

$$K_2 = v_1 v_2 / v_2^2 = N^2 (\gamma + 2\tau) / 3\gamma \quad (6.9)$$

From the last two equations γ/τ was eliminated to yield a cubic in N^2

$$5N^6 - 18N^4 K_2 - 27N^2 (K_2)^2 + 108K_1 (K_2)^2 = 0 \quad (6.10)$$

The significant root of this cubic leads to the values of N in table (6.1) which are analysed in section 6.3.

Calculations were also performed which stem from the assumption

of a cyclization regime based on random flight statistics, which was in no way involved in the calculations of table (6.1). This assumption enters in connection with the parameter λ (eq. (4.32)) and hence the mean bond length l (eq. (4.43)). Two minor complicating factors exist.

- a). The exact gel-point is not known but is estimated to lie in the range $1.1 < R_c < 1.2$. Tabulations are, therefore, presented below to cover a range of assumed values of R_c .
- b). The smallest rings, here those involving two units (four-membered rings), three units (six-membered rings), and perhaps one or two further members of the series, may be expected to deviate from strict random-flight statistics owing to steric factors not known in any detail. The effect of such factors is explored in table (6.2) and fig. (6.2), without actual departure from the principle of random flight statistics, but merely by comparing results for the cases $i_0 = 2$ and $i_0 = 3$. These two schemes differ only in that the latter excludes altogether the formation of four-membered rings (i.e. rings involving two units). Excluded volume effects are neglected for all ring-sizes.

TABLE 6.2Critical Values for $f = 3$, $N = 1.05$ from eq. (6.3)

	R_c	α_c	σ_c	S_α	$S_{\alpha'}$	S_σ	$S_{\sigma'}$
eq.	6.4	4.12	4.13	4.24	4.25	4.26	4.27
	1.539	0.437	0.000	1.098	0.908	1.157	0.952
	1.466	0.496	0.015	1.102	0.904	1.159	0.950
	1.397	0.504	0.031	1.105	0.900	1.160	0.949
	1.332	0.511	0.045	1.108	0.986	1.162	0.948
	1.269	0.518	0.059	1.112	0.893	1.164	0.946
	1.210	0.524	0.073	1.115	0.890	1.165	0.945
	1.153	0.530	0.086	1.118	0.887	1.167	0.944
	1.100	0.535	0.098	1.121	0.884	1.168	0.942
	1.049	0.540	0.110	1.124	0.881	1.170	0.941
	1.000	0.544	0.122	1.127	0.879	1.171	0.940

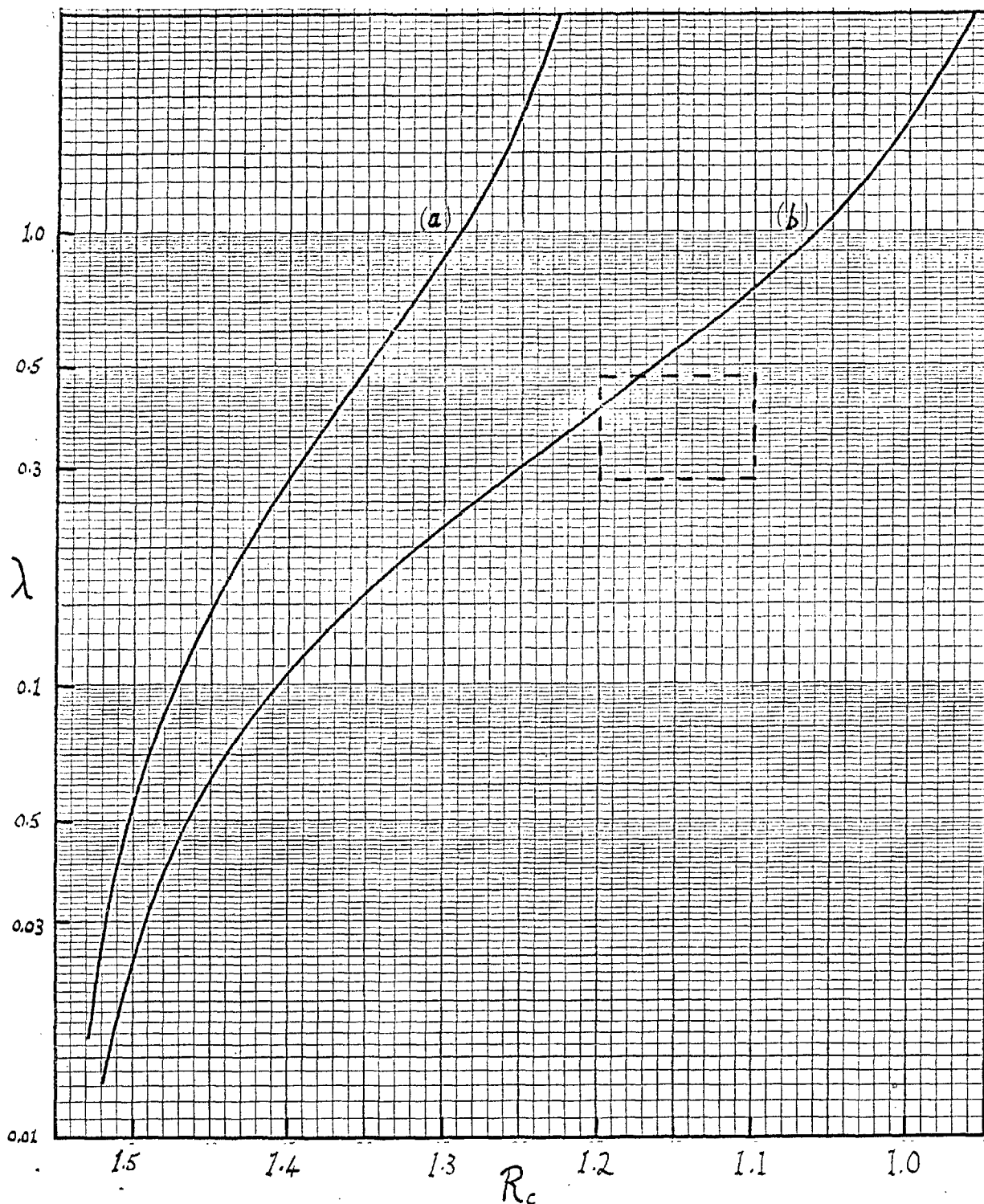


Fig. 6.2 Comparison of experimental gel point with random-flight theory, using plots of λ versus the gel point R_c . The dotted rectangle represents the uncertainty in the measured gel point and in the value of λ calculated from the bond lengths and angles in $\text{POCl}_3/\text{P}_2\text{O}_5$. Plot a: random-flight calculation with minimum ring-size of six atoms ($i_0 = 3$); plot b: same with minimum ring-size of four atoms ($i_0 = 2$).

6.3 Discussion

The theoretical model here proposed can be tested against the data on $\text{POCl}_3/\text{P}_2\text{O}_5$ by Groenweghe, Payne and Van Wazer (1960) in several ways. Firstly, the lpgf of eq. (6.3), which does not assume any configurational (e.g. random flight) scheme for the statistic of cyclization, should lead to a value of N independent of the mole ratio R of phosphorus to chlorine. Table (6.1) shown that this test is very satisfactory, since for the six values of R tabulated $N = 1.049$ with a standard deviation of only 3.86%. This is an improvement over the fit achieved by the original authors of their data to the scheme which neglects the occurrence of cyclization, even though this involved one more adjustable parameter. By putting $\tau = 0$ (neglect of cyclization), we see that the functions K_1 and K_2 (eq. (6.8), (6.9)) become constants; they are, in fact, chemical equilibrium constants and should be independent of R . For the linear FSSE, moreover, the two constants should then be equal since eq. (6.8) and (6.9) yield, for $\tau = 0$, $K_1 = K_2 = N/3$. Since the measured values are not found to be equal, one can fall back on the non-linear FSSE, as did the original authors; this would correspond to eq. (6.2) with $\tau = 0$ and

$$K_1 = \rho(3)/3\rho(2)^2 \quad (6.11)$$

$$K_2 = \rho(2)/3 \quad (6.12)$$

However, even on this assumption, both K_1 and K_2 should still be thermodynamic constants independent of R , and the original authors noted that K_2 varied with R . They calculated average values of $K_1 = 0.490$ and $K_2 = 0.657$ (including measurements at $R = 2.33$) and

respective standard deviations from these values of 32.5 and 22.2%. (These figures are quoted from a later paper by Groenweghe, Van Wazer and Dickinson (1964), in which the designations of K_1 and K_2 were accidentally interchanged). The standard deviations are reduced when the measurements at $R = 2.33$ are discounted (see table (6.1)) but they are still larger than that of the single parameter N used in the model of this work. It is noteworthy that the allowance made for cyclization not only reduces the calculated FSSE to much smaller proportions, satisfactorily represented by the linear approximation, but (with only marginal significance) seems to change its direction. The mean value of N being larger than unity, albeit by only about one standard deviations, suggests a slight preference for the occurrence of branched structures, in contradistinction to the inference drawn from the values of K_1 and K_2 in assumed absence of cyclization.

Accepting the value of $N = 1.05$ (table (6.1)) at its face value, leads, via eq. (3.20), to a decrease in the standard free energy of forming a link of about 50 cal/mole in respect of each link already being carried by either of the units to be joined. On the other hand, Groenweghe, Payne and Van Wazer (1960) deduced effects in the opposite direction of 670 and 920 cal/mole from their interpretation of the mean values of K_1 and K_2 just explained.

Groenweghe, Payne and Van Wazer (1960) also measured, by two concordant methods, the weight fraction w_2 of the dimer pyrophosphoryl dichloride $O = P(Cl)_2 - O - P = O(Cl)_2$ in an equilibrium mixture having the same ratio $R = 2$ as this compound. According to the model

here advocated, this quantity would be calculated from the following equation

$$w_2 = 3 N_0 N_1 (1 - \gamma)^4 \gamma \quad (6.13)$$

From table (6.1), γ is seen to be 0.218 and the normalizing constants N_0 and N_1 are found (using eq. (6.3) and (3.1)) to be 0.7690 and 0.6179 respectively. Hence w_2 is calculated to be 11.6% in excellent agreement with experiment, (viz. 12%).

In view of the cautionary remarks in section (4.5), the successful calculation of w_2 is not conclusive supporting evidence for the model; but it may perhaps be inferred that in cases where the model is well supported by independent evidence, the weight fractions of rather simple species present can be calculated with reasonable confidence by such straightforward means as eq. (6.13).

Beside the constancy of N , the trend of increasing γ with decreasing R in table (6.1) is to be expected from the nature of the model. No clear trend of τ with R is discernible; nor, strictly speaking does the model demand any. However, when the model is supplemented with any reasonable postulates concerning the cyclization regime, τ will be expected to increase with γ . It is concluded that τ (and hence σ) are, in the procedure underlying table (6.1), sensitive to small errors in the v_q . The situation is improved, in this respect, by using the average value of N , viz. 1.05 (table 6.1). When the critical conversion R_c is known in addition, and eq. (4.15) is employed, γ_c and τ_c and hence all statistical parameters are accessible at the gel point. Such calculations are tabulated against R_c in table (6.2). Since for

$\text{POCl}_3/\text{P}_2\text{O}_5$ experimentally $1.10 < R_c < 1.20$, it is seen that the model yields α_c and σ_c values confined to fairly narrow limits, say 0.530 ± 0.005 and 0.087 ± 0.012 respectively. In section 6.4 it is shown that this critical degree of cyclization α_c corresponds well with that predicted on the basis of random flight statistics and the known bond lengths and angles. The critical parameters for $\text{POCl}_3/\text{P}_2\text{O}_5$ collected in table (6.3) are therefore considered to be soundly based. The number average degree of polymerization DP_n is found from the formula (eq. (2.16)):

$$\text{DP}_n = 1/(1 - 1.5\alpha) \quad (6.14)$$

and is in principle measurable for confirmation. The average number of rings per molecule is calculated thus:

$$\text{DR}_n = 1.5 \text{DP}_n \sigma \quad (6.15)$$

TABLE 6.3

Parameters calculated at gel-point for $\text{POCl}_3/\text{P}_2\text{O}_5$,
using $N = 1.05$

α_c	0.530	$\pm$	0.005
σ_c	0.087	$\pm$	0.011
DP_{nc} (eq. (6.14))	4.88	$\pm$	0.18
DR_{nc} (eq. (6.15))	0.64	$\pm$	0.10
$\bar{r}$ (eq. (4.30), $i_o = 2$)	4.73		
$\bar{r}$ (eq. (4.30), $i_o = 3$)	7.67		

The fact that this, even at the gel point, turns out to be 0.64, i.e. well below unity, gives further confidence in the results of the model calculations, since the most serious deviations to be expected would result from substantial amounts of certain fused-ring structures (section (4.3)) which are among the molecules with two or more rings.

6.4 Extension to random flight statistics

Eq. (4.43) is used in table (6.4) to evaluate λ as a function of the mean bond angle β , using the molecular parameters at the head of the table. The requisite bond angles are known for P_4O_{10} in the vapour phase, viz. 123.5° for P-O-P and 101.5° for O-P-O.

TABLE 6.4

Evaluation of λ from eq. (4.43) ($\nu = 2$).

$M = 120$, $d = 1.75$ g.ml (estimated), $l = 1.62$ Å

β	λ
90	1.03
95	0.79
100	0.61
105	0.47
110	0.35
115	0.27
120	0.20
125	0.15

Assuming that the required mean bond angle in the system $\text{POCl}_3/\text{P}_2\text{O}_5$ lies between 105° and 115° , the table shows that λ lies between 0.47 and 0.27.

The functional relation between λ and the gel point R_g ($= 3(1 - \alpha_c - \sigma_c)$) is found from fig. (6.3) for the case $i_o = 2$. This figure (6.3) was constructed by the procedure outlined in section (4.7) and is also shown in an amended form in Appendix C (fig. C1).

Since each repeat unit contributes two ring atoms, $i_o = 2$ corresponds to the inclusion of four-membered rings. The result is plot a in fig. (6.2). An analogous calculation was carried out for $i_o = 3$, i.e. for the limiting ring size of six atoms. The only change is that equation (4.35) takes the form

$$\lambda = \frac{\sigma_c(1 - \alpha_c - \sigma_c)S_\alpha}{A_c n_c S_\sigma [0.164 \alpha_c - 1.094 \sigma_c]} \quad (6.16)$$

and the result is shown as plot b in fig. (6.2). Formally, the wide gap between the two curves displays the important role of the assumption concerning four-membered rings. This is further illustrated (table (6.3) by the mean ring size (eq. (4.30)) $\bar{r} = 4.73$ (using $i_o = 2$) and $\bar{r} = 7.76$ (using $i_o = 3$). Many molecules with four-membered rings involving phosphorus are known but these do not include quadruply connected P. It is apparent from fig (6.2) that the range of λ values calculated is formally in good agreement with the assumption of four-membered rings being present nearly in

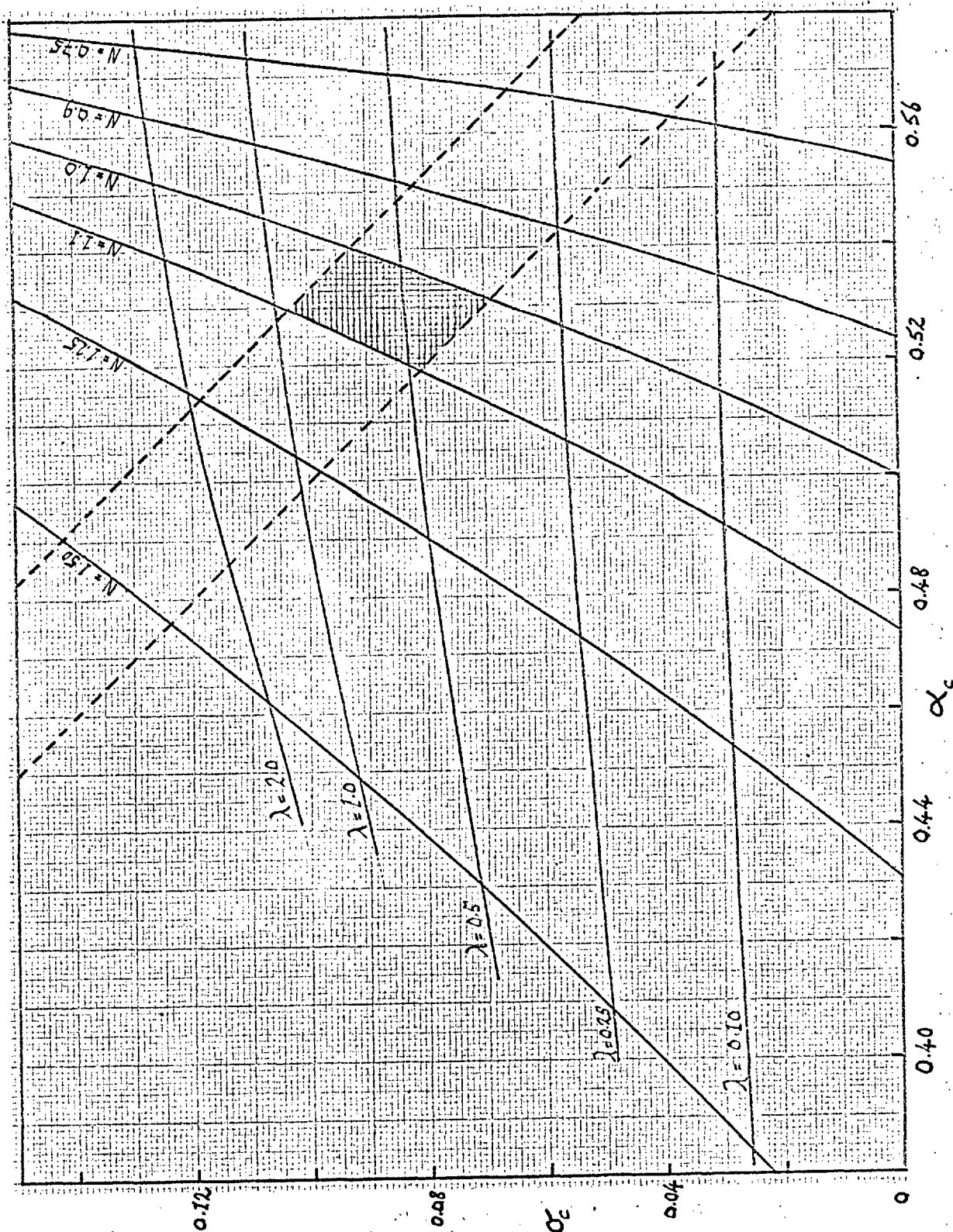


Fig. 6.3 Calculated transformation of $\sigma - \alpha$ plane to $\lambda - N$ plane for trifunctional polycondensation. The dotted lines represent the range of the measured gel point of the system $\text{POCl}_3/\text{P}_2\text{O}_5$, and the shaded area the range of its calculated critical parameters.

the proportions dictated by random flight theory (eq. (4.29)). Deviations of the proportions of small rings from random flight statistics are likely to invalidate any quantitative interpretation of fig. (6.3). Nevertheless, the broad agreement between the gel point measurement and the random-flight theory of cyclization is considered to be strongly significant. The gel point for a classical random polycondensation of $\text{POCl}_3/\text{P}_2\text{O}_5$ would lie at $R_c = 1.50$. The linear substitution effect here deduced from the nmr measurements ($N = 1.05$) would, in the absence of cyclization, raise this slightly, viz. to $R_c = 1.53$. Finally, the cyclization effect deduced from the nmr measurements and from random-flight theory superpose a notable reduction to $R_c = 1.1 - 1.2$ as is found to occur experimentally. Most organic polycondensation systems have more widely spaced functionalities and are hence expected to show lower degrees of cyclization. The present model can be applied to them with even greater confidence. Substitution effects more substantial than that here found may, of course, be expected for other systems. In the reaction between melamine and formaldehyde, this was indeed found to be the case (Gordon, Halliwell and Wilson, 1965), but the data were adequately fitted on the assumption of first-shell and linear effects only.

In the remaining chapters of this thesis a kinetically controlled reaction (the polyesterification of pentaerythritol and adipic acid) is considered. It is shown that the model can be used to analyse different mechanisms for the polymerization reaction as well as statistical quantities such as the gel point.

CHAPTER 7

POLYESTERIFICATION

7.1 Introduction

One of the first definite reports of a study of the chemical reaction between a polyhydric alcohol and a polybasic acid was presented by Smith (1901). However, no exact kinetic studies of polyesterification reactions were made until Kienle and Hovey (1928) commenced a study of the glycerol/phthalic anhydride reaction. Concurrently, Carothers (1940) embarked on his classical research on polyesters. His experiments constitute a landmark in the development of high polymer chemistry and he laid down the experimental foundations for the theoretical developments made later by Flory (1953), Stockmayer (1944) and others. Carothers showed that the physical properties of the product of any polymerization depended on the functionality of the monomers, and that the basic chemical reaction which occurs when a polyhydric alcohol and a polybasic acid react is the same as that for a monohydric alcohol and a monobasic acid.

The formal kinetics of a three dimensional polycondensation are very difficult to analyze, and Kienle and his co-workers (1939, 1940, 1941) soon found that no kinetic equation would cover the whole process. The kinetics of polyesterification are discussed in detail in section (8.2). Most of the published work deals with the glycerol-dibasic acid reaction, where there is the added complication

of the different reactivity of the secondary hydroxyl group. (Gordon (1962) has set out the lpgf for the glycerol/adipic acid reaction, taking into account this different reactivity). The course of these polyesterifications is usually followed up to the gel point by titration of the carboxyl groups; after gelation this method cannot be used owing to partial insolubility. Kienle and his co-workers (1939, 1940, 1941) pursued the course of the reaction through the gel point by measuring the rate of water evolution in a graduated collecting tube. They found that water evolution continues smoothly through the gel point and beyond, with no suggestion of discontinuity in the rate arising from the formation of a gel. This observation is verified in this work (section (7.6)) where the course of the reaction is followed in a sealed system with a pressure transducer.

Gelation in polyfunctional polymerization is taken to be a manifestation of the formation of an "infinite" network (wall-to-wall structure), thus the gel point should coincide with the point at which α (the extent of reaction) reaches its critical value as specified by eq. (2.27). The results of all the work of these polyesterifications (Flory 1953) is that in every case the observed gel point is reached at higher than the theoretical extent of reaction. This is due to the failure of the earlier theories to take into account intramolecular condensation as demonstrated by Stockmayer (1945). By measuring the extent of reaction at the gel point of the reaction between pentaerythritol and adipic acid in

the presence of varying amounts of diluent and extrapolating the results to infinite concentration (where the intramolecular condensation is suppressed), Stockmayer (1945) found that the extent of reaction in the hypothetical system without cyclization agreed within experimental error with that predicted by the random-cross-linking model. This dilution technique has been used in this work (section (7.6)) to study mixtures of different ratios of polyol to acid.

Now that a model has been proposed (section (4.9)) for kinetically controlled reactions with intramolecular and substitution non-random effects, a detailed study of the pentaerythritol/adipic acid reaction was undertaken to investigate the applicability of this model to polyesterification reactions. A similar study was made with 1,1,1-trimethylol ethane, a homologue of pentaerythritol. The majority of the kinetic data were obtained at 175°C. The variation of temperature is, in fact, not of great interest here; the cross-linking and cyclization reaction are expected to have the same activation energies, and all statistical parameters (e.g. the gel point) will then be invariant once the time scale is adjusted to the temperature chosen. At 175°C it was found that the rate of etherification of pentaerythritol was negligible (section (7.6)) and that the gel times for the uncatalysed polyesterification for mixtures of pentaerythritol and adipic acid lay in a convenient range of 35 to 120 minutes.

The apparatus used in this study is described in section (7.3) and the results are presented in section (7.6). A detailed analysis

and discussion of the polyesterification reaction is given in Chapter 8. Firstly the pentaerythritol/adipic acid reaction is briefly reviewed.

7.2 The Pentaerythritol/Adipic Acid Reaction

The first paper dealing in particular with the pentaerythritol (PE) - adipic acid (AA) reaction was published by Cornish (1948). This paper, which contains a comprehensive literature survey, states the problems to be tackled and suggests how Kienle's (1939) apparatus can be modified to study this reaction. No experimental data are presented, in fact the only experimental results are given by Flory (1941), Stockmayer (1945) and Walker and Mackay (1951). In all these cases an 'equivalent' mixture of PE and AA was used, i.e. 1 mole PE and 2 moles AA. Using the random model the gel point condition (eq. (2.37)) predicts a gel point at $\alpha'_c = 1/\sqrt{3} = 0.577$. Flory (1941) reports a value of 0.605, Stockmayer (1945) a value of 0.63, and Walker and Mackay (1951) a value of 0.650. In each case the observed gel point is higher than the random value (0.577), indicating the presence of intramolecular condensation. In this work (section (7.6)) a mean value of 0.623 was observed. The reaction was studied by Stockmayer (1945) at three different temperatures (viz. 130°, 155°, 184°C) with and without the addition of p-toluene sulphonic acid as a catalyst, the gel point was observed to be 0.63 in all cases. The reason for the discrepancy between these studies is unclear. Impurities such as di-, tri-, and polypentaerythritol, all of which have a higher functionality than PE itself, would tend

to cause premature gelation. This might explain the relatively lower gel point obtained by Flory (1941) since his PE contained 49.6% hydroxyl content against the theoretical figure of 50.0%. In the work of Walker and Mackay (1951), the experiments were conducted in an open vessel and thus any loss of adipic acid would lead to an erroneously high result of the gel point as the acid value of the reaction mixture was used to calculate the extent of reaction. The value of the critical extent of reaction of 0.623 in this work (section (7.6)) was found independently from measurements of the amount of water evolved (pressure transducer) and by titration of the carboxyl group content of the reaction mixture.

Price, Gibbs and Zimm (1958) studied the extent of reaction at gelation of mixtures of adipyl chloride and trimethylol ethane (TME) using sym-tetrachloroethane as a solvent. A bulk polymerization of an equivalent mixture of TME and adipic acid was found to gel at a conversion of 0.723, which is to be compared with a value of 0.719 observed in this work (section (7.6)) and a value of 0.707 (eq. (2.38)) for the random-cross-linking model.

There has not been any detailed study of the kinetics of the condensation of polyfunctional alcohols and dibasic acids, although there have been several papers (e.g. Flory 1937, 1939; Davies and Hill 1953) on polyesterification reactions between dibasic acids and glycols. These studies will be discussed in section (8.1) with reference to polyfunctional alcohols.

7.3 Apparatus for studying the Polyesterification Reaction

A furnace has been designed to work in the range $20^{\circ} - 400^{\circ}\text{C}$, controllable to $\pm 0.01^{\circ}\text{C}$. Basically the furnace consists of a 10" diameter aluminium cylinder, 14" high. A 3" dia. hole runs through the axis of this cylinder, and two windows 6" x 2" allow observations to be made of apparatus in this air space. Aluminium inserts are used to vary the size of these windows to suit the experiment being conducted. The furnace contains four heating circuits, two 'ring' heaters in the body of the aluminium block and two wound around the outside of the cylinder, one above and one below the windows. The 'ring' heaters each consist of ~15' 'THERMOCOAX' heating element, type IN.I 10 (supplied by Research and Control Instruments Ltd., London, W.C.1) looped vertically at a fixed distance ($2\frac{1}{2}"$ and 4") from the centre of the cylinder, these heaters have a resistance of ~55 ohms (20°C). The two outer heaters are of Nichrome wire and have a resistance of ~60 ohms (20°C), these two heaters are mainly used as boosters to enable the furnace temperature to be raised quickly. Provision is made for rapid cooling by a system of water channels drilled through the block. Other holes allow temperature sensing elements to be inserted into the furnace. The whole block is thermally insulated with asbestos-glass. Plugs, to which different pieces of apparatus can be attached, close the top of the air space, whilst an axial shaft which projects into the furnace from underneath carries a magnet used as a magnetic stirrer.

For these polyesterification studies the block is thermostatted at 175.0°C . A constant voltage of 120 v. is applied to the inner ring-heater whilst a voltage of 75 v. is switched into the outer ring circuit by a relay (Electromethods 213 B) which is operated by a mercury contact thermometer (Electrical Thermometers Ltd.) having a scale of $0.1^{\circ}\text{C} \equiv 0.1 \text{ mm.}$ which is placed in the block. This contact thermometer allows a switching differential of 0.01°C ., as monitored by a thermistor (STC type Fl5) (the temperature variation of the furnace is shown later in fig. (7.4)); absolute temperatures are measured by a N.P.L. certified thermometer.

The rate of esterification is measured by following the rate of evolution of water in a sealed reaction vessel by means of a pressure transducer. This transducer (Consolidated Electrodynamics type 4-316) (fig. (7.1a)) is designed to measure a differential pressure of $\pm 100 \text{ cm. Hg}$ and can work up to a temperature of 300°C . The sensing elements of this variable-resistance type transducer are unbonded strain gauges connected in a four-arm bridge. Pressure against the diaphragm produces a displacement of the sensing elements, changing the resistance of the active arms and causing an output proportional to the applied pressure. A voltage of 5 volts is applied to the bridge circuit by a Solartron Power Supply Type AS 974 and this corresponds to an output of $\pm 10 \text{ mv.}$ for a pressure differential of $\pm 100 \text{ cm. Hg}$. The reference side of the transducer is sealed off under a pressure of 4 cm. of dry nitrogen. An adapter (fig. (7.1b)) is clamped with an 'O'-ring to the measuring side of the transducer and a glass-to-metal seal is brazed to this adapter

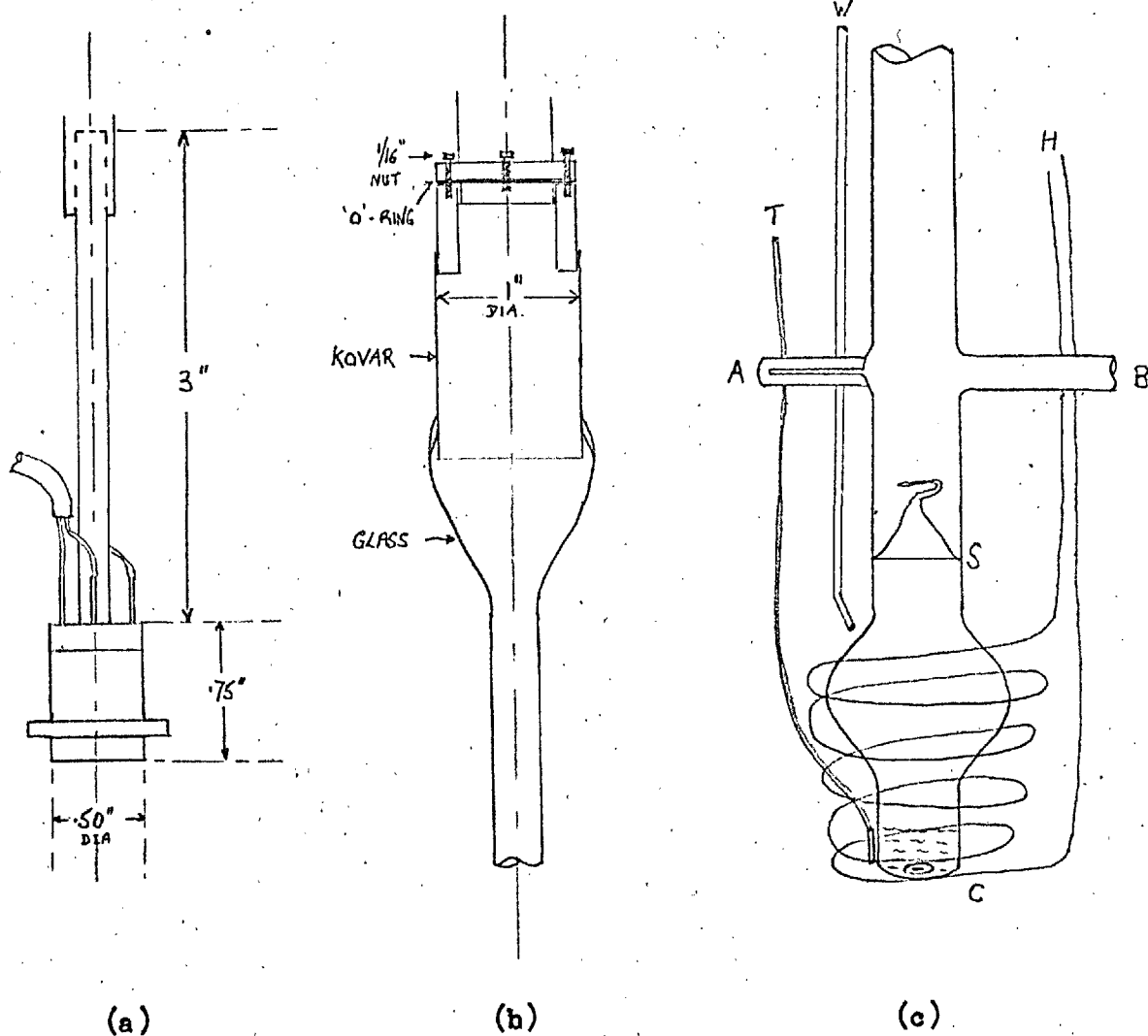


Fig. 7.1 (a) Pressure Transducer

(b) Adapter for connecting reaction vessel to transducer

(c) Reaction Vessel (actual size).

so that the glass reaction vessel can easily be sealed to this unit. The output from the transducer is displayed on a Graphispot type GR VAT recorder (Makers: SEFRAM, Paris; supplied by D-Mac, Guildford, Surrey). This recorder contains a galvanometer to which the output is connected, and the pen carriage automatically follows any deflection of a light spot by the galvanometer mirror. By the use of shunts this recorder has 10 sensitivity ranges from 1000 to 0.25 mV for full scale deflection. For most of this work the range of 5 mV full scale deflection is used. A calibration curve for the transducer at 24° and 175°C. is shown in Fig. (7.2), and this is used to convert the recorder readings directly to absolute pressure. The main disadvantage of the transducer is that it has a thermal zero shift of -0.01% full range/°C although the thermal sensitivity shift is less than $+0.001\%$ FR/°C, (see fig. (7.2)). The combined non-linearity and hysteresis is $\pm 0.16\%$ FR, and the calibration curve remained unaltered over a period of 2 years, it was checked every 3 months.

The reaction vessel is shown in fig. (7.1c) and is described in detail in section (7.4). It is found that when the reaction vessel and transducer are lowered into the furnace it takes a long time (~ 10 mins) for the reaction vessel to come into equilibrium with the temperature of the air space. It is also found that although the block remains constant at $175.0 \pm 0.03^\circ\text{C}$., the air space has a stable vertical gradient of $\sim 0.2^\circ\text{C}/\text{inch}$. To overcome these problems a small heater coil (H, fig. (7.1c)) is placed around the bottom of

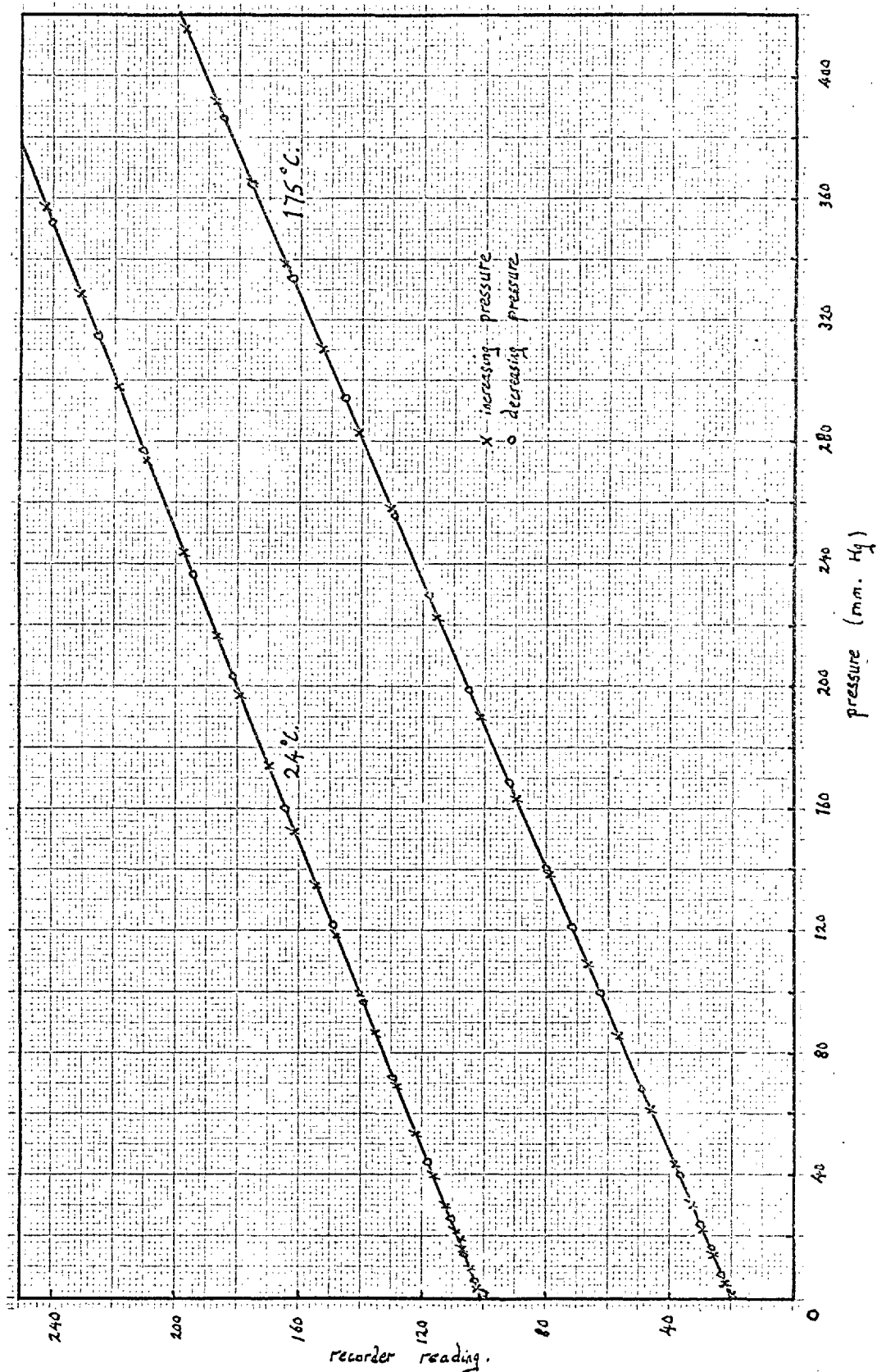


Fig. 7.2 Calibration curve for output of pressure transducer on recorder against absolute pressure.

1 .
the reaction vessel and this is used to raise the temperature of the reaction vessel to that of the block.

A proportional control operates this heater, so that the reaction vessel temperature is automatically kept at the block temperature over a period of several days. The voltage difference between two thermocouples, one in the aluminium block, the other (T) strapped to the side of the reaction vessel, is fed into a microvoltmeter (Pye Nanoammeter type 11360). The amplifier of this instrument delivers a current proportional to the deflection of the meter into an external circuit. A current of 1mA. can be obtained for an input of 100 μ V., i.e. a thermocouple temperature difference of 0.25 °C. This current is further amplified by a factor of 500 before passing into the 10 ohm heater coil around the reaction vessel. In this way the current flowing in the heater circuit is proportional to the temperature difference between the reaction vessel and the block. A simplified circuit diagram of the second D.C. amplifier is shown in fig. (7.3), basically it consists of two directly coupled germanium transistors. A diode in the input side renders the circuit inoperative if the temperature of the reaction vessel exceeds that of the block. The 'set zero' potentiometer allows a constant current to flow through the heater when the thermocouples are balanced. The actual circuit used includes means of supplying a large current to the heater, so that the reaction vessel may be rapidly heated to the required temperature; provision is also made for a larger constant current to be supplied to the heater than the simplified circuit diagram (fig. (7.3)) shows.

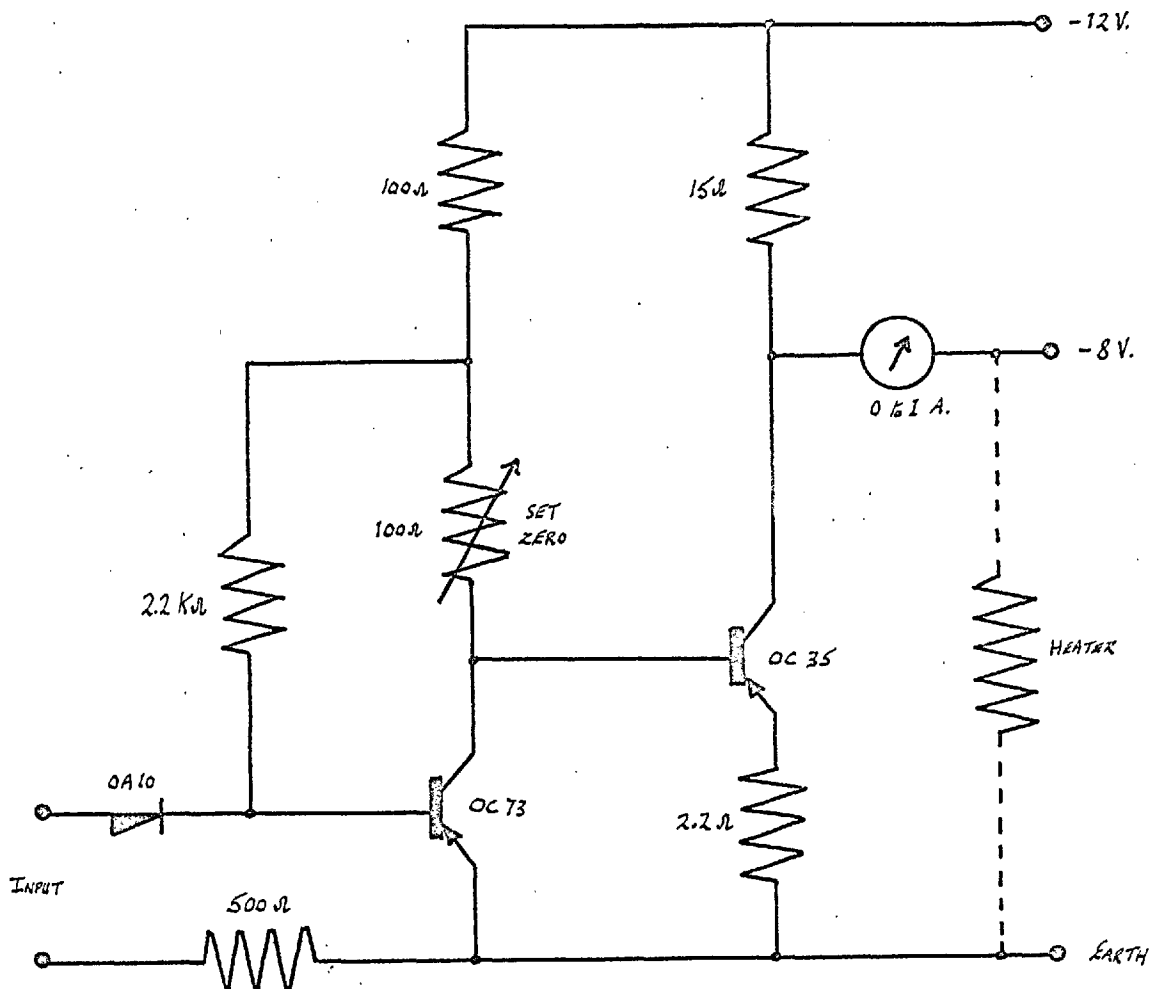


Fig. 7.3 Simplified circuit diagram of D.C. amplifier used in proportional controller.

Performance of Amplifier

Gain	500
Zero Drift	$4.8 \mu\text{A}/^\circ\text{C}$.
Full Scale Output	1 A.
Specified Source Resistance	$> 3 \text{ K}\Omega$
Input Resistance	750Ω
Load Resistance	0.1Ω
(0C 35 passes constant 0.3 A.)	

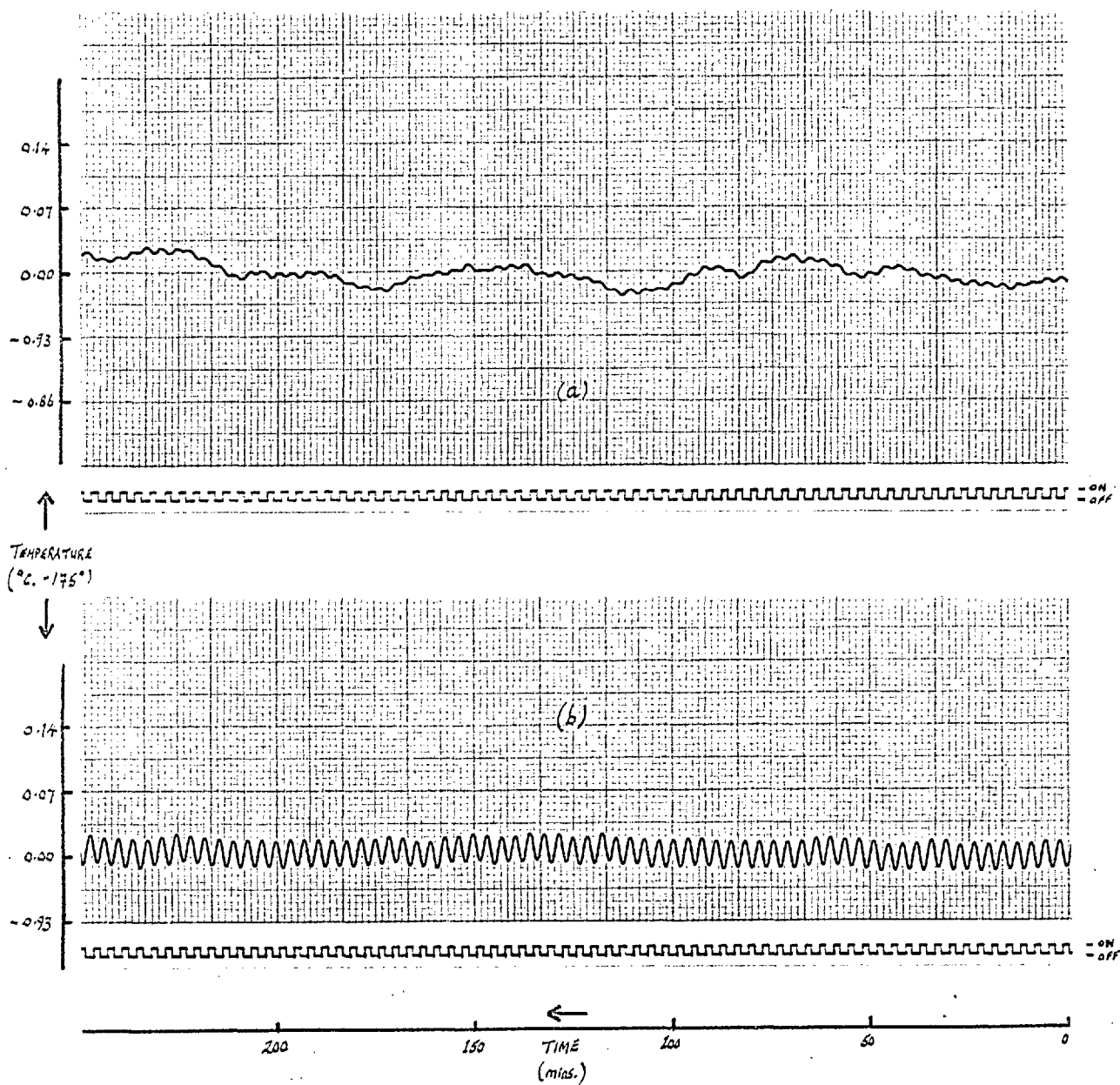


Fig. 7.4 a) temperature variation of reaction vessel
 b) temperature variation of furnace
 (event marker shows switching on and off of
 auxiliary heater).

Figure (7.4a) shows that the temperature variation of the reaction vessel at 175.0°C . was $\pm 0.04^{\circ}\text{C}$. over a period of 240 mins. Fig (7.4b) shows the temperature variation of the block for comparison. This figure (7.4a) was obtained by placing a thermistor in the reaction vessel and making it one arm of a Wheatstone bridge circuit. The out-of-balance current flowing in the circuit is presented on the recorder. Over a period of days the temperature control is certainly better than $\pm 0.1^{\circ}\text{C}$.

As well as the ancillary thermocouple (T) and heater (H), a tube (W) is placed against the reaction vessel (fig. (7.1c)). This allows water to be slowly dropped upon the bottom of the reaction vessel in order to delay commencement of the reaction until the transducer has reached the temperature of the block (as measured by another thermocouple fixed to the transducer). Equilibrium is seen by a constant reading from the transducer, this reading is taken as 'zero' pressure for the experimental run (see fig. (7.5)). The procedure for performing these runs is described in section (7.5).

7.4 Materials

Pentaerythritol was obtained from Eastman Kodak Co. and was purified by recrystallization from 0.005 N HCl; m.p. $261-262^{\circ}\text{C}$. The percentage of hydroxyl groups (acetylation method, Ogg, Porter, Willits 1945) is 49.99%, theoretical 50.00%.

Adipic acid was obtained from B.D.H. and recrystallized from water, m.p. 152.5°C ., % carboxyl group found to be 61.59%, theoretical 61.63%.

Trimethylol ethane (2 - hydroxy methyl - 2 - methyl - propane - 1, 3 - diol) was obtained from Eastman Kodak Co. and purified by two recrystallizations from 50/50 acetone/water mixture; m.p. 201°C., analysis gave 42.42% OH. theoretical 42.45%.

Diomethoxytetraglycol (1, 2 - Bis (2 - methoxyethoxy) ethane) which is used as a diluant, was obtained from Eastman Kodak Co. and purified by distillation, b.p. 167°C./5 cm. Hg.

The reaction mixtures are made up by accurately weighing out finely ground acid and polyol and intimately mixing these in a mortar, this batch (~4g.) is then used for the whole of the kinetic runs for that proportion of acid to alcohol. The equivalence of a mixture is calculated from the known weights of acid and alcohol, and checked by acid-base titration of samples from the batch. The equivalence, E , is defined as the ratio of moles of $-COOH$ to moles of $-OH$ in the mixture. The symbols ${}_1C$ and ${}_2C$ denote the concentration in moles/g. of $-OH$ and of $-COOH$ respectively; thus, $E = {}_2C / {}_1C$. The extent of reaction (β) is defined as the fractional conversion of hydroxyl groups when the acid is in excess in a mixture, and vice versa, i.e. when $E > 1$, $\beta = \beta_{OH} = \beta_1$; and when $E < 1$, $\beta = \beta_{COOH} = \beta_2$. We have that

$$\beta_1 = E \beta_2 \quad (7.1)$$

$$\text{and } \beta_1 = (\alpha_1 + \sigma_1) \quad (7.2)$$

$$\beta_2 = (\alpha_2 + \sigma_2) \quad (7.3)$$

7.5 Procedure

The reaction vessel is shown in fig. (7.1c). An accurately

weighed amount (~100 mg) of the reaction mixture, together with the magnetic stirrer, is placed in the bottom half of the reaction vessel which is then sealed off at point C. It is then sealed to the pressure transducer and connected to a vacuum line (via the side arm B). A heater is wound around the transducer assembly and the top half of the reaction vessel and this section baked at 200°C. under a high vacuum ($<10^{-5}$ mm. Hg) for several hours (usually overnight). The heater is then removed and the system flushed with argon before the break seal (S) is broken. It is necessary to have a pressure of ~50 cm. Hg of argon in the system when breaking the seal (S), otherwise the gas rushing out of the lower part of the reaction vessel carries with it some of the reaction mixture which may then be deposited in the side-arm. The whole system is now pumped down to $\sim 10^{-4}$ mm. Hg and left for several minutes before being filled with argon to a pressure of 5 mm. Hg and being sealed at point B. It was found that if the break-seal (S) was not incorporated, some of the monomer was lost during the long pumping period, leading to irreproducible results.

The thermocouple (T) and heater are now placed around the vessel and also a thermocouple is strapped to the transducer. The top part of the assembly is pre-heated by means of a heater wrapped around the plug to which the transducer-reaction vessel assembly is attached. The complete apparatus is then lowered into the furnace. The lower part of the reaction vessel is cooled by the water spray (W) until the transducer has reached thermal equilibrium (recorder reading

constant) and then rapidly heated (in under 1 min.) to 175°C . Zero time is taken to be the time at which the reaction vessel melts, this coinciding to a pressure increase displayed on the recorder. The proportional controller maintains the reaction vessel at $175.0^{\circ} \pm 0.04^{\circ}\text{C}$. A button magnet is brought directly underneath the vessel and rotated at 65 r.p.m. in order to stir the reaction mixture. The reaction is observed through a window (1" x 1") in the block with the aid of a telescope. During the initial part of the reaction the melt is seen to bubble vigorously; as the reaction proceeds the melt becomes more viscous and the bubbles take longer to rise. The gel point is taken to be the point at which the bubbles cease to rise and the melt remains a 'blown-up' visco-elastic solid; however at this point the stirrer then oscillates, but it is observed that the oscillatory motion is transmitted throughout the whole of the gel. The difference in conversion from the observed gel point and that at which the stirrer becomes stationary is $\sim 1\%$. Figure (7.5) shows the recorder trace for a typical run. The initial fluctuations in the output are due to the cooling of the reaction vessel before the transducer reaches thermal equilibrium. The boost heater to raise the temperature of the reaction vessel to the furnace temperature was switched on a blip A. The reaction starts at blip B on the trace, which corresponds to the reaction vessel attaining a temperature of 175°C . and the reaction mixture melting. The insert shows that part of the trace at which gelation occurred and illustrates the smooth transition through this region. Blip C denotes the point (taken to be the gel point) at

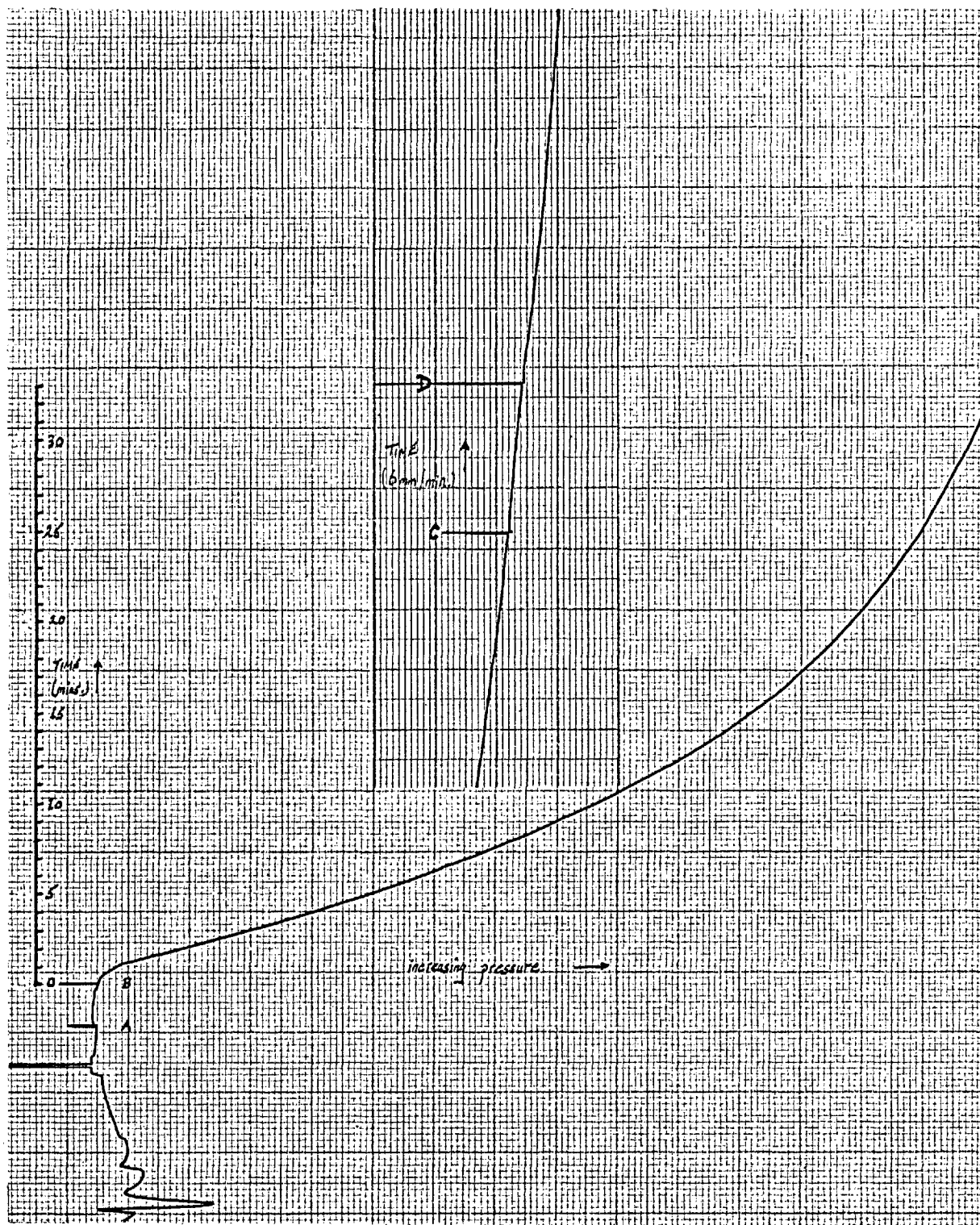


Fig. 7.5 Recorder trace for a typical PE/AA run at 175°C.

Insert shows the gel point region.

which the bubbles in the melt cease to rise, and blip D corresponds to the point at which the stirrer becomes stationary.

The reaction vessel is left in the furnace for a period of 10-15 times the gel time before the apparatus is removed. When the reaction vessel has cooled, it is cut open at point A on the capillary side arm and the volume measured with a gas burette. The gas burette consists of a bulb of known volume (previously calibrated with mercury) which has a tap at each end. The burette is connected to the reaction vessel via the capillary side arm and the whole system evacuated, the pressure being recorded with the transducer. The tap (A) nearest the reaction vessel is closed and the burette allowed to attain atmospheric pressure before the tap (B) is closed; tap (A) is now opened and the new pressure of the system recorded. This procedure is repeated about 8 times.

Let V_1 be the volume of the reaction vessel together with that of the connection with the gas burette up to tap (A), and V_2 be the volume of the gas burette between taps (A) and (B). If P_∞ is atmospheric pressure and P_i the pressure of the system after i increments of gas have been admitted:-

$$P_i V_1 + P_\infty V_2 = P_{i+1} (V_1 + V_2) \quad (7.4)$$

or letting $V_1/V_2 = V$ (7.5)

$$P_\infty - P_i = (P_i - P_\infty) V^i (1 + V)^{1-i} \quad (7.6)$$

thus a plot of $\log (P_\infty - P_i)$ against i has a slope of $\log (V/(1 + V))$, and knowing V_2 and the volume of the connection from the gas burette

to the reaction vessel, the required volume of the reaction vessel can easily be calculated. A typical volume calibration plot is shown in fig. (7.6).

The reaction vessel volume together with the known mass of starting material is used to calculate the theoretical pressure in the reaction vessel that would be attained if the reaction proceeded to 100% conversion. Thus the extent of reaction can be presented as a function of time. The volume of the reaction vessel used in this work is ~40 c.c., and using ~100 mg. of reaction mixture this corresponds to a maximum pressure of ~500 mm. Hg at 175°C.

The concentration dependence of the gel point due to ring formation is investigated by measuring the gel point of mixtures of polyol and acid in the presence of an inert solvent, dimethoxytetraglycol. The procedure is as outlined above, except that the transducer is not used. The reaction vessel is sealed as before to a bulb so that the final volume is ~50 c.c., after evacuating, the apparatus is filled with argon at ~20 cm. Hg. The run is performed in the same manner using the proportional controller to maintain the correct temperature of the reaction vessel. At gelation the apparatus is removed from the furnace and quickly quenched to freeze the reaction. The bottom part of the reaction vessel is cut off and placed in a flask containing 50 ml. of 50/50 ethanol/benzene mixture. This solution is refluxed for 15 hours before cooling. The contents of the flask are now titrated for carboxyl groups with N/10 tetrabutylammonium hydroxide in isopropanol to a phenolphthalein end

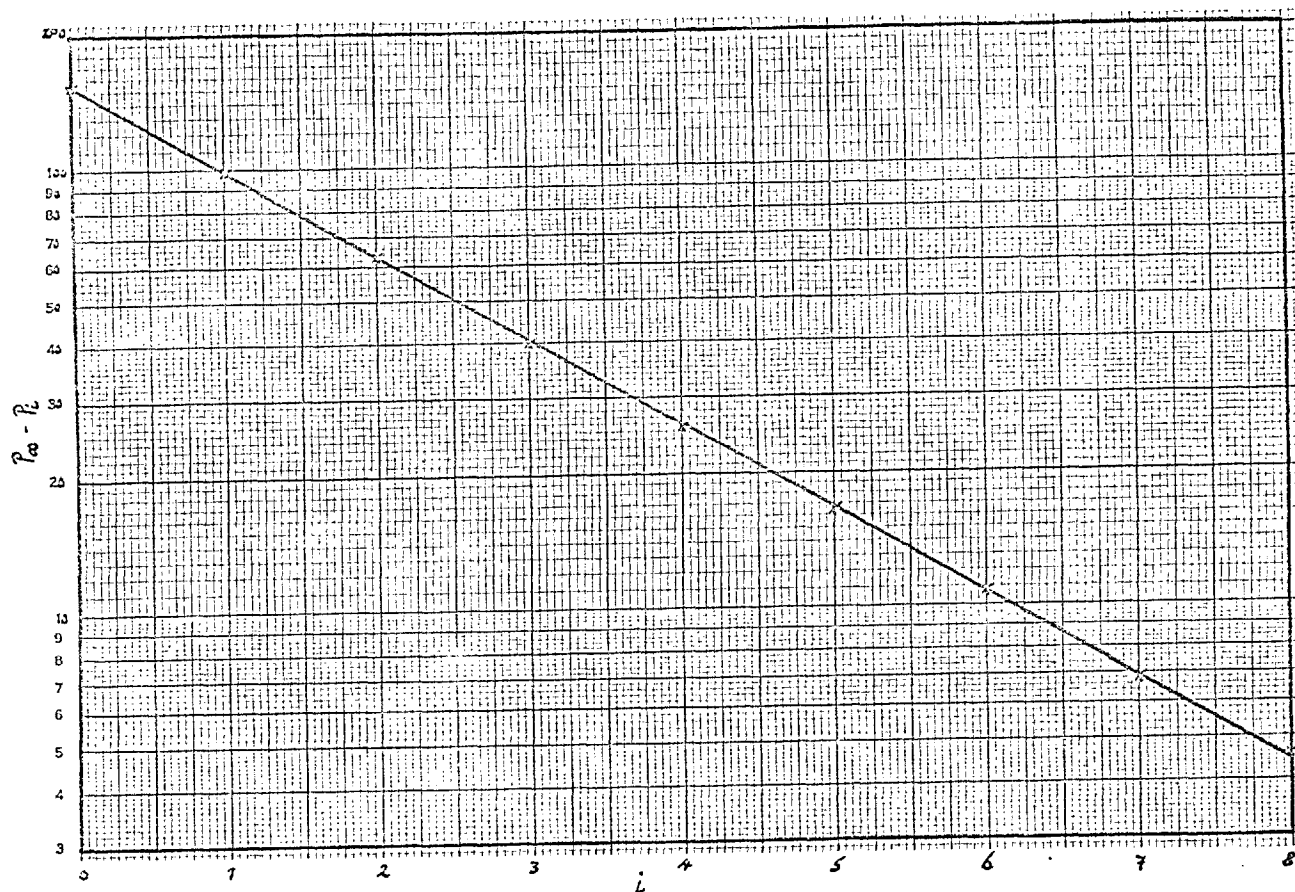


Fig. 7.6 Reaction vessel volume calibration plot.

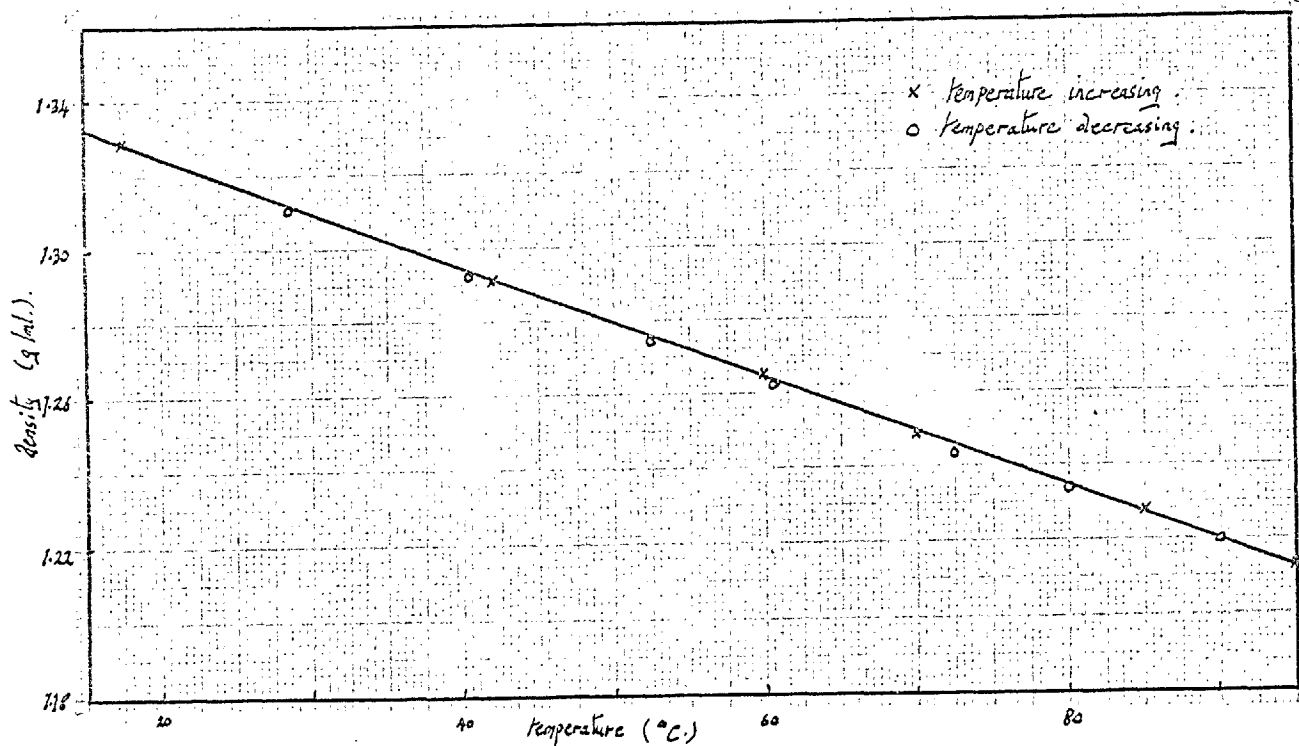


Fig. 7.7 Density of gelled equivalent PE/AA mixture against temperature.

point. This value of the carboxyl content immediately gives the extent of reaction. It is found that sodium or potassium hydroxide lead to the precipitation of a polymer salt and hence fading end points. The only other solvent found suitable for these polyesters was dimethyl formamide, but partial hydrolysis of this solvent leads to irreproducible results. If the reaction is allowed to continue past the gel point, substantially only the sol fraction will be titrated, hence care must be taken to stop the reaction at the onset of gelation.

This titration technique was also used to check the calculation of the extent of reaction as measured by the transducer. The runs were performed with the transducer, but the reaction quenched at some time before gelation and the reaction mixture titrated.

The calculation of the dilution of the system necessitated the determination of the density of the polymer and solvent at 175°C. The density of dimethoxytetraglycol was found using a specific gravity bottle to be 0.9928 g./ml. at 17.5° and 0.8396 g./ml. at 175°C. A density gradient column was set up in order to measure the density of the polymer. A series of glass floats (containing nickel to make them magnetic and manoeuvrable) ~1 mm. in diameter were constructed with densities in the range 0.9 - 1.5 g./ml. Each float is calibrated by measuring its balance point in liquids of known densities, so that its density is known to ± 0.00001 g./ml. The method of construction of these floats is described in detail by Dobson (1965). An equivalent mixture of PE/AA was reacted to gelation and the density of this polymer was measured using the

density gradient tube in the temperature range $15^{\circ} - 95^{\circ}\text{C.}$, as shown in fig. (7.7). Extrapolation of this plot to 175°C. gives a figure of $1.095 \pm 0.005 \text{ g./ml.}$ for the density of this polymer.

The density of the monomers was measured in a simple dilatometer consisting of a bulb and a precision capillary tube. The volume of the dilatometer, calibrated with mercury, was $\sim 0.5 \text{ cc.}$ The density of adipic acid was measured in the range $170^{\circ} - 220^{\circ}\text{C.}$ and at 175°C. is 1.093 g./cc. , the change in density in this range is $-0.0008 \text{ g./cc./}^{\circ}\text{C.}$ Similarly the density of trimethylol ethane was extrapolated to a value of 0.960 g/cc. from measurements in the range $210^{\circ} - 260^{\circ}\text{C.}$ in which the density change is $-0.00074 \text{ g/cc./}^{\circ}\text{C.}$ Owing to decomposition it was only possible to measure the density of pentaerythritol at just above its melting point, i.e. at 260°C it was found to be 1.08 g/cc. Assuming the same density temperature coefficient as trimethylolethane the extrapolated value at 175°C. is 1.14 g/cc.

7.6 Results

Preliminary work was aimed at measuring the kinetics of etherification of pentaerythritol. This reaction was catalysed with p-toluene sulphuric acid and studied in the range $195^{\circ} - 230^{\circ}\text{C.}$ This single component polycondensation is, of course, easier to treat statistically than a two component system. It was observed that although runs performed under identical conditions were reproducible, however at different catalyst concentrations and different temperatures, the gel points were not at the same fractional conversion. The reaction products were always coloured dark brown and had a characteristic

odour. It was also observed that when the reaction was allowed to continue for many times the gel time, the pressure in the system did not level off at a pressure corresponding to 100%, but continued to increase.

When pure pentaerythritol is heated at temperatures above 200°C. in vacuo it was found that it slowly decomposed evolving gases with a mean molecular weight of 32, and no gelation was observed, although the final pressure corresponded to an extent of reaction, based on the assumption that etherification was occurring and only water was being evolved, of greater than 100%. The products of this reaction had the same colour and characteristic odour as those of the catalysed reaction. Mass spectra and infra red analysis of the products of this decomposition reaction showed the presence of aliphatic saturated and unsaturated aldehydes (e.g. acetaldehyde, α -methyl acrolein). This preliminary work showed that pentaerythritol was thermally unstable above 200°C. and unsuitable for etherification studies which require higher temperatures than polyesterification reactions. As no gelation was observed in the uncatalysed experiments, it cannot be assumed that etherification is the primary reaction in this thermal decomposition of PE. The presence of carbonyl groups in the reaction products shows that C - C and C - O bonds are being broken, and this will have a pronounced effect on polymer chains and hence will cause a delay in gelation in the catalysed polyetherification reaction. In preliminary work in these laboratories, this delay had previously been attributed solely to intramolecular condensation.

These studies were a natural prologue to the investigation of the polyesterification reaction, and showed that at 175°C. the rate of etherification of PE catalysed by acids can be neglected in comparison with the rate of esterification. Runs performed with pure pentaerythritol, adipic acid, or trimethylolethane all showed negligible increase in pressure in the apparatus when left for periods of a day (the maximum time any polyesterification run was studied) at 175°C.

As a check on the method of measuring pressure to calculate the extent of reaction, a series of runs were performed in which the mixture was quenched at varying extents of reaction before the gel point. The reaction mixture was then titrated for carboxyl groups (section (7.5)). The extent of reaction calculated from the pressure reading and from the titration is compared in table (7.1); the excellent agreement shows that the pressure technique can be used with confidence for following the course of the reaction.

TABLE 7.1

Comparison of conversions as measured by transducer and titration.

Method	Extent of Reaction (β)				
pressure	0.235	0.478	0.537	0.610	0.624 *
titration	0.236	0.482	0.540	0.608	0.624 *

(* gel point)

To test the reproducibility of the experiments, two mixtures of the same equivalence were prepared and the rate curves (extent of reaction (β) against reduced time - gel time taken to be unity) of these mixtures at 175°C. were virtually identical (fig. (7.8a, b)). Another run was performed at 170°C. and the kinetic curve (fig. (7.8c)) was again superposable on the plot for the same mixture at 175°C. (fig. (7.8a)).

Various experiments were performed to confirm that under the experimental conditions used the polyesterification is kinetically controlled, i.e. that the backward rate constant is negligible. By increasing the quantity of starting material in the reaction vessel the pressure of water vapour in the system at any stage of the reaction is proportionally increased above the normal conditions. Doubling the amount of starting material left the rate curve unchanged (fig. (7.9a, c)). A series of runs were carried out in which varying amounts of water were added to the system before the reaction vessel was sealed off. Even when the initial water vapour pressure is similar to the maximum pressure in the normal experiments (i.e. ~50 cm. Hg), the kinetic curve is still superposable on the mean rate curve for that mixture (fig. (7.9 b, c)). A similar experiment with an equivalent mixture ($E = 1$) of TME/AA at 175° with an initial water pressure of 32 cm. Hg is compared with the mean of the kinetic data for the same mixture under normal conditions in table (7.2).

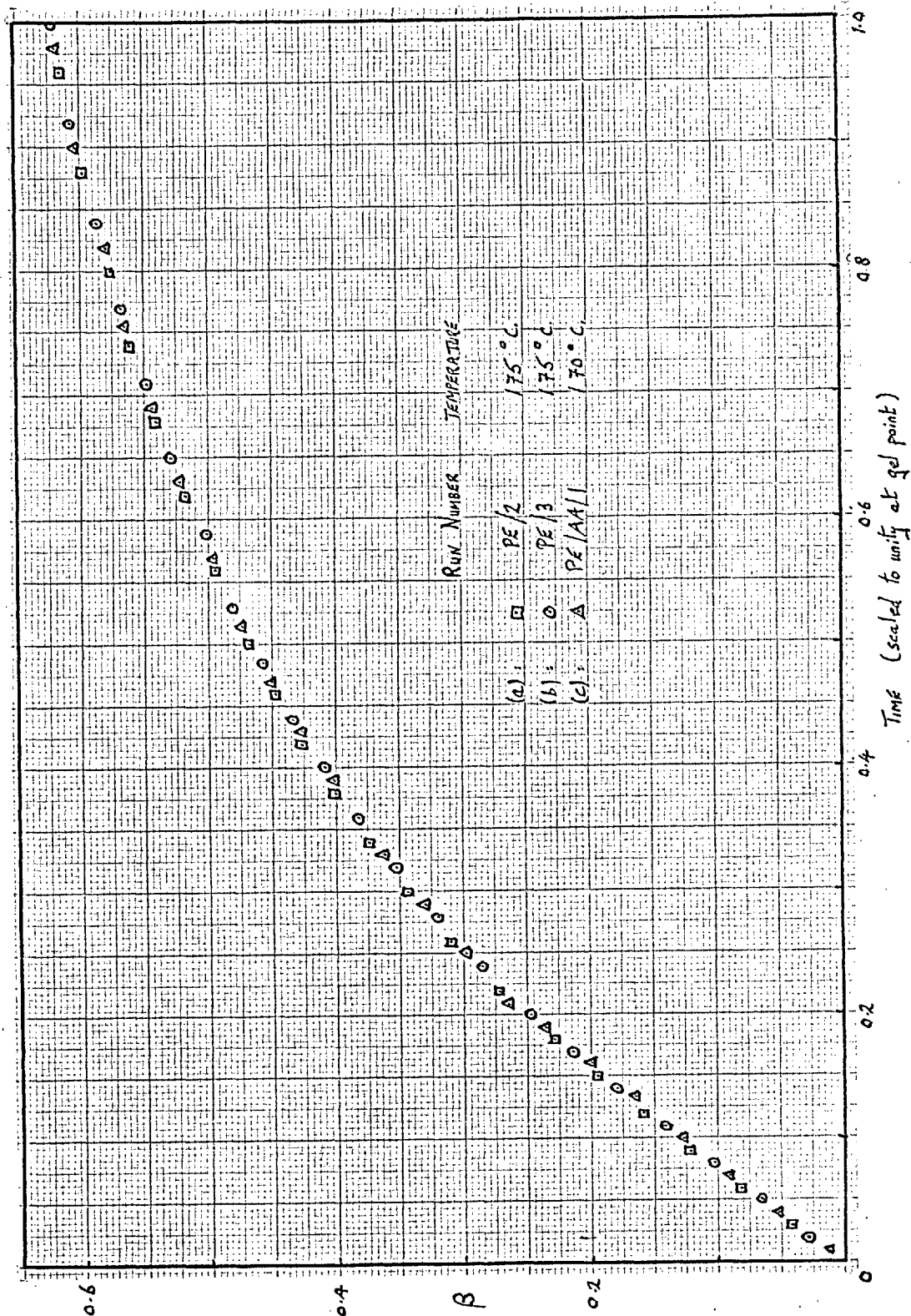


Fig. 7.8 Conversion against time plots for different equivalent mixtures of PE/AA.

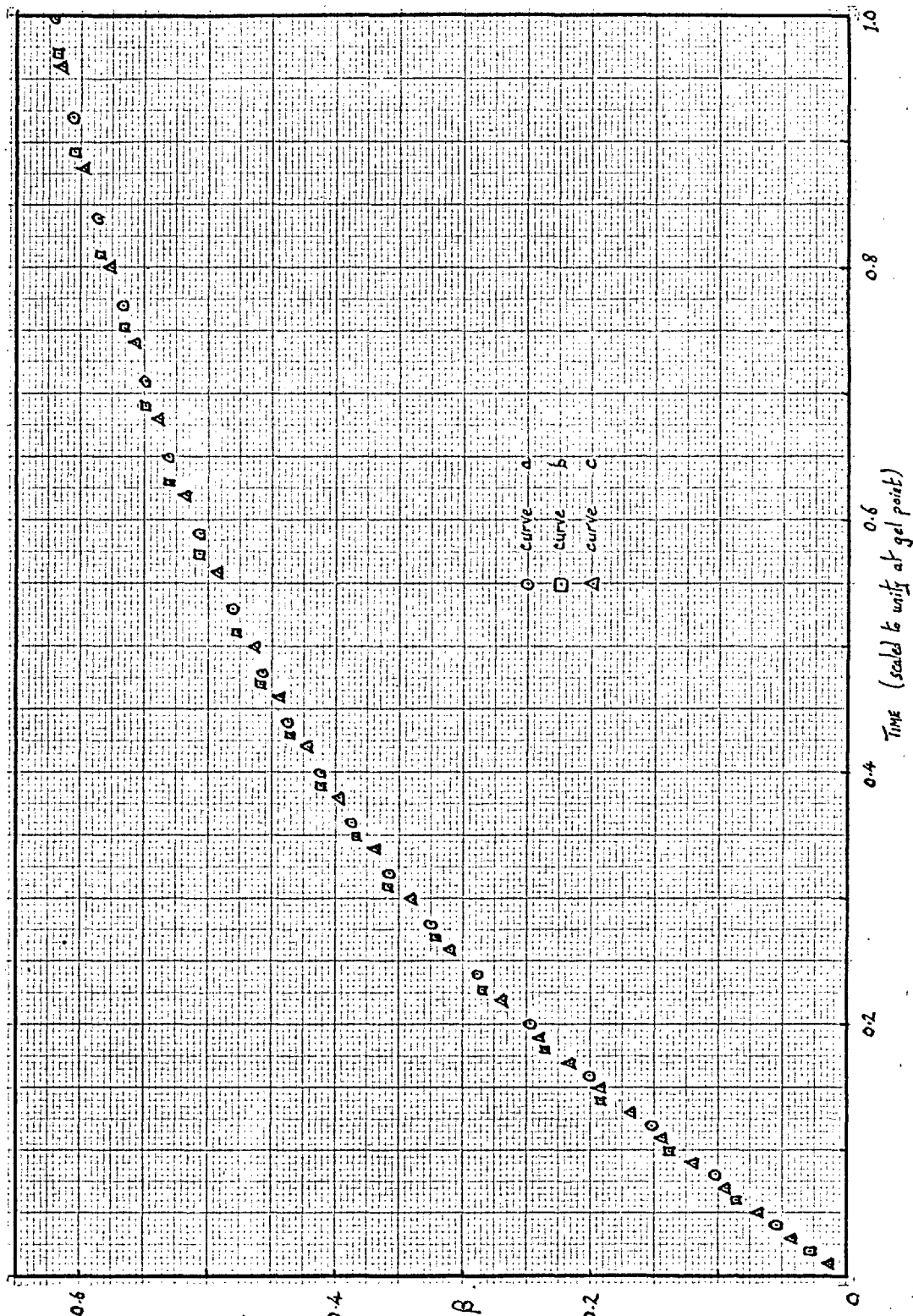


Fig. 7.9 Conversion against time plots for an equivalent mixture of PE/AA at 175°C.

- (a) pressure of 120 cm. Hg corresponds to $p = 1$
- (b) initial water pressure of 48 cm. Hg
- (c) mean of rate curve of runs performed under normal conditions.

TABLE 7.2

Comparison of conversion/time data for an equivalent mixture of TME/AA at 175°C. TME refers to mean of 4 runs performed under normal conditions (see table 7.6), TME/W refers to a run with an initial water pressure of 32 cm. Hg.

TIME	CONVERSION (μ)	
	TME	TME/W
0.05	0.096	0.105
0.10	0.191	0.211
0.15	0.277	0.289
0.20	0.350	0.361
0.30	0.459	0.465
0.40	0.535	0.540
0.50	0.589	0.593
0.65	0.647	0.650
0.80	0.685	0.686
1.00	0.719	0.721
GEL TIME		
(mins.)	58	60

From these results it is assumed that under the normal experimental conditions used in this work (section (7.5)), the polyesterification is irreversible up to the region of the gel

point. The forward reaction cannot be driven to 100% conversion (see below) in a reasonable time, but this is attributed to the onset of diffusion control when the free functionalities attached to the gel become isolated from each other, rather than to irreversibility.

A series of runs (between 3 and 6) were performed under normal conditions with each of 5 different mixtures of PE/AA and 3 mixtures of TME/AA, all at 175.0°C. The experimental conditions, gel point data and final conversions of these runs are summarized in table (7.3). An arithmetic mean of the gel point and gel time (and standard deviations) for each mixture, which will be used in the subsequent analysis (section (8.3)), is shown in table (7.4). Since the main interest lies in the region up to the gel point, in order to compare the kinetic curves of each run of a given mixture, a series of points (~ 100) was taken from the recorder chart for each run. A polynomial was fitted to these points on a computer and this polynomial was then used to calculate the extent of reaction (β_{calc}) at 50 fixed intermediate reduced times (the gel point being as always at time unity). The difference between the experimental and calculated extent of reaction at the observed time values is shown in fig. (7.10) for a typical run. The mean of the calculated extent of reaction for each run at these 50 time values was used to construct a mean kinetic curve for each mixture. The kinetic data of each run are tabulated in Appendix E, whilst these mean curves are presented in tables (7.5), (7.6). The extent of reaction of a

TABLE 7.3

Summary of experimental data, 175°C.

Run No.	Equiv.	P _{max} (mm. Hg)	Gel time (t _g) (mins.)	Gel conv.	Final Conv. (time > 20t _g)
Pentaerythritol/Adipic acid					
PE/1	1.00	466	38.0	0.634	0.93
PE/2	1.00	580	35.0	0.624	0.87
PE/3	1.00	528	30.0	0.622	0.89
PE/4	1.00	518	28.0	0.625	0.90
PE/5	1.00	695	34.0	0.619	0.87
PE/6	1.00	514	35.0	0.617	0.91
PE/7	0.50	560	112.0	0.796	0.89
PE/8	0.50	547	119.0	0.801	0.88
PE/9	0.50	521	103.0	0.809	0.93
PE/10	0.75	500	40.5	0.683	0.93
PE/11	0.75	604	41.0	0.679	0.95
PE/12	0.75	521	41.5	0.676	0.94
PE/13	1.50	465	31.0	0.742	0.96
PE/14	1.50	462	36.0	0.719	0.93
PE/15	1.50	472	38.0	0.741	0.97
PE/16	1.50	527	33.0	0.730	0.95
PE/17	1.50	570	34.0	0.744	0.96
PE/18	1.50	517	38.0	0.743	0.92
PE/19	2.00	470	46.0	0.877	0.98
PE/20	2.00	414	53.0	0.866	0.98
PE/21	2.00	462	54.0	0.872	0.94
PE/22	2.00	478	58.0	0.862	0.93
PE/23	2.00	442	63.0	0.860	0.93

TABLE 7.3 (cont.)

Run No.	Equiv.	P _{max} (mm. Hg)	Gel time (t _g) (mins.)	Gel conv.	Final Conv. (time > 20t _g)
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Trimethylolethane/Adipic acid

TME/1	1.00	486	55.5	0.717	0.88
TME/2	1.00	510	60.0	0.718	0.89
TME/3	1.00	607	57.0	0.719	0.90
TME/4	1.00	544	58.0	0.723	0.89
TME/5	0.67	553	124.0	0.863	0.97
TME/6	0.67	497	112.0	0.854	0.96
TME/7	0.67	488	115.0	0.850	0.96
TME/8	0.67	510	118.0	0.862	0.97
TME/9	0.67	503	108.0	0.862	0.96
TME/10	0.67	470	135.0	0.856	0.95
TME/11	1.50	504	71.0	0.872	0.97
TME/12	1.50	503	86.0	0.860	0.96
TME/13	1.50	496	87.0	0.866	0.95
TME/14	1.50	479	80.0	0.869	0.97
TME/15	1.50	523	73.5	0.870	0.94
TME/16	1.50	499	68.5	0.872	0.92

TABLE 7.4

Gel point data, 175°C.

Pentaerythritol/Adipic acid

Equiv. (E)	Random (α_r)	Conversion (β_g)	Time (mins.)
0.50	0.816	0.802 (± 0.006)	111 (± 8.0)
0.75	0.667	0.680 (± 0.004)	41 (± 0.5)
1.00	0.577	0.623 (± 0.006)	33 (± 1.5)
1.50	0.707	0.737 (± 0.010)	35 (± 3.0)
2.00	0.816	0.867 (± 0.007)	55 (± 6.0)

Trimethylol ethane/Adipic acid

0.67	0.866	0.858 (± 0.005)	119 (± 2.0)
1.00	0.707	0.719 (± 0.003)	58 (± 10)
1.50	0.866	0.868 (± 0.005)	78 (± 8.0)

representative run from each mixture of PE/AA and TME/AA is tabulated up to 20 times the gel time in table (7.7), (7.8).

Although points can be read off the recorder chart to ± 0.1 mm. corresponding to ± 0.0002 in β_{exp} , the error of ± 1 mm. in both the initial zero point and in the gel point leads to an estimated experimental error of ± 0.004 in the absolute values of the extent of reaction (β_{exp}).

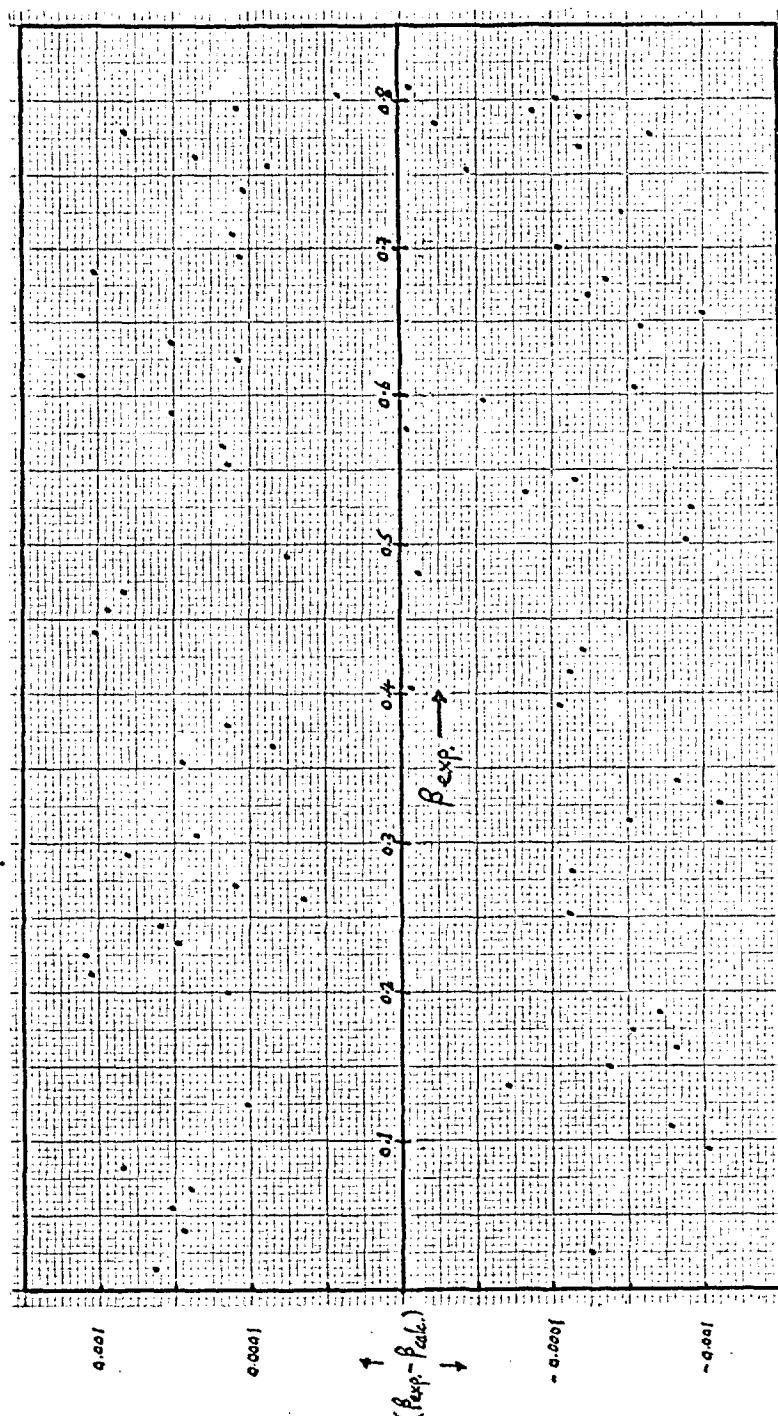


fig. 7.10 Difference plot of $(\beta_{exp} - \beta_{calc})$ against β_{exp} for run PE/7, (shown on a log scale). The value of β_{calc} is computed, from a polynomial fitted to the experimental points, at the same time value as β_{exp}

Mean kinetic data up to the gel point (time unity) for PE/AA at 175°C.

TIME	EQUIVALENCE (E)				
	0.50	0.75	1.00	1.50	2.00
0.00	0.0000	0.0000	0.0000	0.0000	0.0000
0.01	0.0471	0.0100	0.0140	0.0163	0.0254
0.02	0.0938	0.0377	0.0281	0.0322	0.0503
0.03	0.1382	0.0562	0.0420	0.0481	0.0746
0.04	0.1795	0.0744	0.0555	0.0639	0.0993
0.05	0.2175	0.0924	0.0687	0.0796	0.1237
0.06	0.2523	0.1101	0.0817	0.0952	0.1482
0.07	0.2841	0.1272	0.0945	0.1106	0.1726
0.08	0.3133	0.1439	0.1072	0.1257	0.1967
0.09	0.3401	0.1600	0.1198	0.1406	0.2204
0.10	0.3649	0.1755	0.1324	0.1551	0.2435
0.11	0.3878	0.1905	0.1449	0.1694	0.2660
0.12	0.4091	0.2049	0.1572	0.1834	0.2878
0.13	0.4290	0.2189	0.1694	0.1972	0.3088
0.14	0.4476	0.2324	0.1814	0.2107	0.3290
0.15	0.4650	0.2455	0.1931	0.2240	0.3484
0.16	0.4814	0.2583	0.2046	0.2370	0.3670
0.17	0.4967	0.2707	0.2157	0.2498	0.3850
0.18	0.5112	0.2827	0.2266	0.2625	0.4023
0.19	0.5246	0.2944	0.2372	0.2748	0.4190
0.20	0.5376	0.3058	0.2475	0.2870	0.4352
0.22	0.5611	0.3275	0.2673	0.3106	0.4660
0.24	0.5820	0.3480	0.2862	0.3333	0.4949
0.26	0.6006	0.3673	0.3042	0.3551	0.5219
0.28	0.6172	0.3853	0.3214	0.3759	0.5470
0.30	0.6320	0.4023	0.3379	0.3958	0.5702
0.32	0.6452	0.4183	0.3536	0.4149	0.5915
0.34	0.6570	0.4335	0.3686	0.4331	0.6111
0.36	0.6678	0.4479	0.3829	0.4504	0.6291
0.38	0.6775	0.4616	0.3964	0.4669	0.6458
0.40	0.6865	0.4747	0.4092	0.4825	0.6614
0.42	0.6949	0.4871	0.4214	0.4973	0.6759
0.44	0.7027	0.4988	0.4330	0.5112	0.6896
0.46	0.7100	0.5100	0.4439	0.5244	0.7024
0.48	0.7169	0.5205	0.4544	0.5369	0.7143
0.50	0.7234	0.5305	0.4644	0.5488	0.7256
0.53	0.7323	0.5445	0.4787	0.5657	0.7411
0.56	0.7404	0.5577	0.4921	0.5816	0.7553
0.59	0.7476	0.5701	0.5048	0.5967	0.7683
0.62	0.7541	0.5817	0.5168	0.6111	0.7804
0.65	0.7601	0.5926	0.5281	0.6247	0.7914
0.68	0.7655	0.6026	0.5387	0.6375	0.8014
0.71	0.7706	0.6119	0.5486	0.6495	0.8103
0.74	0.7754	0.6206	0.5580	0.6606	0.8185
0.77	0.7798	0.6289	0.5670	0.6711	0.8262
0.80	0.7839	0.6367	0.5756	0.6810	0.8334
0.84	0.7885	0.6461	0.5866	0.6936	0.8419
0.88	0.7923	0.6547	0.5969	0.7056	0.8490
0.92	0.7959	0.6636	0.6065	0.7166	0.8564
0.96	0.7994	0.6715	0.6156	0.7268	0.8624
1.00	0.8024	0.6797	0.6234	0.7367	0.8675

TABLE 7.6

Mean kinetic data up to gel point (time unity) for TME/AA at 175°C.

TIME	EQUIVALENCE (E)		
	0.67	1.00	1.50
0.00	0.0000	0.0000	0.0000
0.01	0.0471	0.0105	0.0381
0.02	0.0935	0.0389	0.0761
0.03	0.1380	0.0581	0.1129
0.04	0.1802	0.0774	0.1481
0.05	0.2198	0.0965	0.1816
0.06	0.2571	0.1157	0.2134
0.07	0.2918	0.1347	0.2436
0.08	0.3243	0.1536	0.2725
0.09	0.3546	0.1723	0.3000
0.10	0.3827	0.1908	0.3264
0.11	0.4089	0.2089	0.3516
0.12	0.4332	0.2266	0.3757
0.13	0.4558	0.2439	0.3986
0.14	0.4768	0.2607	0.4205
0.15	0.4963	0.2770	0.4413
0.16	0.5144	0.2927	0.4610
0.17	0.5312	0.3079	0.4797
0.18	0.5470	0.3225	0.4973
0.19	0.5617	0.3365	0.5140
0.20	0.5754	0.3499	0.5298
0.22	0.6004	0.3752	0.5589
0.24	0.6225	0.3984	0.5849
0.26	0.6420	0.4200	0.6085
0.28	0.6593	0.4399	0.6299
0.30	0.6747	0.4586	0.6493
0.32	0.6884	0.4760	0.6671
0.34	0.7008	0.4924	0.6833
0.36	0.7120	0.5076	0.6981
0.38	0.7223	0.5219	0.7117
0.40	0.7319	0.5351	0.7241
0.42	0.7407	0.5475	0.7355
0.44	0.7489	0.5590	0.7461
0.46	0.7565	0.5697	0.7559
0.48	0.7635	0.5799	0.7650
0.50	0.7700	0.5894	0.7736
0.53	0.7789	0.6029	0.7854
0.56	0.7870	0.6153	0.7959
0.59	0.7947	0.6267	0.8051
0.62	0.8020	0.6371	0.8132
0.65	0.8087	0.6466	0.8202
0.68	0.8145	0.6554	0.8265
0.71	0.8195	0.6636	0.8321
0.74	0.8241	0.6712	0.8373
0.77	0.8287	0.6783	0.8421
0.80	0.8336	0.6848	0.8466
0.84	0.8399	0.6926	0.8521
0.88	0.8449	0.7000	0.8570
0.92	0.8497	0.7068	0.8609
0.96	0.8533	0.7127	0.8646
1.00	0.8579	0.7191	0.8682

TABLE 7.7

Kinetic data for mixtures of PE/AA, 175°C.

(GEL TIME at time unity)

Equivalence (E) (Run No.)	0.50 (PE/8)	0.75 (PE/11)	1.0 (PE/3)	1.5 (PE/18)	2.0 (PE/21)
Gel Time (mins.)	119	41	30	34	54
TIME	EXTENT OF REACTION (β_{exp})				
0.05	0.215	0.075	0.065	0.074	0.130
0.10	0.352	0.151	0.129	0.147	0.247
0.20	0.529	0.287	0.246	0.287	0.435
0.30	0.629	0.393	0.336	0.403	0.572
0.40	0.684	0.474	0.410	0.489	0.661
0.50	0.721	0.532	0.466	0.556	0.725
0.65	0.758	0.592	0.530	0.631	0.793
0.80	0.782	0.636	0.576	0.688	0.839
1.00	0.801	0.679	0.622	0.744	0.872
1.10	0.807	0.696	0.638	0.764	0.885
1.25	0.822	0.720	0.667	0.792	0.899
1.50	0.836	0.748	0.695	0.829	0.912
1.75	0.843	0.773	0.721	0.851	0.922
2.00	0.854	0.790	0.743	0.869	0.928
2.50	0.860	0.820	0.773	0.889	0.932
3.00	0.864	0.834	0.790	0.902	0.935
4.00	0.871	0.864	0.822	0.912	0.938
5.00	0.874	0.899	0.841	0.917	0.939
6.00	0.876	0.915	0.852	0.918	0.940
8.00	0.877	0.931	0.866	0.919	0.942
10.0	0.877	0.939	0.877	0.920	0.943
12.0	0.877	0.943	0.884	0.921	0.943
15.0	-	0.945	0.887	0.922	0.944
20.0	-	0.946	0.888	0.922	0.944

TABLE 7.8

Kinetic data for mixtures of TME/AA, 175°C.

(GEL TIME at time unity)

Equivalence (E)	0.067	1.00	1.50
(Run No.)	(TME/10)	(TME/2)	(TME/16)
Gel Time (mins.)	135	60	68.5

TIME	EXTENT OF REACTION (β_{exp})		
0.05	0.221	0.081	0.190
0.10	0.387	0.164	0.340
0.20	0.577	0.322	0.533
0.30	0.676	0.446	0.647
0.40	0.733	0.534	0.722
0.50	0.771	0.592	0.773
0.65	0.809	0.650	0.825
0.80	0.836	0.687	0.851
1.00	0.856	0.718	0.872
1.10	0.864	0.733	0.876
1.25	0.873	0.758	0.883
1.50	0.888	0.773	0.887
1.75	0.896	0.791	0.891
2.00	0.902	0.803	0.894
2.50	0.909	0.832	0.897
3.00	0.919	0.843	0.900
4.00	0.927	0.852	0.904
5.00	0.935	0.859	0.907
6.00	0.944	0.865	0.909
8.00	0.946	0.876	0.911
10.0	0.947	0.884	0.913
12.0	0.947	0.890	0.915
15.0	-	0.893	0.916
20.0	-	0.894	0.916

The results of the dilution experiments in which the gel point conversion is measured by titration (section (7.5)) as a function of the volume of the system are presented for the PE/AA system in table (7.9) and for the TME/AA system in table (7.10). The dilution, D , of the reaction mixture is defined as

$$D = \frac{\text{solvent vol.} + \text{polymer vol.}}{\text{polymer vol.}} \quad (7.7)$$

In fig. (7.11), (7.12) the values of β_c are plotted against D and the least squares line through these points is extrapolated to zero volume ($D = 0$). The value obtained at $D = 0$ is the critical extent of reaction (α_c) in the absence of cyclization and is compared with the random value (eq. (2.38)) in table (7.11) together with the standard deviation of the observed β_c from the least squares line and the coefficient d_1 of the equation for this line which takes the form

$$\beta_c = \alpha_c + d_1 D \quad (7.8)$$

TABLE 7.9

PE/AA dilution results, 175°C.

Equivalence (E)	$C_{OH}^{\circ} \times 10^3$ equiv./g.	D (eq. (7. 7))	β_c
1.0	9.34	1.00	0.624
1.0	8.47	1.13	0.635
1.0	6.97	1.44	0.640
1.0	6.28	1.64	0.644
1.0	6.21	1.66	0.653
1.0	5.88	1.77	0.673
1.0	5.13	2.07	0.690
1.0	4.74	2.26	0.696
1.5	6.96	1.00	0.741
1.5	5.25	1.43	0.777
1.5	5.23	1.43	0.759
1.5	4.36	1.78	0.805
1.5	4.18	1.87	0.805
1.5	4.06	1.93	0.796
2.0	5.55	1.00	0.868
2.0	5.05	1.13	0.878
2.0	4.86	1.19	0.914
2.0	4.77	1.21	0.888
2.0	4.71	1.23	0.890
2.0	4.19	1.42	0.908
2.0	3.96	1.52	0.938
2.0	3.65	1.68	0.918

TABLE 7.10

TME/AA dilution results, 175°C.

Equivalence (E)	$C_{OH} \times 10^3$ equiv./g.	D (eq. (7.7))	β_c
1.0	8.84	1.00	0.728
1.0	7.07	1.33	0.738
1.0	6.32	1.52	0.759
1.0	5.94	1.63	0.772
1.0	5.24	1.89	0.775
1.5	6.68	1.00	0.868
1.5	5.50	1.28	0.880
1.5	5.16	1.39	0.889
1.5	4.61	1.59	0.906
1.5	4.27	1.73	0.910
1.5	3.95	1.90	0.912

TABLE 7.11Least squares data and extrapolated value of α_c from
fig. (7.11), (7.12)

PE/AA (fig. (7.11))

Equivalence (E)	α_c	d_1 (eq. (7.8))	standard deviation	α_c^* (eq. (2.38))
1.00	0.561	0.059	± 0.008	0.577
1.50	0.670	0.070	± 0.009	0.707
2.00	0.790	0.085	± 0.013	0.816

TME/AA (fig. (7.12))

1.00	0.667	0.059	± 0.006	0.707
1.50	0.814	0.054	± 0.004	0.866

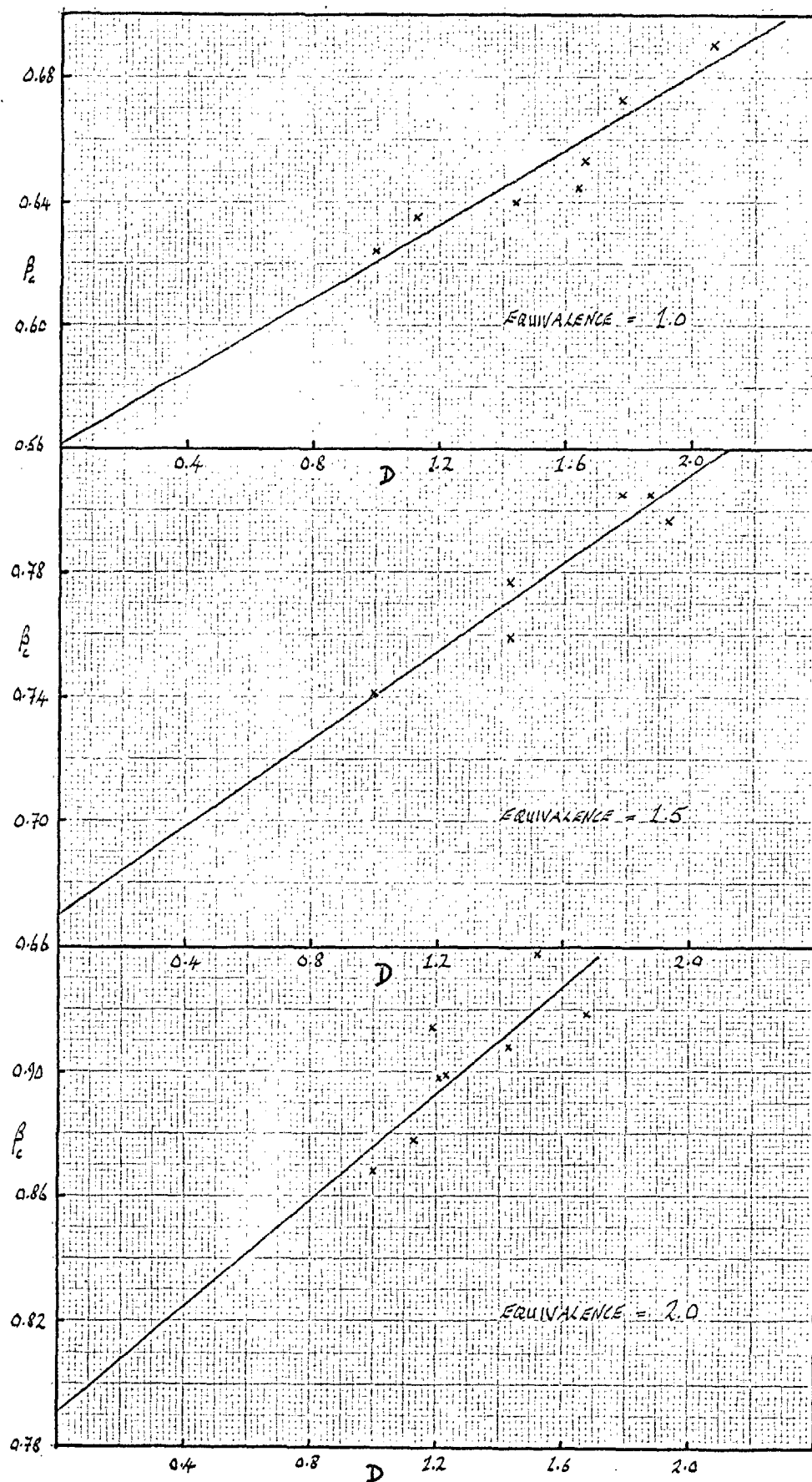


Fig. 7.11 β_c against D for PE/AA, 175°C.

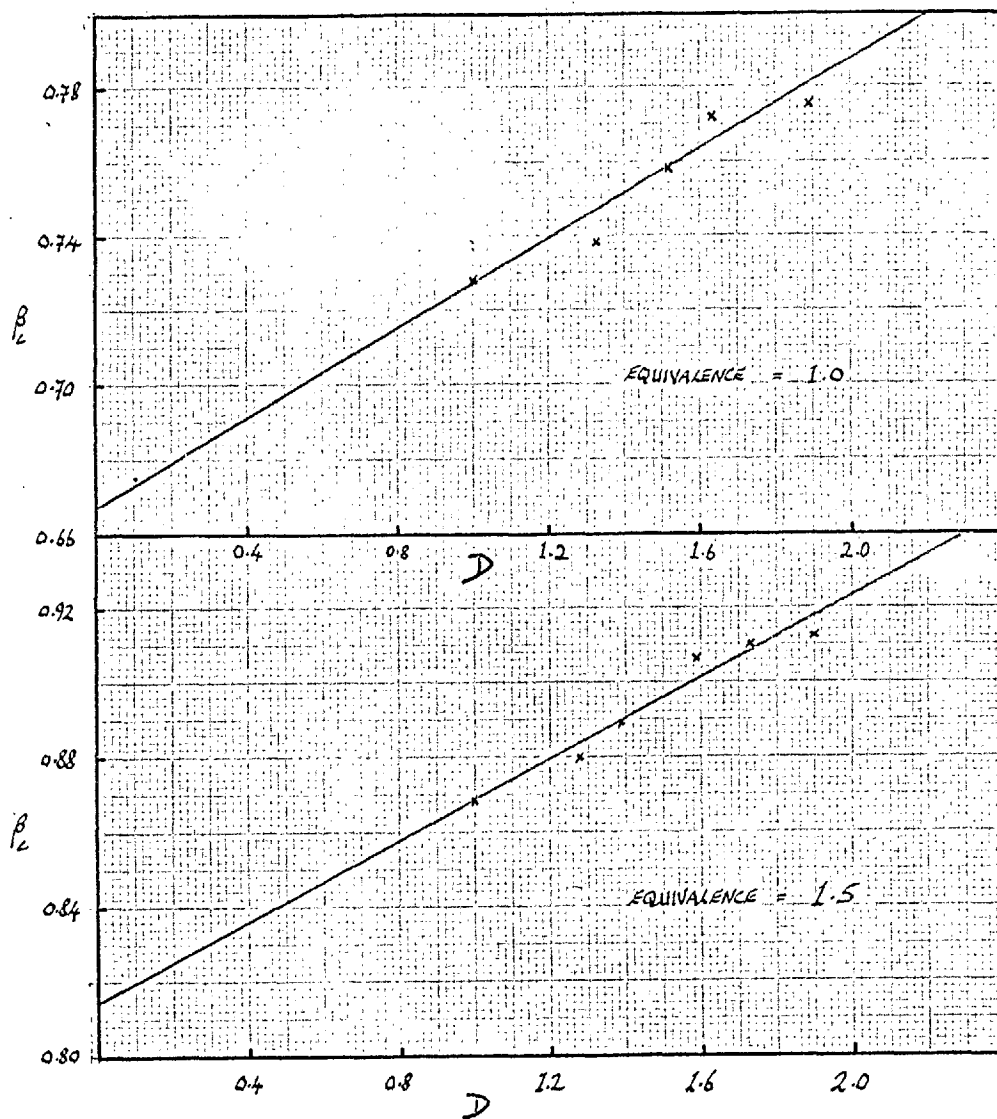


Fig. 7.12 β_2 against D for TME/AA, 175°C.

CHAPTER 8

ANALYSIS OF POLYESTERIFICATION RESULTS

8.1 Introduction

It is a surprising fact that despite their great technological importance many of the principal features of polyesterification reactions are unresolved by the published studies of these processes. Thus, there is uncertainty on such items as the order of the reaction, and whether this is markedly dependent upon the medium; the incidence of equilibrium in the condensation; the possibly determining influence of the rate of removal of water, etc. The most complete summary of earlier published results is given by Kuchler (1951) in an account which indicates the doubtful aspects. Many experimental studies on the polycondensation reaction between dibasic acids and glycols have been reported by various authors, among them Menshytkin (1882), Dostal and Raff (1936), Flory (1937, 1939), Rafikov and Korshak (1949), Colonge and Stuchlik (1950), Davies and Hill (1953), Tang and Yao (1959), and others, but quite varied results were obtained.

According to Flory (1937), polyesterification in the absence of a foreign acid, owing to the catalytic effect of the dibasic acid molecule, is a third-order reaction. Tang and Yao (1959) attempted to show that polyesterification is provoked by the catalysis by hydrogen ions. When the dibasic acid and the polyol react in an equivalent ratio in the presence of a (strong) foreign acid, the

hydrogen ion derives mainly from the catalyst and the polyesterification is thus a second-order reaction. On the other hand, in the "uncatalysed" esterification, the hydrogen ions come from the ionization of the dibasic acid, and the reaction is a $2\frac{1}{2}$ -order reaction. When the acid and polyol react in a non-equivalent ratio, the order of the reaction is more complicated, but their results were found to be in good agreement with the hydrogen ion catalytic mechanism. Tang and Yao (1959) also re-examined the data of previous workers and they were all found to conform to their proposed mechanism.

The kinetic equation derived from this hydrogen ion mechanism has recently been criticized (Wu, Ling and Ma, 1963) on the grounds that the equilibrium constant for the ionization of the acid is a function of the extent of reaction. It was assumed in the derivation of the kinetic equation that it remained constant. If the dielectric constant of the reaction medium decreases as a function of conversion, the electrostatic forces between positive and negative ions are increased, and the formation of undissociated acid molecules is favoured. In the course of the polyesterification reaction the disappearance of polar hydroxyl and carboxyl groups replaced by less polar ester groups will cause the dielectric constant of the reaction medium to fall with conversion. Wu, Ling and Ma (1963) estimated the ionization constant from measurements of the conductivity of the reaction system. They found that the equilibrium ionization constant (K_e) of carboxylic acid group in the system ethylene glycol/adipic acid at 100°C. decreased by three orders of magnitude in the range $0 < \beta < 0.65$, and

when $\beta > 0.65$ the conductance of the reaction system is as small as that in deionized water. By plotting $-\log (K_e)$ against the extent of reaction β , they obtained a linear reaction. However a $2\frac{1}{2}$ -order plot $((1 - \beta)^{-3/2} \text{ vs } t)$ of data obtained for the reaction between ethylene glycol and adipic acid at 140°C . is almost linear up to $\sim 80\%$ reaction, after which there is a slight downward curvature. Clearly, if K_e varies by several orders of magnitude during the reaction such a plot would have a very pronounced downward curvature, even at low conversions, and hence it must be assumed that the hydrogen ion is not the catalysing species for the uncatalysed polyesterification reaction. This is confirmed by the observation that the conductivity of the system at high extents of reaction is extremely small.

In the next section (8.2) the pentaerythritol/adipic acid results are analyzed with the aim of determining the kinetic order of the reaction. The effect of the non-random contributions to the apparent order of the polyesterification is discussed. Having fixed the order of the reaction and incorporated it into the differential rate equations, the linear substitution parameters N_1 , N_2 are estimated in section (8.3) from the concentration dependence of the gel points. Using these values the cyclization parameter (λ) is found by fitting the experimentally observed gel points for different mixtures. As a check on the values obtained for these non-random parameters (N_1 , N_2 , λ), the rate curve is computed for each mixture and compared with the observed rate curves in section (8.4). Before a final discussion of the results is given the post-gel model is used to compare the observed conversion at several points after the gel point with various

values of the parameter m which is a measure of the effect of the network on the cyclization reaction. A graph showing how σ increases with α through the whole of the reaction will be presented in section (8.5).

8.2 Kinetic order of polyesterification

For a random cross-linking reaction, the rate of the polyesterification process can be written for the n^{th} -order reaction normally contemplated as

$$-d[\text{COOH}]/dt = k[\text{OH}][\text{COOH}]^{n-1} \quad (8.1)$$

where concentrations are expressed as equivalents of the functional groups. By so expressing the rate, the complications of writing a separate rate equation for the reaction of each molecular species with every other are avoided. In adopting this procedure we imply that the reaction is random, i.e. there are no substitution or cyclization effects. It has been shown (Flory 1939, 1940) that the course followed by mono- and polyesterifications are similar, and the rate constant k does not, therefore, appreciably change as the size of the reacting molecules increases. Analysis of more exact data here presented shows that there is, nevertheless, a slight dependence of this kind in that at least one substitution parameter deviates significantly from unity. However, before attempting to analyse deviations from randomness, one must clearly test how good a fit is obtainable, in terms of eq. (8.1), i.e. assuming the random scheme.

8.2.1 Attempted fitting of random condensation kinetics

Letting the initial concentrations of the carboxyl group and of the hydroxyl group be denoted by C_0 and C_0/E respectively, $[\text{COOH}] = C$,

and $a = (1 - E)/E$, and substituting these into eq. (8.1), we obtain:

$$-dC/dt = k (aC_0 + C) C^{n-1} \quad (8.2)$$

Assuming no volume shrinkage on reaction, the solutions of eq. (8.2) for $n = 2$, $2\frac{1}{2}$ and 3 can be written down in terms of the extent of reaction $\beta_2 (= (C_0 - C)/C_0)$:

$n = 2$:

$$(a = 0) \quad (1 - \beta_2)^{-1} = kC_0 t + 1 \quad (8.3)$$

$$(a \neq 0) \quad \log(1 + a (1 - \beta_2)^{-1}) = kaC_0 t + \log(1 + a) \quad (8.4)$$

$n = 2\frac{1}{2}$:

$$(a = 0) \quad (1 - \beta_2)^{-3/2} = 1.5 kC_0^{3/2} t + 1 \quad (8.5)$$

$$(a > 0) \quad (1 - \beta_2)^{-1/2} + (a)^{-1/2} \tan^{-1}((1 - \beta_2)/a)^{1/2} \\ = 0.5 k a C_0^{3/2} t + 1 + a^{-1/2} \tan^{-1}(a)^{-1/2} \quad (8.6)$$

$$(a < 0) \quad -(1 - \beta_2)^{-1/2} + 0.5 (-a)^{-1/2} \log \left[\frac{(1 - \beta_2)^{1/2} + (-a)^{1/2}}{(1 - \beta_2)^{1/2} - (-a)^{1/2}} \right] \\ = 0.5 k a C_0^{3/2} t - 1 + 0.5 (-a)^{-1/2} \log \left[\frac{1 + (-a)^{1/2}}{1 - (-a)^{1/2}} \right] \quad (8.7)$$

$n = 3$:

$$(a = 0) \quad (1 - \beta_2)^{-2} = 2kC_0^2 t + 1 \quad (8.8)$$

$$(a \neq 0) \quad a(1 - \beta_2)^{-1} - \log(1 + a (1 - \beta_2)^{-1}) \\ = k a^2 C_0^2 t + a - \log(1 + a) \quad (8.9)$$

The rate curves (Table 7.5, 7.6) obtained for different mixtures of PE/AA and TME/AA at 175° C. are plotted according to eq. (8.3) - (8.9) in figs. (8.1) - (8.5). These plots are used to determine the order of the reaction and inspection shows that a second-order reaction can

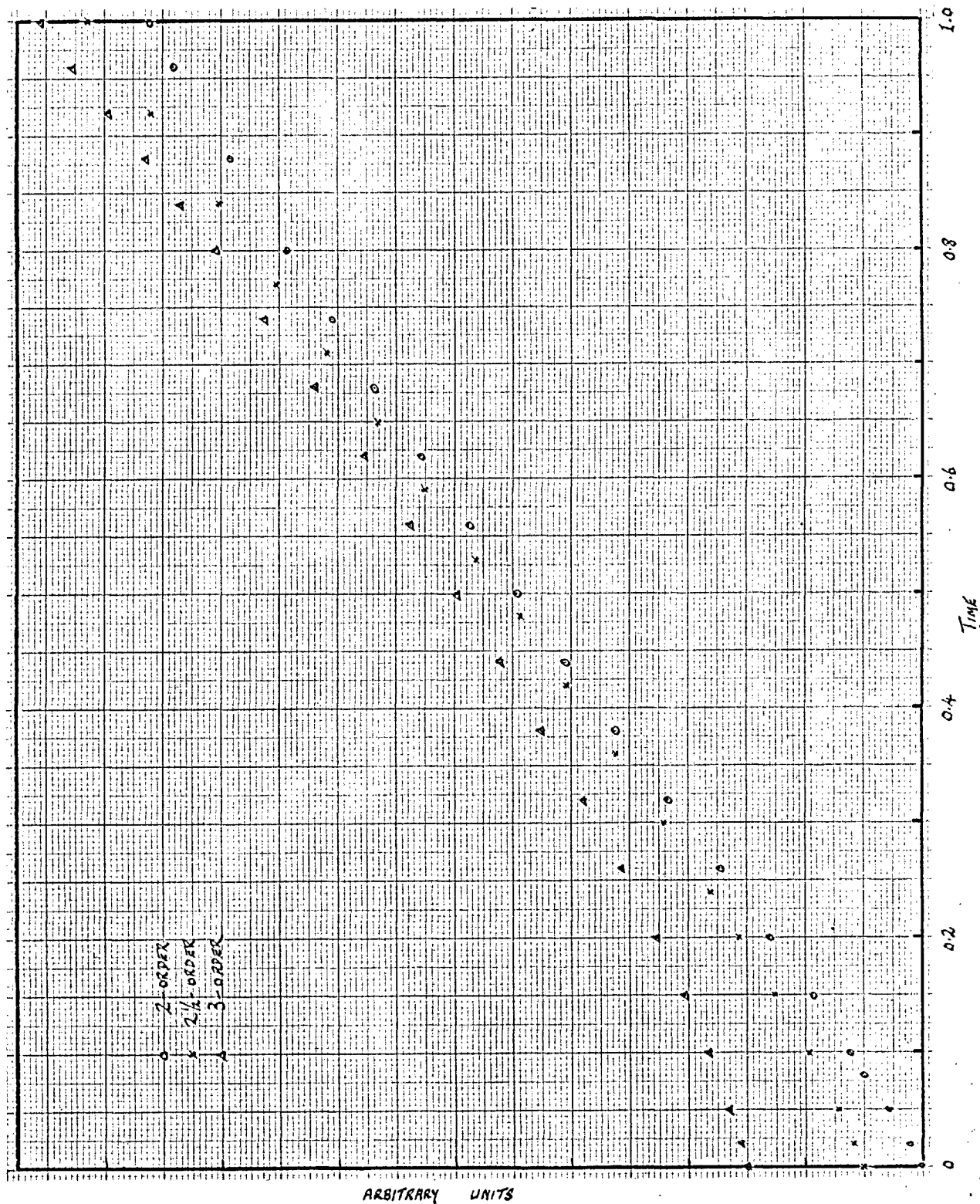


Fig. 8.1 Kinetic data: PE/AA, $E = 1.0$, 175°C .

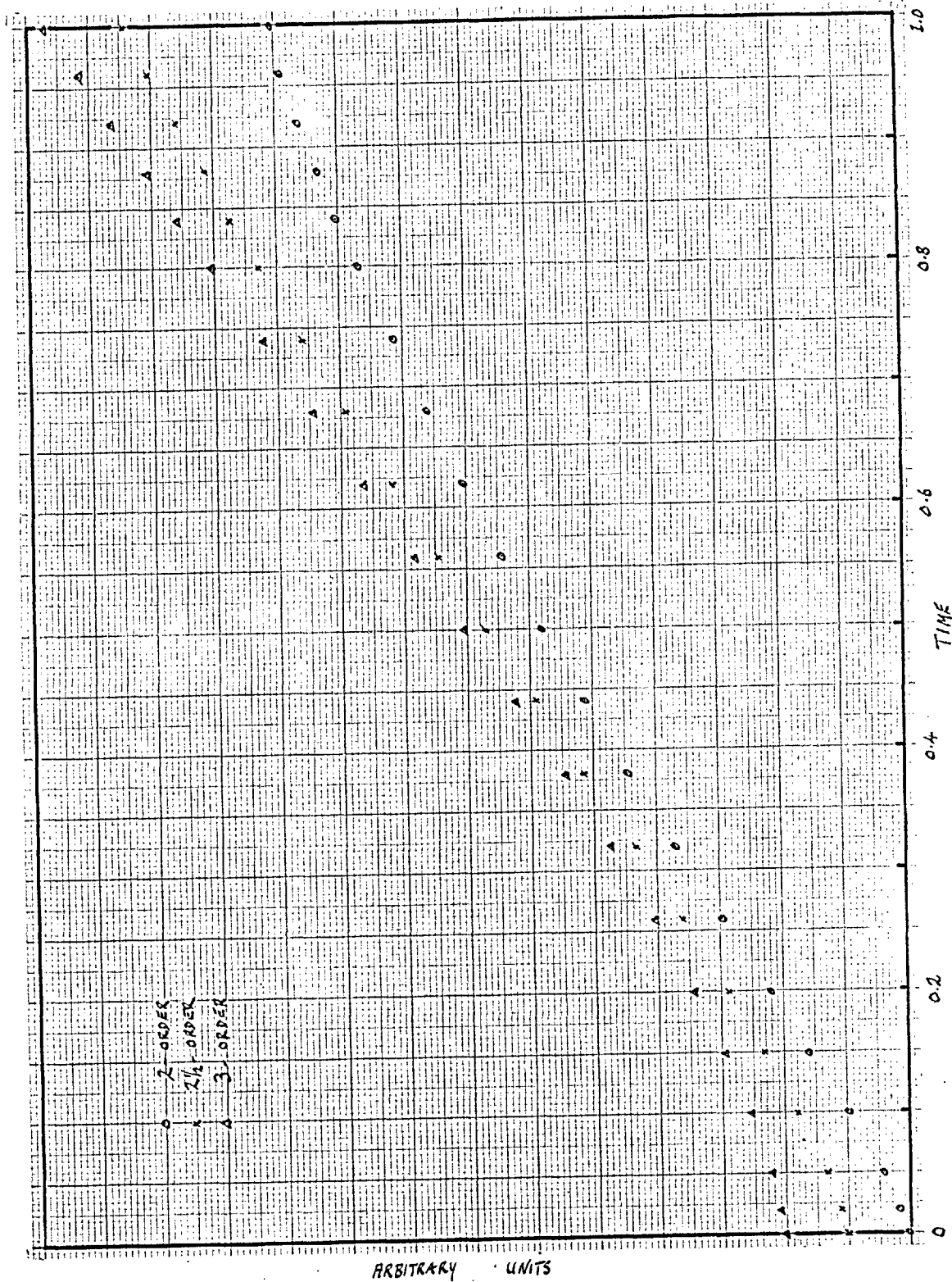


Fig. 8.2 Kinetic data: TME/AA , $E = 1.0$, $175^\circ C$.

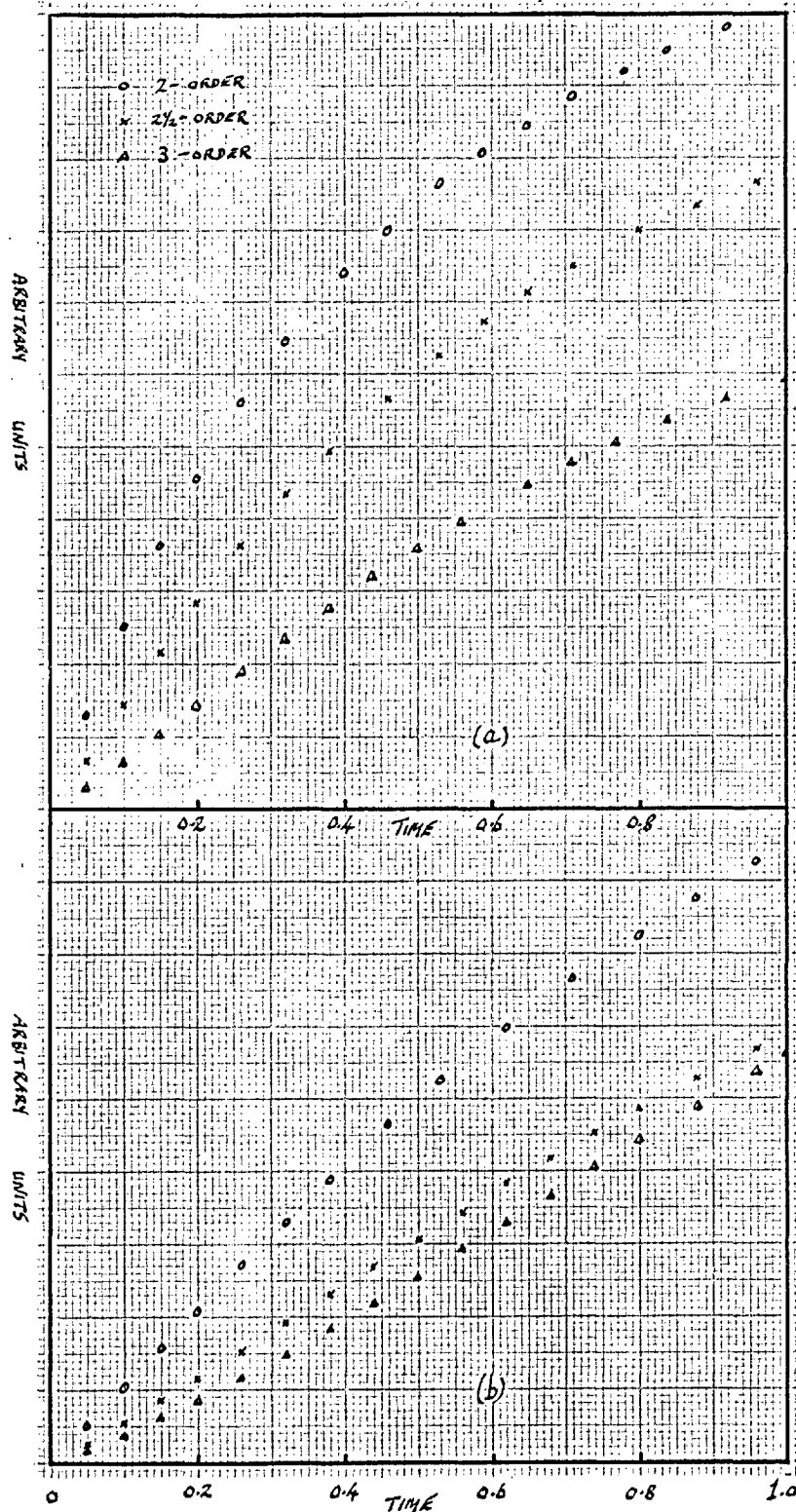


Fig. 8.3 Kinetic data: PE/AA, (a) $E = 0.50$, 175°C .

(b) $E = 0.75$, 175°C .

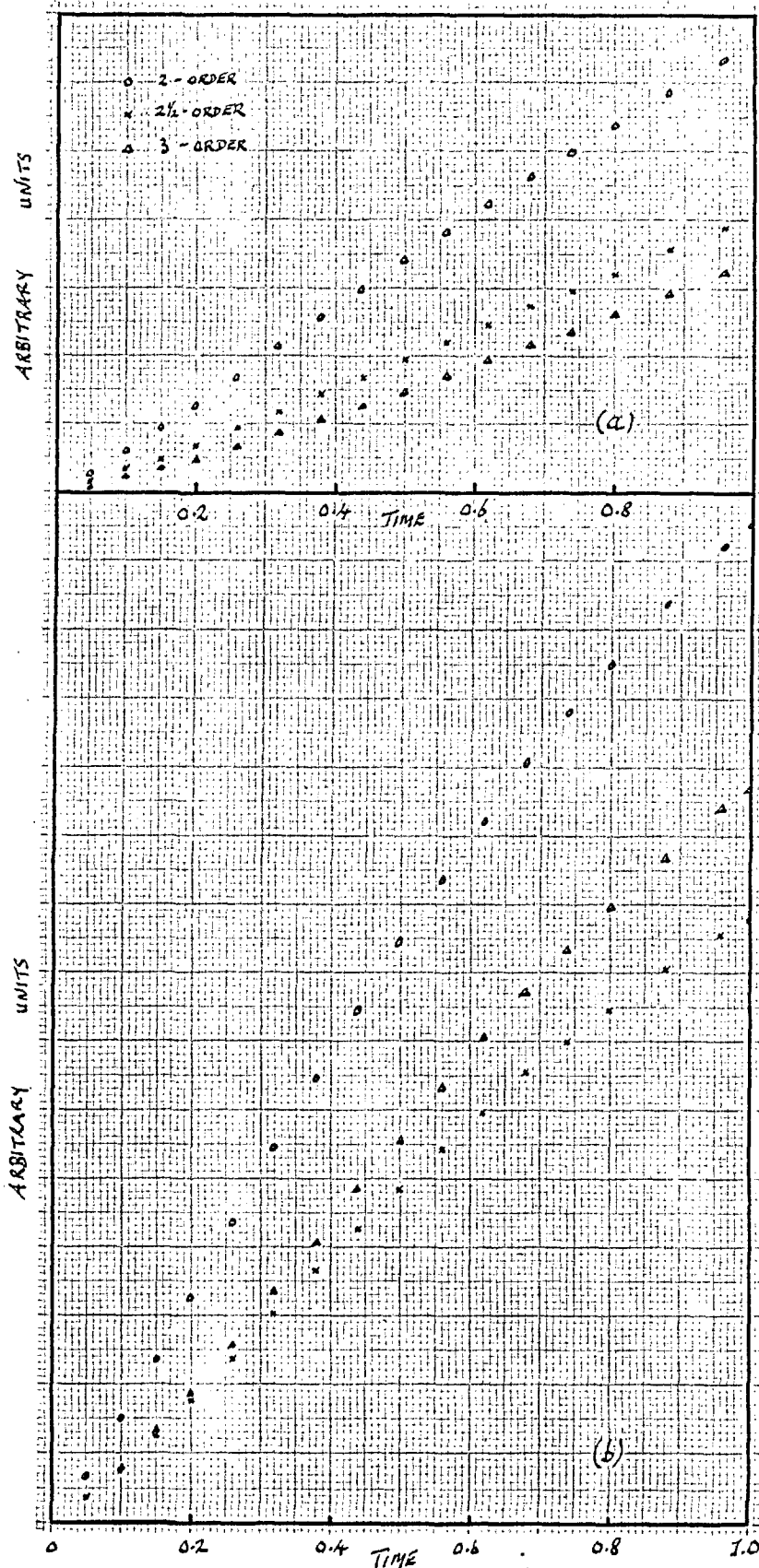


Fig. 8.4 Kinetic data: PE/AA (a) $E = 1.5$, 175°C .
(b) $E = 2.0$, 175°C .

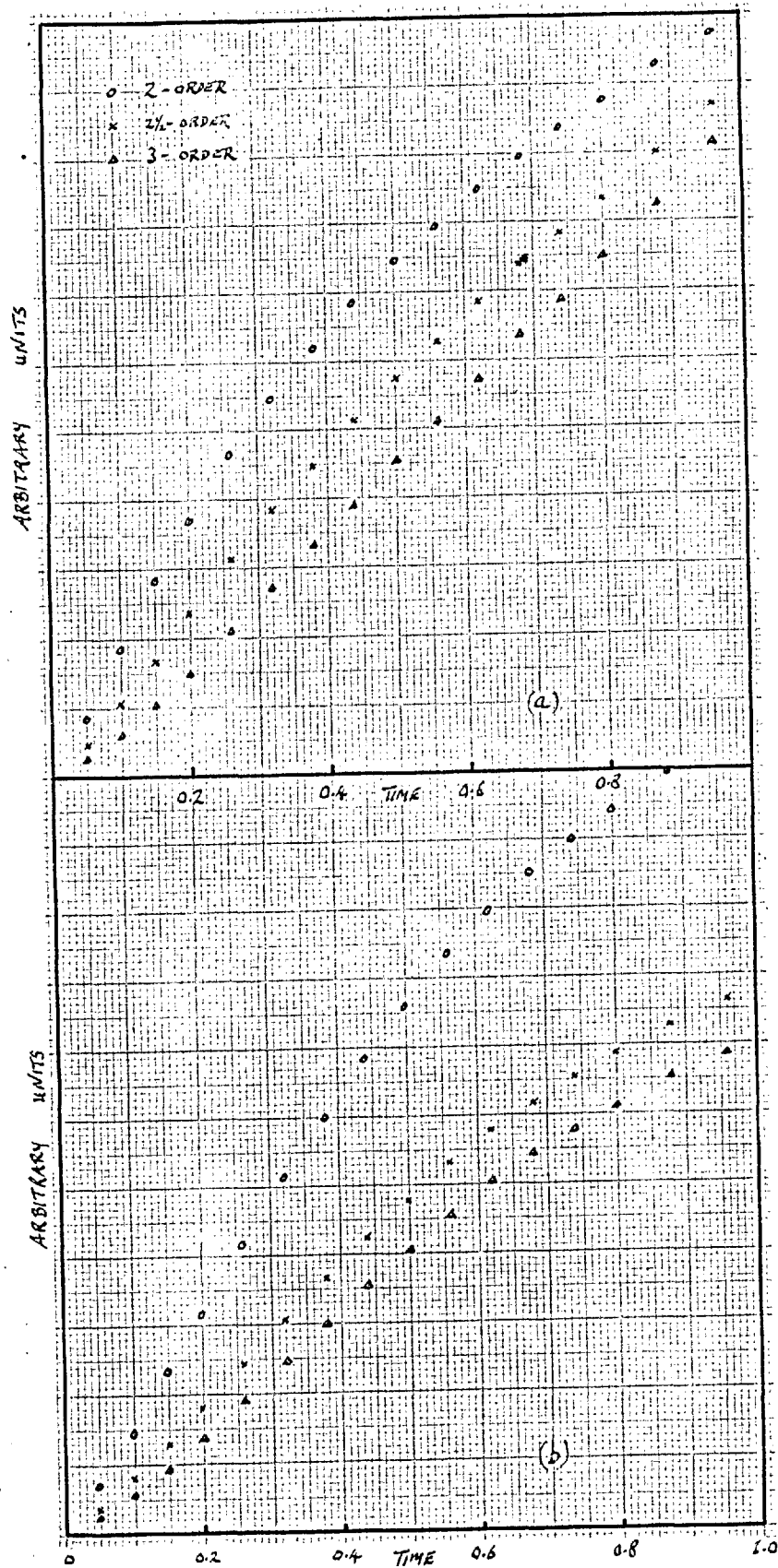


Fig. 8.5 Kinetic data: TME/AA (a) $E = 0.67$, 175°C .
 (b) $E = 1.50$, 175°C .

be rejected. However it is not easy to distinguish between a $2\frac{1}{2}$ - and 3-order reaction and inspection of the plots for the two equivalent mixtures (fig. (8.1), (8.2)) shows that the results are best represented by a random $2\frac{1}{2}$ -order reaction. This finding agrees satisfactorily with the conclusion of Tang and Yao (1959) based on their analysis of other polyesterification data. However, the degree of fit (linearity) of the $2\frac{1}{2}$ -order plot is not within experimental error. Even if it were, we would regard it as fortuitous in view of three independently measurable effects which, in theory, all lower the apparent reaction order. These are:

- (i) The incursion of cyclization reactions, which are superposed on the cross-linking reaction underlying eq. (8.1), and which generally increase in rate with overall conversion, since large molecules, bearing many pendent free functionalities, afford more opportunity for cyclization than small molecules.
- (ii) One of the two linear substitution parameters, that for OH groups, can be shown to be significantly larger than unity.

(iii) The shrinkage occurring as a result of the polyesterification reaction should also lead to a measurable increase in reaction rate.

The first two of these effects can be assessed by gel point measurements and the third by density measurements, and they must not be neglected in attempts to fit the kinetic measurements. It will be shown (section (8.3)) that when these three factors are built into the scheme, an improved fit of the data is obtained, provided the rate of link formation is taken to be proportional to $[\text{OH}][\text{COOH}]^2$ rather than $[\text{OH}][\text{COOH}]^{3/2}$. This finding contradicts the notion of hydrogen ion

catalysis and disposes of the difficulties associated with variations, discussed in section (8.1), in the ionization constant K_2 . The conclusion that the kinetics, when suitably corrected for the three effects mentioned above, are basically third-order, can be checked by examining the initial rates, which are not affected by such corrections, over a range of the initial composition E of the mixtures. Moreover, this examination confirms the plausible surmise made by earlier workers (Flory, 1939) that the overall order of these reflects an order of unity with respect to OH and an order of two with respect to COOH.

8.2.2. Analysis of initial rates for different compositions E

Details of the initial rates of all runs performed on PE/AA and TME/AA are recorded in Table (8.1), (8.2). The values of $d\alpha/dt$ shown were obtained as follows. From each run 100 to 120 points were read from the pressure/time recorder graph (e.g. Fig. (7.5)). Pressure values were converted to conversion (β) and a least-square fitting of a linear combination of the first sixteen Chebyshev polynomials were performed. The standard deviation for this fitting varied within the range 0.03 and 0.13% for the various runs, (a plot of the difference between the observed conversion and the conversion calculated using the Chebyshev polynomial has been given in Fig. (7.10)). For each run the Chebyshev polynomial was used to compute the conversion at 50 intermediate times between zero time and the gel time (taken as time unity). Thus at these 50 time points relative to the gel time, a value of the conversion is obtained for each run. A mean of these values is used as the representative kinetic data for that mixture.

TABLE 8.1

INITIAL RATE OF POLYESTERIFICATION

System	E	$\Delta \alpha_1 / \Delta t$ $\text{min}^{-1} \times 10^2$	Mean $\Delta \alpha_1 / \Delta t$ $\text{min}^{-1} \times 10^2$
PE/AA	0.50	2.08; 2.10; 2.17	2.12
PE/AA	0.75	3.61; 3.90; 2.85	3.45
PE/AA	1.00	3.10; 3.10; 4.40	
		3.60; 7.40; 3.60	4.20
PE/AA	1.50	4.60; 4.90; 4.20	
		4.40; 4.30; 5.10	4.58
PE/AA	2.00	4.90; 4.00; 4.30	
		5.70; 4.25	4.63
TME/AA	0.67	2.28; 2.88; 2.88	
		2.95; 2.68; 2.35	2.67
TME/AA	1.00	3.7; 2.8; 3.7	
		3.4	3.40
TME/AA	1.50	5.1; 4.6; 4.1	
		5.4; 4.7; 5.7	4.93

TABLE 8.2

Rate Constants from initial rates (Table (8.1))

SYSTEM	E	C_a equiv/g $\times 10^2$ (from ingredients)	k_x^* (equiv/g) $^{-1}$ min $^{-1}$ (2-order)	k_x^* (equiv/g) $^{-3/2}$ min $^{-1}$ (2 $\frac{1}{2}$ -order)	k_x^* (equiv/g) $^{-2}$ min $^{-1}$ (3-order)	k_x^* (equiv/g) $^{-3}$ min $^{-1}$ (4-order)
PE/AA	0.50	7.09	2.99	35.5	421	5950
PE/AA	0.75	8.44	4.09	44.5	484	5740
PE/AA	1.00	9.34	4.50	46.5	482	5150
PE/AA	1.50	10.4	4.49	43.2	424	4070
PE/AA	2.00	11.1	4.17	39.6	376	3380
TME/AA	0.67	7.51	3.55	41.0	473	6300
TME/AA	1.00	8.84	3.85	40.9	435	4920
TME/AA	1.50	10.0	4.93	49.3	493	4930
Mean			4.07	42.6	448	5055
Standard Deviation			0.56	4.01	38.2	910
Standard Deviation/Mean %			13.9	9.41	8.53	18.0

(It is this mean kinetic curve that is used for a complete fitting of the kinetics at $E = 1$ discussed in section (8.4)). These mean conversion/time results have been recorded previously in Tables (7.5), (7.6) for the different mixtures of PE/AA and TME/AA. The individual kinetic data for each run, together with its standard deviation from the mean, are tabulated in Appendix E.

The initial rates, as shown in Table (8.1), were obtained as $\Delta \alpha_1 / \Delta t$ (where α_1 is the fractional conversion of hydroxyl groups) from the least squares Chebyshev polynomial at points near the origin ($\beta < 0.05$) where deviations from linearity are found to be negligible.

Inspection of the tabulated initial $\Delta \alpha_1 / \Delta t$ values of replicate runs shows that their reproducibility is only moderate by general standards for kinetic experiments. However, as shown in Table (8.2), the mean values of the sets of (from three to six) replicates are sufficiently accurate to confirm that, over the range of E values studied, the initial rates are proportional to $[\text{OH}][\text{COOH}]^2$, since this assumption leads to minimal values of the standard deviation shown.

Of the four parameters k_∞^* , N_1 , N_2 and λ^* (defined in eq. (8.13)) only the first is connected with the absolute time scale inherent in initial rate measurements. The other three concern the statistical factors, such as degrees of cyclization, critical conversion, etc., which are independent of the absolute time scale. The lack of high reproducibility in the initial rates at constant E , revealed in Table (8.1), reflects entirely a lack of reproducibility in k_∞^* , i.e. in the absolute time scale. This is confirmed by re-scaling all the runs so that unit time corresponds to their observed gel times, when

they become superposable to a very marked degree, see Appendix E. For example for the equivalent ($E = 1$) mixture of PE/AA (Table E.1) the mean of the standard deviation of the six runs from the mean rate curve is 0.89%. The use of the gel point as a statistical reference point is, of course, well known (Gordon and Roe, 1956).

It is not surprising that the statistics of the polycondensation reactions should be so much more accurately reproducible than their absolute time scale. The statistics, for instance, depend on absolute conversions which are independent of temperature, or traces of adventitious catalysts, and on ratios of rate constants which are expected to be practically independent of these same variables. (Thus λ^f is proportional to the ratio $k_{\sigma}^f/k_{\alpha}^f$, while the N_i are ratios of rate constants referring to the real and fictitious 'random' system).

Because of the lack of sufficiently reproducible k_{α}^f thus brought to light, no attempt to fit runs over the whole range of compositions E to a single set of the four parameters can succeed. The parameters N_1 , N_2 and λ^f would merely acquire fluctuations in their attempt to balance out the scatter in k_{α}^f , and these fluctuations would be large in comparison with the real deviations of N_1 and N_2 from unity and λ^f from zero, i.e. from the values pertaining to the classical random reaction scheme.

Fortunately, however, it is not necessary to fit a single set of values of all four parameters to all the rate curves. The broad consistency of the kinetic and statistical behaviour having once been demonstrated over the range of compositions, it suffices to extract the optimum fit for the central composition, ($E = 1$). This composition is

the one which previous workers confined their attention (Stockmayer 1945, Walker and Mackay, 1951), and for which the critical conversions and gel times are easiest to measure. (Gelation occurs at the lowest conversion and the rate at the gel point is at its maximum at $E = 1$. Both these factors benefit the accuracy of measurement). The broad consistency over the whole range of E values is attested as follows:

- (i) the assumed proportionality of the initial rates to $[\text{OH}][\text{COOH}]^2$ gives optimum fit over the whole range (Table (8.2)) and the same scheme gives optimum fit to the individual rate curve as a whole for $E = 1$ (see section (8.3) below).
- (ii) The best values for N_1 and N_2 from the gel point statistics over the range of compositions also give the optimum fit to the whole rate curve at $E = 1$ for PE/AA.
- (iii) The consistency of the statistical behaviour is attested by the satisfactory verification of the linear relation linking λ^f to $1/E$ (figs. (8.7), (8.8), see section (8.3)).
- (iv) The optimum set of the four parameters determined (section (8.4)) for the mean of the PE/AA runs at $E = 1$ also fit very closely the whole kinetic behaviour of the mean of the three runs at $E = 0.75$ (see fig. 8.11), for which the mean time scale happens to agree closely, as is evident from the near identity of the k_x^* values from the initial rates (484 and 482 equiv.⁻² g² min⁻¹ resp., see Table (8.2)).

8.3 Kinetic equations and Gel Points

A third-order reaction scheme may now be incorporated into the kinetic rate equations (eq. (4.55)) which may be written for a polyesterification in terms of $d({}_1P_{i,j})/dt$ and $d({}_2P_{i,j})/dt$, where subscript 1 refers to unit 1 (polyol, functionality f_1) and subscript 2 refers to unit 2 (acid, functionality f_2):

$$\begin{aligned} -d({}_1P_{i,j})/dt = & k_s' \left\{ N_1^{i+j} k_1 {}_1P_{i,j} - N_1^{i+j-1} (k_1 + 1) {}_1P_{i-1,j} \right\} \\ & \times \langle N_2^{i+j} k_2 \rangle \langle k_2 \rangle ({}^sC_2^0)^2 \\ & + k_s' i \left\{ N_1^{i+j} k_1 {}_1P_{i,j} - N_1^{i+j-1} (k_1 + 1) {}_1P_{i-1,j} \right\} \\ & \times \langle N_2^{i+j} i k_2 \rangle \langle k_2 \rangle {}^sC_2^0 \sum_{x=2}^{\infty} {}_2m_x(x)^{-3/2} / \langle i k_2 \rangle \quad (8.10) \end{aligned}$$

a similar expression holds for $d({}_2P_{i,j})/dt$ in which the subscripts 1 and 2 are interchanged. In eq. (8.10) the parameters are defined as:

N_s : linear substitution parameter of type s unit

${}^sC_2^0$: initial concentration of type s functionalities
in mixture of equivalence E

and

$$k_s = (f_s - i - j) \quad (8.11)$$

The quantity

$${}_s m_x = \frac{\langle k_s i {}_sP_{i,j} \rangle}{\langle i {}_sP_{i,j} \rangle} \left[\frac{\langle i(i-1) {}_1P_{i,j} \rangle \langle i(i-1) {}_2P_{i,j} \rangle}{\langle i {}_1P_{i,j} \rangle \langle i {}_2P_{i,j} \rangle} \right]^{(x-2)/2} \quad (8.12)$$

represents the mean number of reaction partners available to a free functionality on a type s unit for forming a ring of x units.

The initial conditions are

$${}_sP_{0,0} = 1; \quad {}_sP_{i,j} = 0 \text{ for } i > 0$$

There are $\left[(f_1 + 1)f_1/2 + (f_2 + 1)f_2/2 + 2 \right]$ of these simultaneous

first-order differential equations and a computer program to solve these by step-by-step integration has been written; the method is outlined in Appendix F. For a given system the parameters f_1 , f_2 , ν , and C_2^0 are fixed, leaving us with k_α^* , k_σ^* , N_1 , N_2 , which can be adjusted but which should be constant over a range of initial E values (polyol/acid ratio). A cyclization parameter is defined (c.f. eq. (4.31))

$$\lambda^E = k_\sigma^* / (k_\alpha^* C_2^0 \nu^{3/2}) \quad (8.13)$$

and thus in eq. (8.10) we are left with three parameters to evaluate for the system, i.e. λ^E , N_1 , N_2 , apart from a scaling factor for the time t .

In order to compare mixtures of different equivalence it is convenient to refer this cyclization parameter (λ^E) to that of the equivalent ($E = 1$) mixture, i.e. to λ^1 . Letting the molar volume of the equivalent weight of type s unit be v_s we have (assuming ideal mixing):

$$C_2^0 = E(v_1 + v_2) C_2^0 / (v_1 + E v_2) \quad (8.14)$$

and incorporating eq. (8.14) in (8.13)

$$\lambda^E E(v_1 + v_2) = \lambda^1 v_1 + E v_2 \lambda^1 \quad (8.15)$$

and thus a plot of λ^E against $1/E$ should be linear.

A correction is now included into the differential rate equations (eq. (8.10)) to take into account the volume change in the system due to reaction progress. This is, of course, only a minor correction but it included for the sake of completeness. It will affect the cross-linking reaction more than the cyclization reaction

(the former has a factor $(^fC_2^o)^2$ whilst the latter has a factor $(^fC_2^o)$). Accordingly, this correction will have only a small effect on the magnitude of the cyclization parameter λ^f . Assuming the molar volume of unit 1 (V_1) is the same as that of unit 2 (V_2), the mole fraction of unit 1 is

$$x_1 = 1/(1 + f_1 E/f_2) \quad (8.16)$$

and hence the molar volume of an ideal mixture at conversion

$\beta_1 (= E \beta_2)$ is

$$\begin{aligned} V_m^\beta &= V_m^o - k''(\text{moles of bonds formed}) \\ &= V_m^o - k'' f_1 \beta_1 x_1 \end{aligned} \quad (8.17)$$

Let there be a fractional contraction μ in the volume of the system at 100% conversion, i.e.

$$k'' f_1 x_1 = \mu V_m^o \quad (8.18)$$

and defining

$$k' = k'' f_1 / V_m^o \quad (8.19)$$

we have

$$k' = \mu (1 + f_1/f_2) \quad (8.20)$$

In terms of the initial concentration $(^fC_2^o)$ of carboxyl functionalities, we have at a conversion β_1

$$(^fC_2^\beta) = (^fC_2^o) / (1 - k' \beta_1 / (1 + f_1 E/f_2)) \quad (8.21)$$

Working through this treatment with values of the molar volume of PE and AA, and of the density of the polymer (section (7.5)) results in a value of μ (eq. (8.18)) of 0.18. A value of $\mu = 0.15$ ($k' = 0.45$) (based on an initial assumption of a 15% contraction) has, however, been used in the subsequent work in which eq. (8.21) is incorporated as a factor on the right-hand side of the differential rate equations

(8.10): i.e.

$$\begin{aligned}
 -d \langle i P_{i,j} \rangle / dt = k_a^* \left\{ N_1^{i+j} k_1 i P_{i,j} - N_1^{i+j-1} (k_1 + 1) i P_{i,j-1} \right\} \langle N_2^{i+j} k_2 \rangle \\
 \times \langle k_2 \rangle ({}^E C_2^0)^2 / \left[1 - k' (\langle i_1 \rangle + \langle j_1 \rangle) / (1 + f_1 E / f_2) \right]^2 \\
 + k_a^* i \left\{ N_1^{i+j} k_1 i P_{i,j} - N_1^{i+j-1} (k_1 + 1) i P_{i,j-1} \right\} \langle N_2^{i+j} i k_2 \rangle \\
 \times \langle k_2 \rangle ({}^E C_2^0) \sum_{x=x_0}^{\infty} x m_x (x\nu)^{-3/2} / \left[\langle i k_2 \rangle (1 - k' (\langle i_1 \rangle + \langle j_1 \rangle) / (1 + f_1 E / f_2)) \right]
 \end{aligned} \quad (8.22)$$

It is shown (see Appendix D) that this shrinkage correction factor k' has only a small effect on the cyclization component σ at constant λ^E and the effect of k' on the rate curve is shown later in fig. (8.10).

The gel point condition is seen from eq. (4.52) to be, in terms of the $i P_{i,j}$:

$$\langle i(i-1) i P_{i,j} \rangle \langle i(i-1) i P_{i,j} \rangle = \langle i i P_{i,j} \rangle \langle i i P_{i,j} \rangle \quad (8.23)$$

Thus by solving the differential rate equations (8.22) until this condition (eq. (8.23)) is satisfied and evaluating α_1 , α_2 , σ_1 , σ_2 from the following equations

$$\alpha_s = \langle i i P_{i,j} \rangle / f_s \quad (8.24)$$

$$\sigma_s = \langle j j P_{i,j} \rangle / f_s \quad (8.25)$$

the extent of reaction

$$\beta_c = \alpha_c + \sigma_c \quad (8.26)$$

at the gel point may be computed as a function of λ^E , N_1 , and N_2 .

As always the results are presented in terms of β_c which is the larger of β_{1c} and β_{2c} , and we always have

$$\beta_{1c} = E \beta_{2c} \quad (8.27)$$

The above procedure has been performed (see Appendix F for computer

program) for the cases $f_1 = 3, 4$ (e.g. TME and PE) and $f_2 = 2$ (e.g. AA) and the results are summarized in Appendix D.

In order to find the value of the two linear substitution parameters (N_1, N_2) the results of the concentration dependence of the gel points (Table (7.9), (7.10)) are used. The extrapolation of the plots of critical conversion against dilution to zero volume gives the value of α_c (Table (7.11)), i.e. the critical conversion in the absence of cyclization. This corresponds to the case $\lambda^E = 0$, and the value of α_c as a function of N_1 , and N_2 for this case is given in Appendix D for different mixtures of polyol to acid. Thus for each pair of values of E and α_c a plot of N_1 against N_2 can be constructed and hence the intersection of such plots for a given system gives an estimate to these parameters. Such plots are given in fig. (8.6a) for the PE/AA system and in fig. (8.6b) for the TME/AA system. Unfortunately owing to the scatter on the dilution experiment results and the long extrapolation (fig (7.11), (7.12)) the value of N_1 and N_2 deduced from fig. (8.6) can only be used as a rough guide to their magnitude and these figures obviously do not uniquely determine N_1 and N_2 . However, these figures make it likely that in both systems, both linear substitution parameters lie in the range $0.9 \leq N_1, N_2 \leq 1.6$, whilst $1 \leq N_1 \times N_2 \leq 1.6$. A value of $N_1 > 1$ is in agreement with the observation that for both systems the extreme mixture with excess polyol gels earlier than the conversion predicted even by the random model without cyclization. Since the dilution experiments confirm the presence of cyclization reactions in these systems this observation confirms not only the presence of

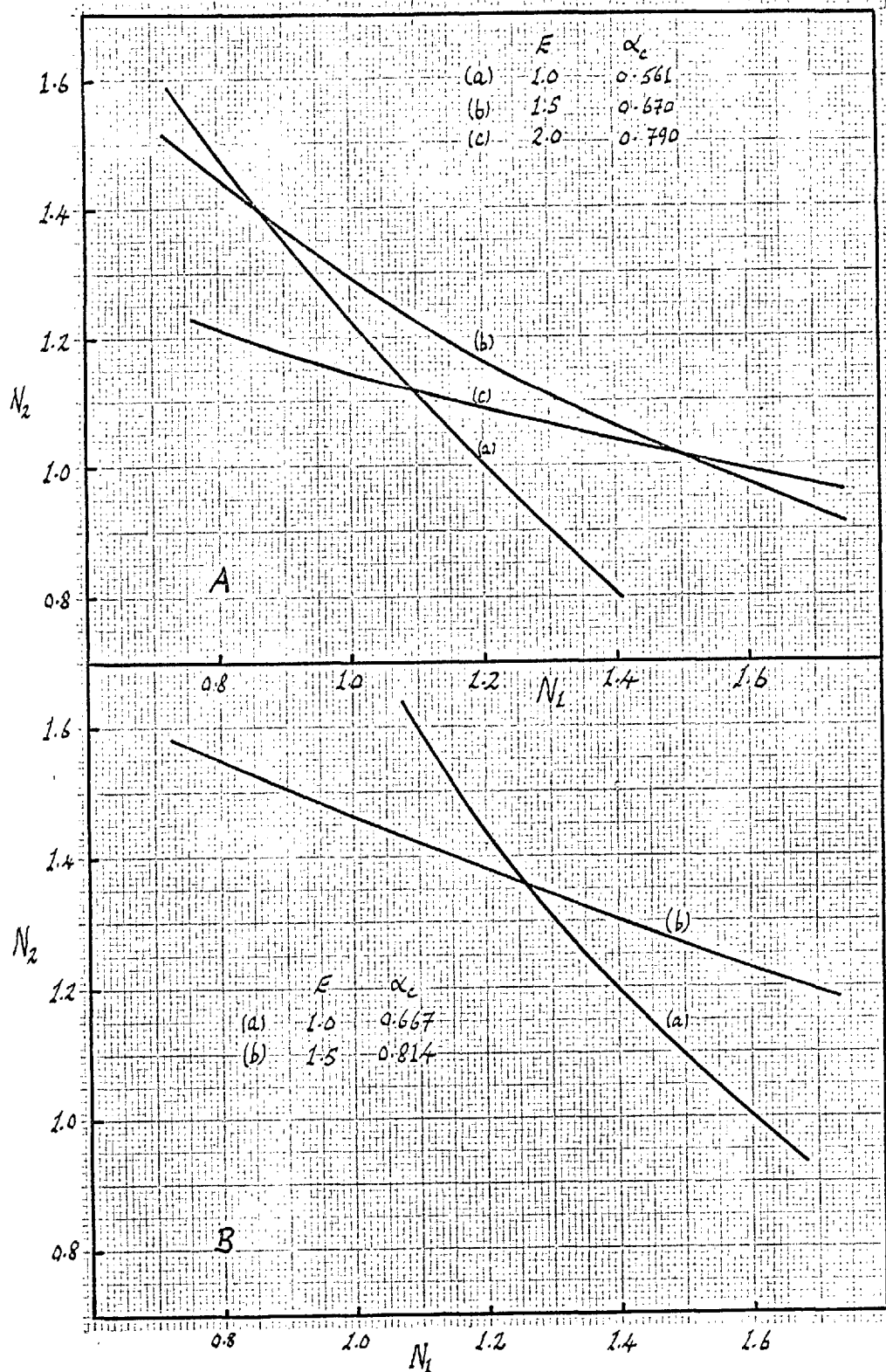


Fig. 8.6 N_2 against N_1 for fixed α_c : A; PE/AA
B; TME/AA

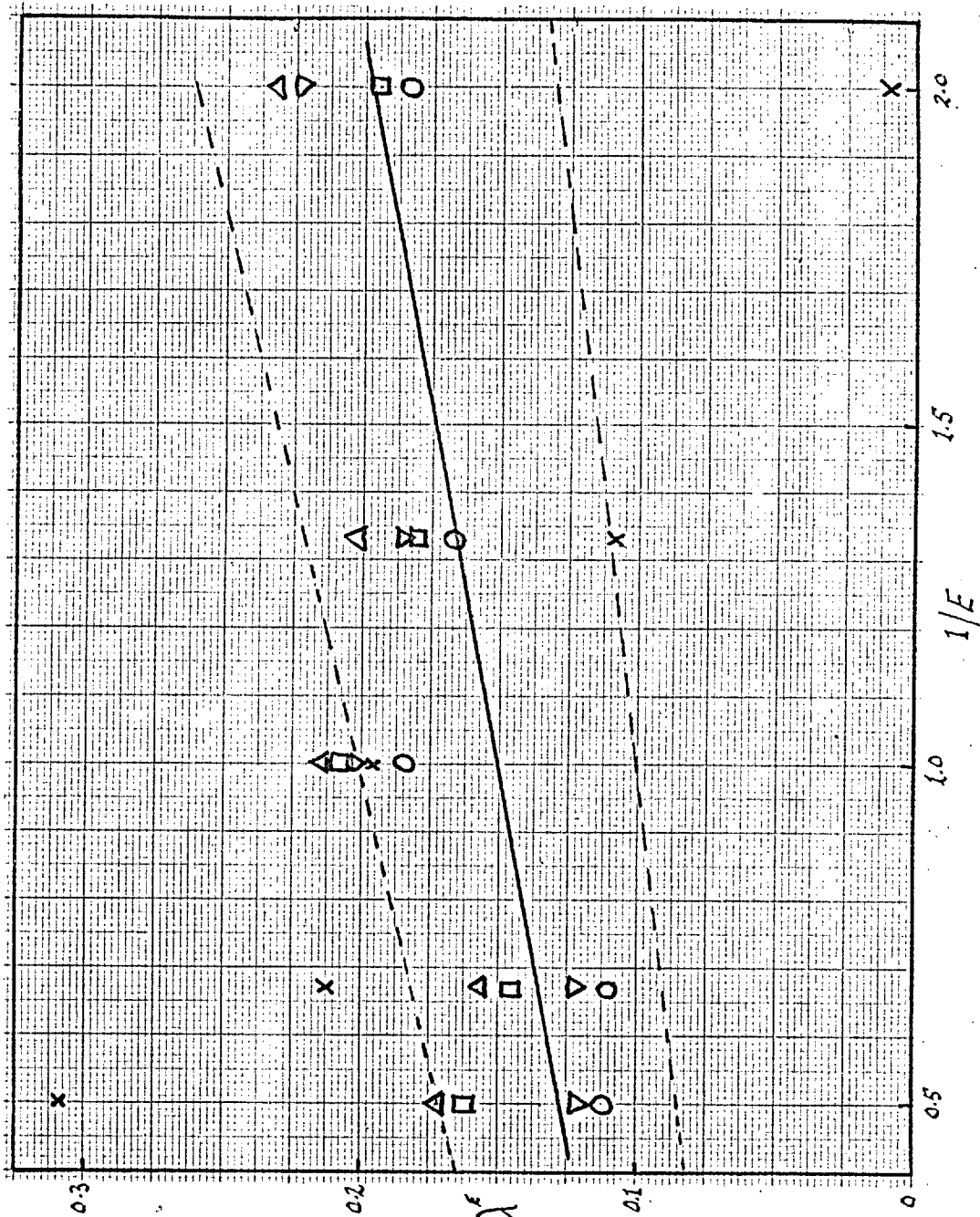


Fig. 8.7 λ^E versus $1/E$: PE/AA

	N_1	N_2
x	1.0	1.5
o	1.5	0.9
□	1.5	1.0
△	1.6	1.0
▽	1.6	0.9

Lines obey theoretical relationship (eq. (8.15))
with $v_2/v_1 = 2.3$

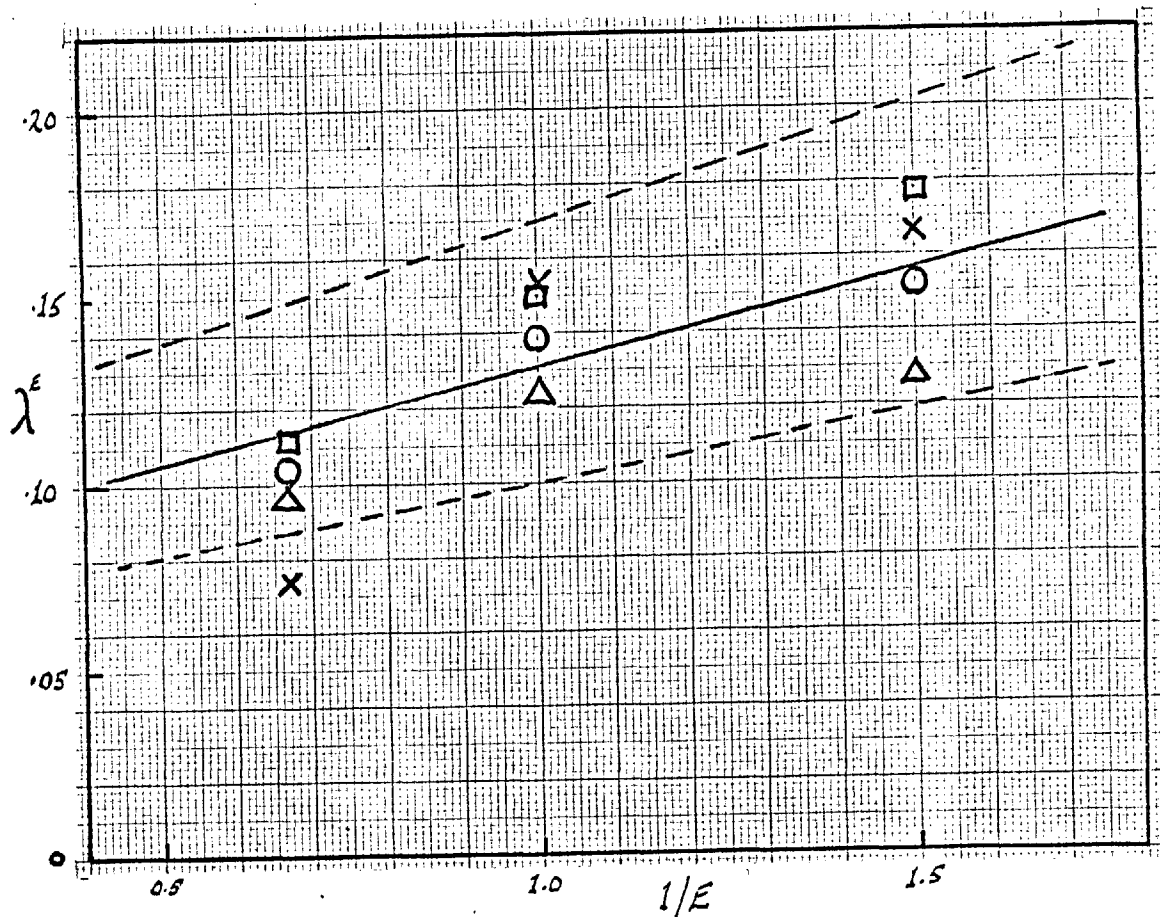


Fig. 8.8 λ^E versus $1/E$: TME/AA

	N_1	N_2
Δ	1.4	1.2
$\times$	1.5	1.1
$\circ$	1.5	1.2
$\square$	1.6	1.2

Lines obey theoretical relationship (eq. (8.15))
with $v_2/v_1 = 1.7$

a substitution effect on one of the monomers, but that the value of the substitution parameter of the polyol (N_1) is greater than unity. (A value of N_1 greater than unity corresponds to the favouring of the formation of branched molecules and hence premature gelation).

Much better estimates of N_1 and N_2 are obtained when the cyclization parameters λ^f are calculated from the gel points (Table 7.4) and the values of N_1 and N_2 are chosen so that the optimum fit is obtained to eq. (8.15). Working in the range $0.9 \leq N_1, N_2 \leq 1.6$ we can take a pair of values of N_1 and N_2 and compute the value of λ^f which corresponds to the observed β_c . A plot of λ^f against $1/E$ should be linear (eq. (8.15)) and the ratio of the slope to the intercept should give the ratio of the equivalent volume of the acid to polyol, which has been experimentally measured (section (7.5)). For the PE/AA system the ratio is 2.3, and for the TME/AA system it is 1.7. Such plots are shown in Fig. (8.7), (8.8) for the two systems, and the lines drawn obey the theoretical relationship based on the measured ratio of the equivalent volumes of polyol to acid. The values of λ^f as a function of N_1 and N_2 to fit the observed β_c are recorded later in Table (8.3), (8.4). From these plots it is estimated that for the PE/AA system $N_1 = 1.5 \pm 0.1$, $N_2 = 0.9 \pm 0.1$; and for the TME/AA system $N_1 = 1.5 \pm 0.1$, $N_2 = 1.2 \pm 0.1$.

8.3.1 Check of λ^f against random-flight statistics

The value of λ^f from the above fitting may now be used to calculate the mean bond length from random flight statistics (see section (4.8)). For a mixture containing one mole COOH and one mole OH, the molar volume /COOH functionality is 96.5 cc. for the PE/AA system and 108 cc.

for TME/AA, (the molar volumes of the monomers have been given in section (7.5)), i.e. the mean volume (V) associated with each COOH functionality is 160 and 180 Å³ in the PE/AA and TME/AA system respectively. From eq. (4.43) we have

$$1 = 0.5 \sqrt{3/\pi\nu} \left[V/\lambda^3 \right]^{1/3} \quad (8.28)$$

for a random walk which preserves a tetrahedral valence angle. Using values of $\nu = 11$; $\lambda^3 = 0.15$ for PE/AA, $\lambda^3 = 0.14$ for TME/AA (see figs. 8.7, 8.8) in eq. (8.28) give $l = 1.5$ and 1.6 Å for the PE/AA and TME/AA systems respectively. These mean bond lengths compare favourably with the C - C bond length (1.54 Å), bearing in mind that 7 out of 11 bonds in a ring are C - C, whilst the remaining 4 are C - O which do not preserve the tetrahedral valence angle.

Excluded volume effects, which have been neglected in the present theory, would lead to larger apparent bond lengths (lower λ^3 values). In solvent free melts, these effects should be small, and it is gratifying that both the POCl₂/P₂O₅ (chapter 6) and the polyol/AA systems yield apparent bond lengths from the random flight theory which agree closely with the actual known bond lengths.

8.4 Comparison of theoretical and experimental rate curve for E = 1

The experimental rate curve (Table (7.5)) for the equivalent mixture ($E = 1$) is now compared with the calculated rate curve obtained by integrating the kinetic rate equations (8.22). These equations are solved by step-by-step integration (see Appendix F) and at each step the value of α and σ are calculated from eq. (8.24), (8.25). For a given pair of N_1 and N_2 values the value of λ^f is adjusted to fit the observed mean gel point (β_g), an arbitrary value

of k_{α}^* is chosen for the calculation, and this is scaled to fit the observed mean gel time, these two critical parameters have been listed in Table (7.4). The rate equations (8.22) are solved up to the gel point (eq. (8.23)) and a least-squares polynomial (order 8) fitted to the resulting $\beta_{cal} (= (\alpha + \sigma))$ versus time curve. The value of β_{cal} is then computed from the polynomial at the same 50 time intervals relative to the gel time as used to tabulate the experimental mean rate curve. We therefore know the functional relationship:

$$\beta_{cal} = f(k_{\alpha}^*, \lambda^E, N_1, N_2; E, t) \quad (8.29)$$

For each mixture (E fixed) we have the 50 mean measurements of β_{exp} as a function of time (t) from which to determine the set of unknown constants ($k_{\alpha}^*, \lambda^E, N_1, N_2$). It is customary to search for that set of constants that will minimise the error square sum (F):

$$F = \sqrt{\left(\sum_{i=1}^{50} [\beta_{exp,i} - \beta_{cal,i}]^2 \right) / 50} \quad (8.3)$$

The results of this procedure are shown in Table (8.3) for the whole range of PE/AA compositions studied for different pairs of N_1 and N_2 values.

It can be seen from Table (8.3) that for the equivalent ($E = 1$) mixture the best fit is obtained with values of $N_1 = 1.5$ and $N_2 = 0.9$ which are the central values of the range estimated for these parameters from the gel points of different PE/AA compositions (section (8.3)). A difference plot of the experimental and calculated curves using these parameters is shown in Fig. (8.9). This is, of course, not the least squares fit to the experimental curve as we have

TABLE 8.3

FITTING OF PE/AA GEL POINT DATA

E t_g (mins)		0.50 0.802 111			0.75 0.680 41			1.00 0.623 35			1.50 0.737 35			2.00 0.867 55		
N_1	N_2	$k_{\alpha} \times 10^{-3}$	λ^E	$F \times 10^2$	$k_{\alpha} \times 10^{-3}$	λ^E	$F \times 10^2$	$k_{\alpha} \times 10^{-3}$	λ^E	$F \times 10^2$	$k_{\alpha} \times 10^{-3}$	λ^E	$F \times 10^2$	$k_{\alpha} \times 10^{-3}$	λ^E	$F \times 10^2$
1.0	1.5	.365	.010	5.88	.591	.108	0.77	.638	.199	2.09	.539	.213	1.50	.430	.310	3.03
1.1	1.3	.353	.046	6.30	.565	.114	0.55	.600	.190	1.53	.501	.200	0.89	.391	.254	4.03
1.1	1.5	.326	.064	6.95	.526	.140	0.72	.562	.218	1.10	.469	.226	0.72	.366	.315	4.62
1.2	1.5	.294	.115	7.96	.475	.171	1.50	.504	.236	0.43	.417	.240	1.42	.319	.320	6.05
1.3	1.1	.317	.123	7.40	.501	.144	1.15	.525	.194	0.57	.431	.151	1.18	.326	.193	5.84
1.3	1.3	.289	.144	8.26	.462	.175	1.79	.486	.227	0.44	.399	.208	1.82	.302	.267	6.69
1.3	1.5	.268	.162	8.86	.433	.200	2.25	.458	.253	0.68	.376	.253	2.30	.285	.326	7.24
1.4	0.9	.327	.144	7.06	.511	.135	0.94	.529	.171	0.64	.431	0.94	1.00	.324	.104	5.67
1.4	1.1	.290	.167	8.26	.459	.172	1.82	.480	.211	0.47	.391	.165	1.93	.294	.200	6.86
1.4	1.2	.276	.177	8.71	.441	.187	2.18	.462	.228	0.68	.377	.195	2.30	.283	.239	7.30
1.5	0.9	.300	.184	7.85	.470	.161	1.54	.488	.187	0.35	.395	.108	1.66	.295	.112	6.55
1.5	1.0	.282	.196	8.50	.445	.180	2.03	.463	.208	0.59	.376	.146	2.18	.281	.163	7.18
1.5	1.1	.268	.207	9.00	.425	.197	2.44	.444	.227	0.92	.360	.178	2.60	.270	.208	7.67
1.5	1.3	.245	.227	9.79	.393	.227	3.05	.414	.259	1.37	.336	.234	3.24	.252	.281	8.44
1.6	0.9	.278	.221	8.54	.437	.184	2.09	.453	.202	0.62	.366	.121	2.24	.273	.120	7.24
1.6	1.0	.261	.232	9.16	.414	.203	2.57	.432	.223	1.00	.349	.158	2.75	.260	.171	7.84
1.6	1.1	.248	.244	9.66	.396	.220	2.97	.414	.242	1.31	.335	.191	3.19	.250	.215	8.32
1.6	1.2	.237	.254	9.99	.381	.235	3.29	.399	.258	1.57	.323	.220	3.49	.241	.253	8.71

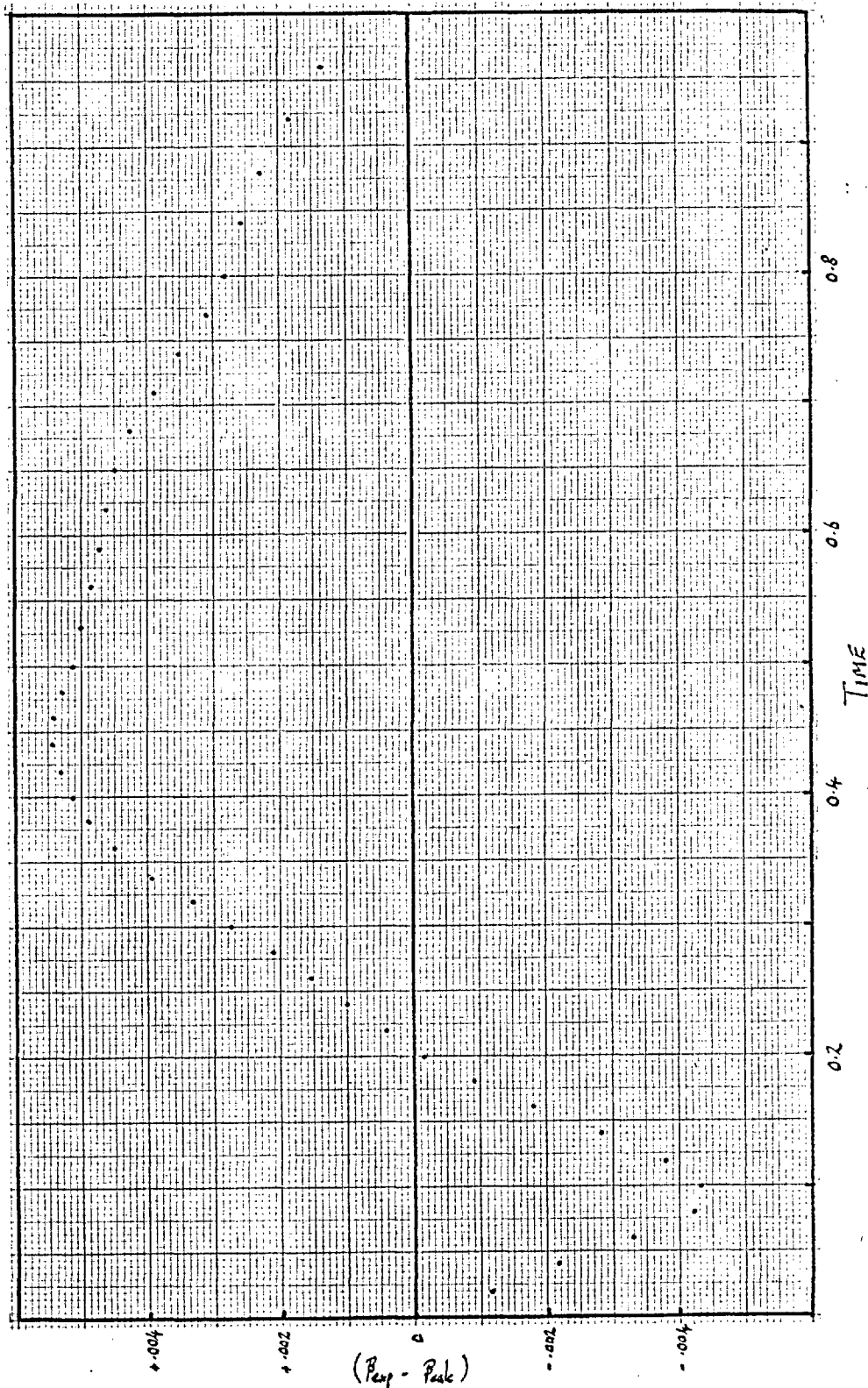


Fig. 8.9 Difference Plot, $(\beta_{exp} - \beta_{calc})$ against time. PE/AA
 $E = 1$; $N_1 = 1.5$, $N_2 = 0.9$, $k_u^* = 488 \text{ (equiv/g)}^{-2} \text{ min}^{-1}$,
 $\lambda' = 0.187$, $k' = 0.45$

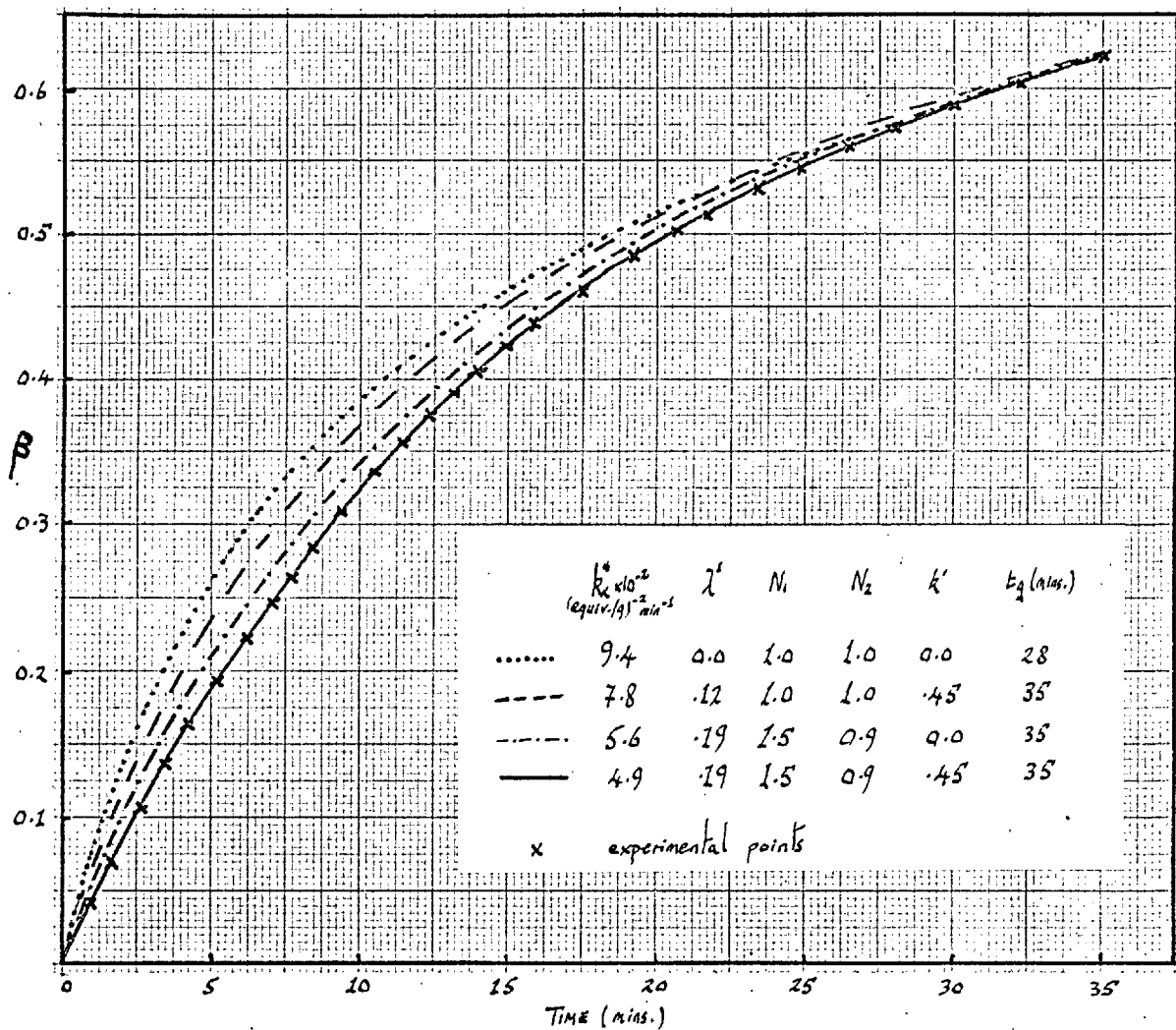


Fig. 8.10 Comparison of experimental and theoretical rate curves for equivalent ($E = 1$) mixture of PE/AA, 175°C.

superposed the condition that the theoretical curve must fit the observed gel point. The experimental rate curve is shown in Fig. (8.10) together with that calculated from (i) the random cross-linking model ($N_1 = N_2 = 1$, $\lambda^1 = 0$); (ii) the cyclization model without substitution effect ($N_1 = N_2 = 1$, $\lambda^1 = 0.118$), (iii) the non-random model without the shrinkage correction ($N_1 = 1.5$, $N_2 = 0.9$, $\lambda^1 = 0.186$, $k' = 0$, and (iv) the best fit obtained ($N_1 = 1.5$, $N_2 = 0.9$, $\lambda^1 = 0.187$, $k' = 0.45$). In all cases, except (i), the value of k_x^* and λ^1 were chosen so that the gel time and gel conversion agreed with that observed; in the random-model curve (i) the value of k_x^* was chosen so that the gel point ($\alpha_c^* = 0.577$) coincided with the observed time at which this conversion was reached. These curves illustrate the effect on the non-random contributions on the rate curve and show that the observed curve could not be adequately fitted without their inclusion.

The relatively high value of the error square sum (F) of the non-equivalent mixtures (Table 8.3) compared with F for the case $E = 1$ reflects the low value of k_x^* compared with that calculated from the initial rates (Table 8.2) which must be used to fit the observed mean gel times. It is because of the lack of sufficient reproducibility of k_x^* (and hence of the gel times) that the kinetic curves cannot be fitted over the whole range of composition E to a single set of the four parameters (k_x^* , λ^1 , N_1 , N_2). For the mean of the three runs at $E = 0.75$ the value of k_x^* happens to agree closely to that found for the case $E = 1$. Fig. (8.11) shows a comparison of the experimental and theoretical rate curves ($E = 0.75$). This figure also

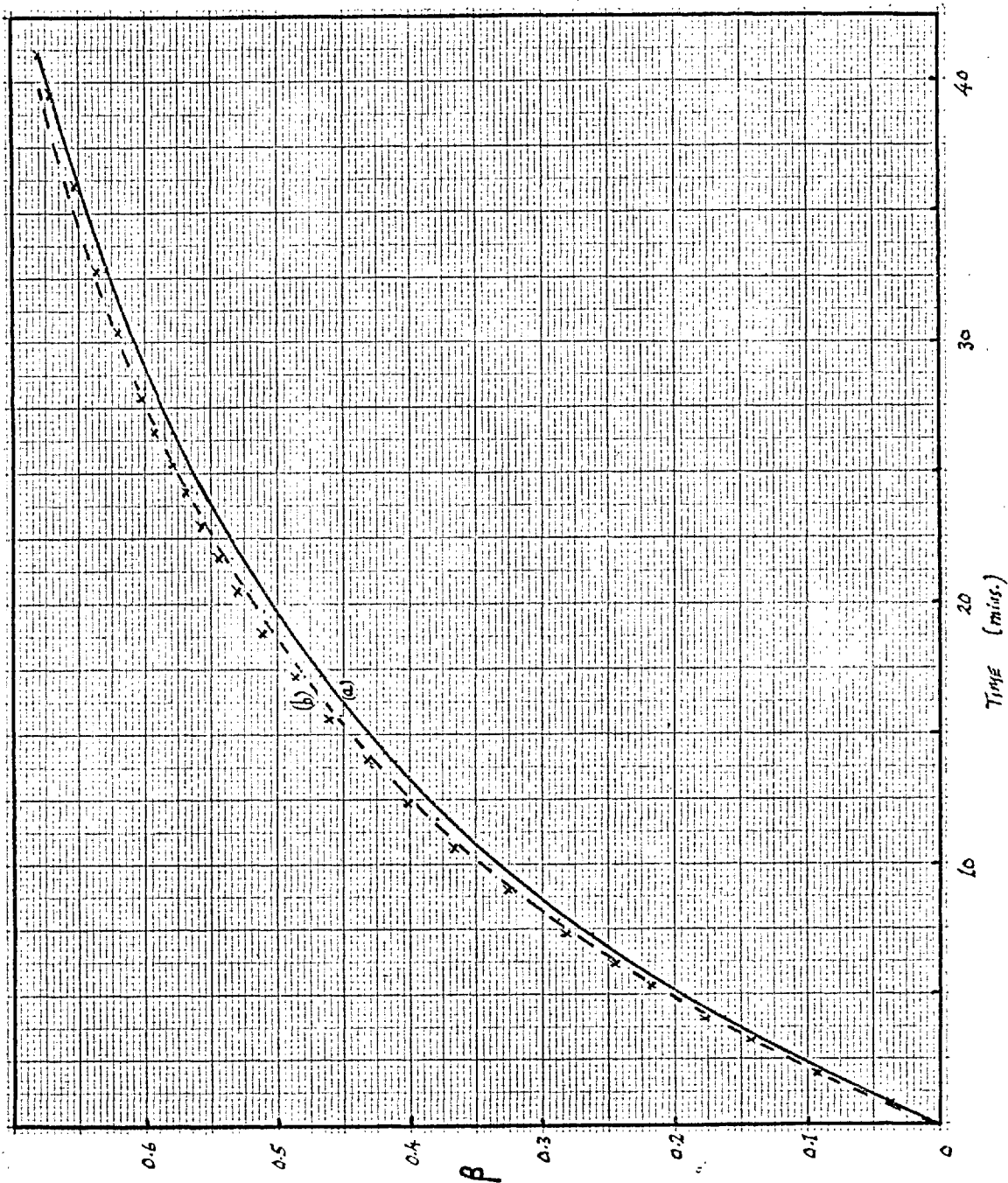


Fig. 8.11 Comparison of experimental (x) and theoretical rate curves; PE/AA, $E = 0.75$, 175°C . $N_1 = 1.5$, $N_2 = 0.9$, $k' = 0.45$, $\lambda^{0.75} = 0.161$

a) $k_x^* = 470 (\text{equiv/g})^{-2} \text{min}^{-1}$

b) $k_x^* = 490 (\text{equiv/g})^{-2} \text{min}^{-1}$

shows the theoretical rate curve using the same value of k_x^* as calculated for the optimum fit to the equivalent mixture ($N_1 = 1.5$, $N_2 = 0.9$).

8.4.1 Fitting of the TME/AA system

The comparison of the experimental rate curves for TME/AA (Table (7.6)) with the theoretical ones was performed in the same manner as given above for the PE/AA system, and the results are summarized in Table (8.4). The central values of $N_1 = 1.5$ and $N_2 = 1.2$ obtained from the analysis of the critical conversions in section (8.3) are used as representative for comparing the rate curve for the equivalent mixture with the theoretical rate curve, and this is shown in fig. (8.12), together with the 'random' rate curve. A complete analysis over the composition range is not attempted because of the lack of reproducibility of k_x^* as discussed in section (8.2).

It is concluded from the analysis of the rate curves of the equivalent mixtures that they could not be adequately fitted unless both cyclization and substitution effects are included in the rate equation. The rate curves of these equivalent mixtures of PE/AA and TME/AA can be fitted within experimental error with this non-random model, using the values for the non-random parameters (N_1 , N_2 , λ^f) obtained by fitting the observed gel points over a range of composition E.

Table (8.5) lists the calculated values of α_c and α_s for all the mixtures using the values of the linear substitution parameters that were obtained from the analysis of the critical conversions

TABLE 8.4
FITTING OF TME/AA GEL POINT DATA

		0.67			1.00			1.50		
		0.858			0.720			0.868		
		119			57.6			77.7		
E β_c t_c (mins)										
N_1	N_2	k_A^t	λ^t	$F \times 10^2$	k_A^t	λ^t	$F \times 10^2$	k_A^t	λ^t	$F \times 10^2$
1.0	1.4	743	.011	2.11	840	.090	3.78	545	.120	3.77
1.1	1.4	668	.048	1.44	754	.106	2.90	484	.127	4.81
1.2	1.4	609	.081	1.25	688	.122	2.17	437	.134	5.76
1.2	1.5	586	.088	1.30	664	.134	1.94	422	.156	6.07
1.3	1.1	651	.091	1.32	722	.096	2.54	455	.060	5.34
1.3	1.3	586	.106	1.34	659	.124	1.84	415	.117	6.26
1.3	1.5	541	.119	1.65	613	.148	1.38	387	.163	6.93
1.4	1.0	643	.112	1.29	710	.094	2.45	444	.034	5.48
1.4	1.1	603	.119	1.26	671	.110	2.00	420	.067	6.07
1.4	1.2	571	.127	1.43	640	.125	1.64	401	.097	6.59
1.5	0.9	646	.130	1.31	708	.090	2.52	440	.003	5.39
1.5	1.0	600	.138	1.24	664	.108	1.98	414	.041	6.12
1.5	1.1	564	.146	1.46	630	.123	1.55	392	.074	6.74
1.5	1.2	534	.153	1.76	600	.138	1.23	374	.104	7.28
1.5	1.3	510	.160	2.06	576	.151	1.00	360	.130	7.71
1.5	1.5	473	.174	2.55	538	.175	0.80	336	.177	8.48
1.6	0.9	606	.155	1.20	666	.103	2.10	413	.011	5.98
1.6	1.0	564	.162	1.40	626	.120	1.58	389	.048	6.72
1.6	1.1	530	.170	1.76	594	.136	1.19	369	.081	7.35
1.6	1.2	503	.177	2.14	567	.150	0.93	352	.111	7.92

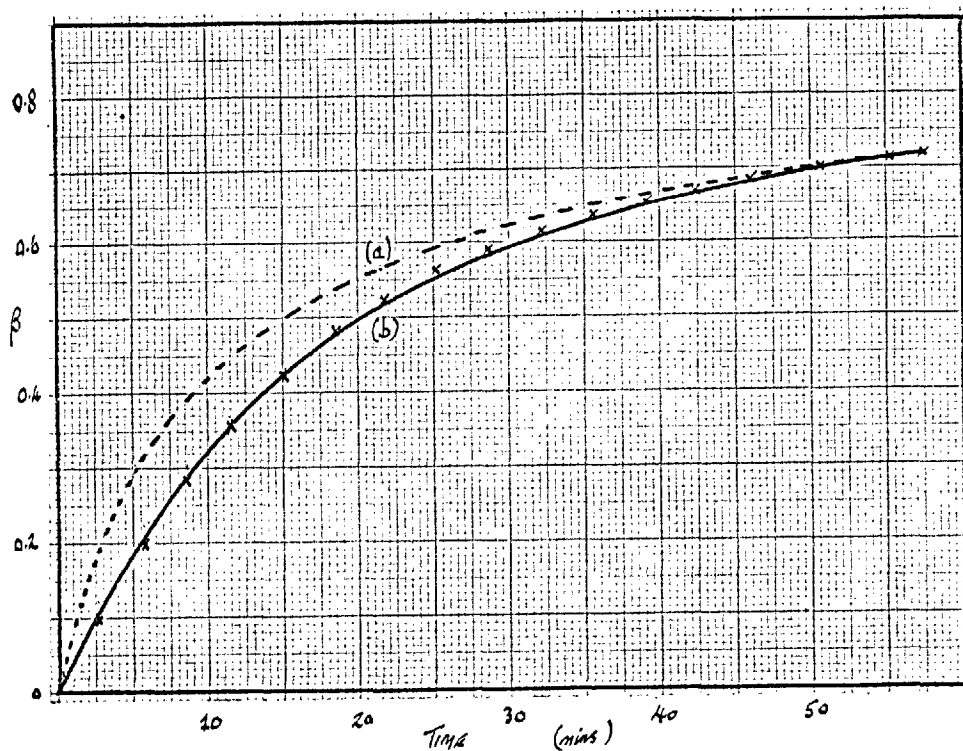


Fig. 8.12 Comparison of experimental (x) and theoretical rate curves TME/AA, $E = 1.0$, 175°C .

- a) $N_1 = 1.5$, $N_2 = 1.2$, $k' = 0.45$, $\lambda' = 0.138$, $k_x^* = 600$
 $(\text{equiv/g})^{-2} \text{min}^{-1}$
- b) $N_1 = 1.0$, $N_2 = 1.0$, $k' = 0.00$, $\lambda' = 0.000$, $k_x^* = 995$
 $(\text{equiv/g})^{-2} \text{min}^{-1}$

(section (8.3)). These values are considered soundly based now that the broad consistency of the kinetic and statistical behaviour has been demonstrated over the range of compositions.

TABLE 8.5

CRITICAL DEGREES OF CROSS-LINKING AND CYCLIZATION

System	E	N ₁	N ₂	λ^e	α_c	α_c
PE/AA	0.50	1.5	0.9	0.184	0.744	0.058
PE/AA	0.75	1.5	0.9	0.161	0.629	0.051
PE/AA	1.00	1.5	0.9	0.187	0.565	0.058
PE/AA	1.50	1.5	0.9	0.108	0.703	0.034
PE/AA	2.00	1.5	0.9	0.112	0.832	0.035
TME/AA	0.67	1.5	1.2	0.153	0.811	0.047
TME/AA	1.00	1.5	1.2	0.138	0.677	0.043
TME/AA	1.50	1.5	1.2	0.104	0.836	0.032

8.5 Post-gel model

It is interesting to use the values of the non-random parameters deduced for the equivalent mixture for PE/AA in conjunction with the post-gel model developed in chapter 5 to overcome the divergence, implied by the model, in the rate of cyclization at the gel point, which is not, of course, observed. A parameter m was introduced which is the maximum number of ties (lines to infinity) allowed to radiate from the path between two functionalities if cyclization between them is to be allowed. It is again emphasised that this is

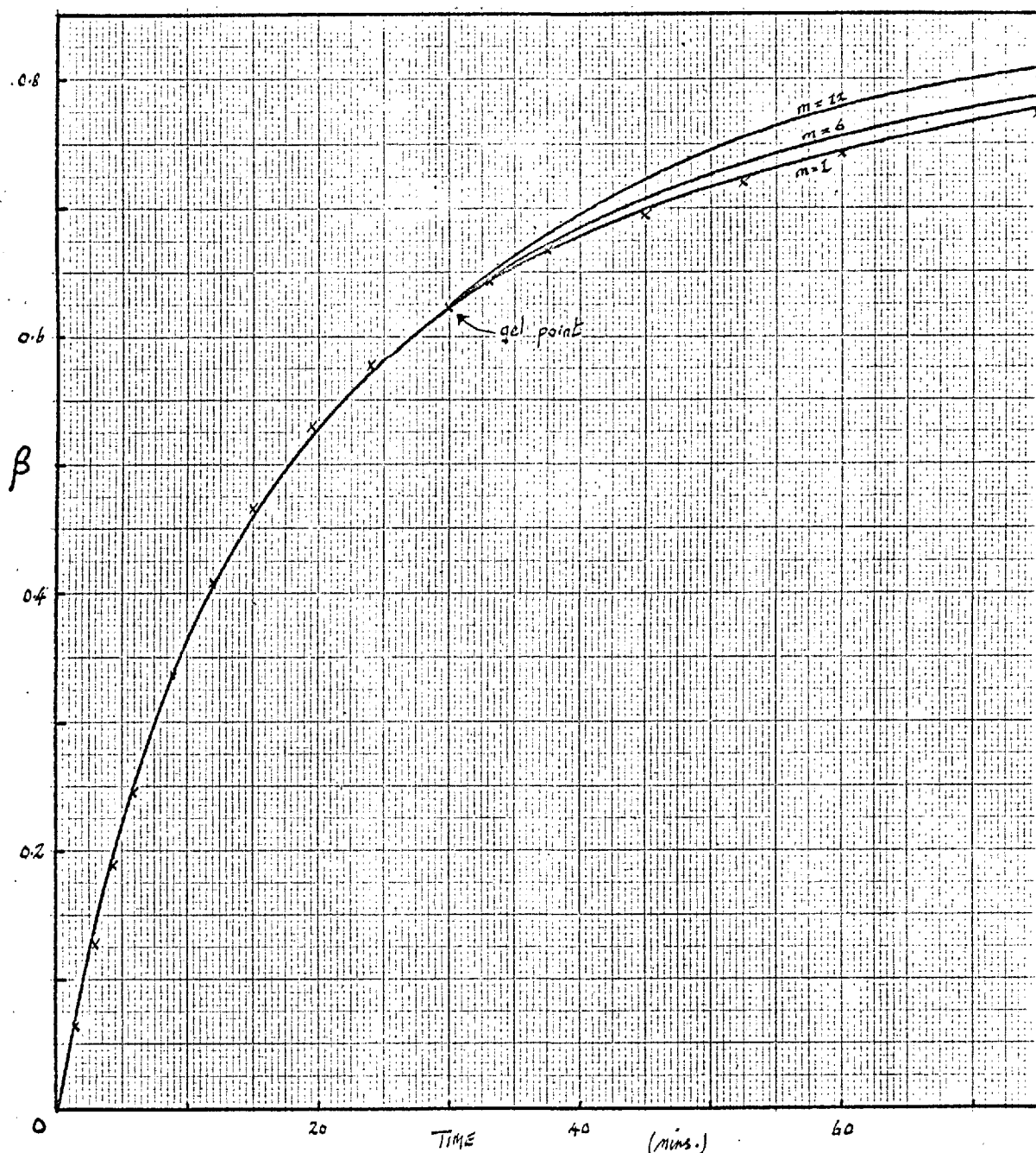


Fig. 8.13 Comparison of experimental rate curve (x) for equivalent ($E = 1$) mixture of PE/AA, 175°C. (run no. PE/3, Table 7.7) with theoretical curve using post-gel model (section (5.3)).
 $N_1 = 1.5$, $N_2 = 0.9$, $k' = 0.45$, $\lambda' = 0.187$, $k_x^* = 569$
 (equiv/g) $^{-2}$ min $^{-1}$

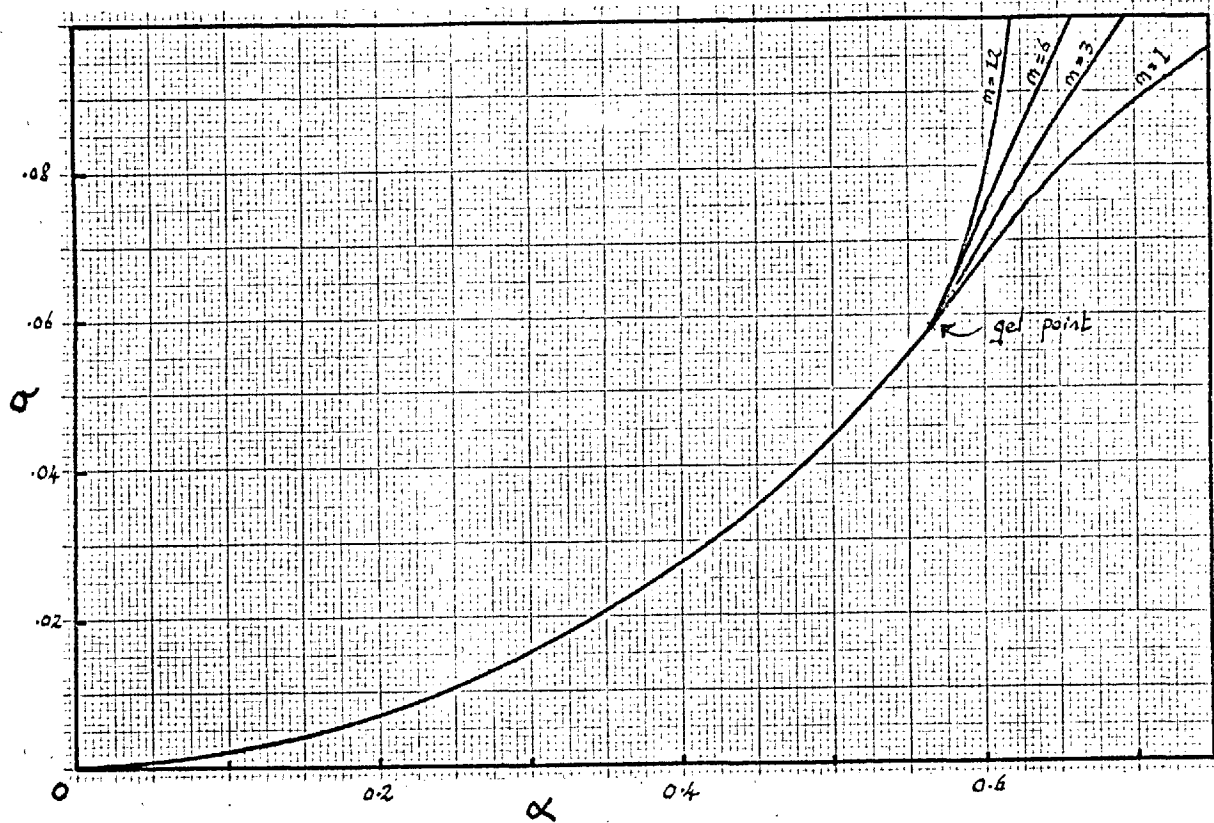


Fig. 8.14 Plot of σ against α for equivalent mixture of PE/AA.

$$N_1 = 1.5, N_2 = 0.9, k' = 0.45, \lambda^1 = 0.187$$

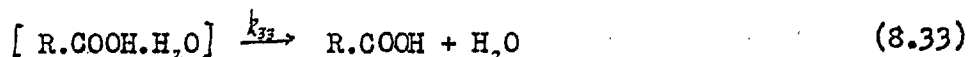
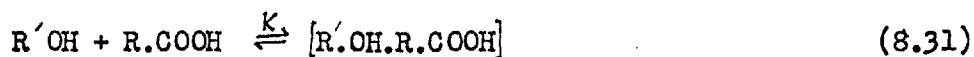
a crude model and is only expected to be of service for a small degree of conversion after the gel point. Figure (8.13) shows the rate curve for an equivalent mixture of PE/AA (run no. PE/3, see Table (7.7)) together with the theoretical rate curve computed for different values of m (eq. (5.12)). The systematic deviations of the experimental points from the theoretical curve are due to the fact that the parameters chosen fit the mean of the rate curves and not this curve in particular. This figure illustrates that the observed rate is best represented by a value of the post-gel cyclization parameter (m) of unity, i.e. a model that prohibits cyclization between functionalities which have one or more ties radiating from the path linking them.

Figure (8.14) shows a plot of σ versus α for this mixture and illustrates the manner in which σ increases rapidly near the gel point, i.e. the rate of cyclization increases when there is a large number of branched structures and correspondingly many functionalities in a molecule available for intramolecular condensation.

8.6 Discussion

The main outcome of this analysis of the polyesterification data is a justification of the inclusion of non-random terms into the differential rate equations. The non-random effects are seen to mask the order of the reaction leading some workers (Tang and Yao, 1959) to conclude that the uncatalysed polyesterification is $2\frac{1}{2}$ -order and catalysed by hydrogen ions. Our detailed analysis confirms Flory's (1937) conclusion that it is in fact third-order,

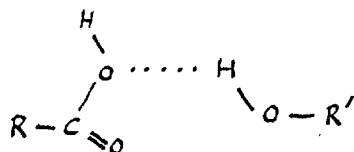
i.e. catalysed by undissociated acid molecules in the absence of a strong acid catalyst. Early work on the simple esterification of acetic acid and methanol in the absence of a catalyst (Rolfe and Hinshelwood, 1934) concluded that this reaction was catalysed by undissociated acetic acid. Similarly Williamson and Hinshelwood (1934) found that in the presence of an added strong acid the reaction is almost exclusively catalysed by hydrogen ions, i.e. a second-order reaction. We may therefore speculate concerning the mechanism of the uncatalysed polyesterification. A simple scheme consists of three steps:



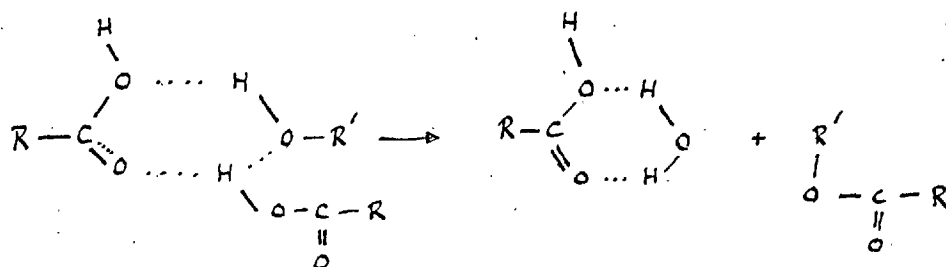
The only slow step is (8.32), and the rate equation is

$$\begin{aligned} \frac{d[OH]}{dt} &= -k_{32}[R'.OH.R.COOH][R.COOH] \\ &= -k_{32}K[R'.OH][R.COOH]^2 \end{aligned} \quad (8.34)$$

The complex $R.OH.R.COOH$ could be hydrogen bonded, i.e.



and the transition state in the slow step could be of a similar type



It is implied in the kinetic treatment (eq. (8.22)) that the equilibrium constant K of complex formation is merely a factor in both k_x^* and k_σ^* and that K is truly constant throughout the reaction: in particular, it is assumed that there is no substitution effect on K itself (eq. (8.31)), but that all substitution effects are confined to the step of (8.32). Since the substitution parameter (N_2) for $COOH$ for the cross-linking reaction is found to be 1.0 ± 0.2 i.e. within experimental error, there is practically no substitution effect ($N_2 = 1$), this treatment is particularly reasonable for an intermediate complex of form $[R.COOH]^2$ rather than $[R'.COOH.R.OH]$. Moreover, the same kinetic equations would result if the pre-equilibrium concerned the formation of a complex, not between $R'.OH$ and $R.COOH$ (eq. (8.31)), but between two $R.COOH$. Instead of eq. (8.32), one would then require this complex to collide with $R.OH$ to form the ester and a hydrated $R.COOH$. This scheme has the advantage that monocarboxylic acids are known to form hydrogen-bonded dimers corresponding to just the kind of complex here required. No further evidence is here presented to discriminate between the two schemes just proposed.

In retrospect it is a little disappointing that dilution experiments have not achieved accuracy sufficient to uniquely determine the linear substitution parameters, although the extrapolated value of α_c could be used to estimate the magnitude of these effects. The main difficulty arises in experimentally determining the gel point to sufficient accuracy, this is particularly difficult in the non-equivalent mixtures in which the gel point occurs at high conversions where the rate of reaction is comparatively slow due to the third-order reaction. However, the gel points were satisfactorily analyzed in terms of the three non-random parameters (N_1 , N_2 and λ^c) and the magnitude of the cyclization parameter is in excellent agreement with that predicted by random flight statistics. The value of the linear substitution parameter (N_1) of the polyol, though small (a value of $N_1 = 1.5$ corresponding to a non-random contribution to the activation energy of 360 cal/mole at 175°C., (eq. (3.20), (4.44)) is significantly greater than unity. At first sight it is a little surprising that this is in a direction which favours the condensation of functionalities on units which already bear reacted functionalities. However, it is known that in the solid state pentaerythritol is hydrogen-bonded (Llewellyn, Cox, & Goodwin, 1937) and it is conceivable that even in the melt some hydrogen bonds exist which must be broken when the first functionality of a unit condenses, it then becomes progressively easier for the remaining functionalities to react. This would account for a value of N_1 greater than unity.

The slight deviation of the linear substitution parameter for adipic acid from unity ($N_2 = 0.9$ to 1.2) in the two systems is not thought to be significant.

The excellent fitting of the rate curve for the equivalent mixtures of the two systems gives confidence to the use of the non-random model to other polycondensation systems. Although no attempt was made to fit the rate curves for all the non-equivalent mixtures, owing to the irreproducibility of k_x^* , to a single set of the four parameters, the fitting of the $E = 0.75$ for PE/AA with the same parameters as for the equivalent ($E = 1$) mixture is encouraging.

One proposal for confirmation of the present work by further research concerns the measurement of σ in terms of number average degrees of polymerization DP_n for direct comparison with theoretical calculations of σ . Tables of α and σ as functions of N_1 , N_2 and λ^E are given in Appendix D for various mixtures of $f_1 = 4$ (e.g. PE), 3 (e.g. TME) and $f_2 = 2$ (e.g. AA) monomers. Fig. (8.14) illustrates how σ varies as the reaction proceeds and such σ against α plots are experimentally accessible.

It is concluded that by using the theory of branching process as a common mathematical framework, the classical theory of polycondensation can be adequately generalized to include the two major sources of non-randomness, i.e. substitution effects and intramolecular condensation. In this thesis, the two extreme cases of thermodynamically and kinetically controlled reactions have been

satisfactorily treated using the non-random model. The inclusion of the non-random effects which are independently measured, e.g. by gel point determinations, is justified since the data could not be adequately analysed without reference to such effects.

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Appendix A

Statistical Parameters for Equilibrium Controlled
Polycondensation

The general link probability generating function for a f-functional polycondensation has been given (eq. (4.19)) as

$$\mathbb{F}_0(\theta) = N_0 \sum_{i=0}^f \sum_{j=0}^{f-i} g(i, j, k) \theta_\alpha^i \theta_\sigma^j \theta_\omega^k / (i!j!k!) \quad (\text{A.1})$$

where

$$g(i, j, k) = f! \gamma^i (i\tau)^j (1-\gamma)^k N^{(i+j)(i+j-1)} \quad (\text{A.2})$$

The statistical parameters that are used in the equilibrium treatment are defined in terms of $\mathbb{F}_0(\theta)$ in section (4.6). They are here formulated in terms of γ , τ , and N using eq. (A.1) and eqs. (4.12) - (4.14), (4.16), (4.17):

$$f \propto N_0 \sum_{i=1}^f \sum_{j=0}^{f-i} g(i, j, k) / ((i-1)!j!k!) \quad (\text{A.3})$$

$$f \sigma = N_0 \sum_{i=0}^f \sum_{j=1}^{f-i} g(i, j, k) / (i!(j-1)!k!) \quad (\text{A.4})$$

$$a = N_1 \sum_{i=2}^f \sum_{j=0}^{f-i} g(i, j, k) / ((i-2)!j!k!) \quad (\text{A.5})$$

$$n = N_1 \sum_{i=1}^f \sum_{j=0}^{f-i} g(i, j, k) / ((i-1)!j!k!) \quad (\text{A.6})$$

$$A = \left[\sum_{i=1}^f \sum_{j=0}^{f-i} g(i, j, k) / ((i-1)!j!(k-1)!) \right] / \left[\sum_{i=0}^f \sum_{j=0}^{f-i} g(i, j, k) / (i!j!(k-1)!) \right] \quad (\text{A.7})$$

rewriting eqs. (A.3) - (A.7):

$$\alpha = \gamma N_0 / N_1 \quad (\text{A.8})$$

$$\sigma = (f-1) \gamma \tau N^2 N_0 C \quad (\text{A.9})$$

$$a = (f-1) \gamma N^2 N_1 D \quad (\text{A.10})$$

$$n = (f-1)(1-\gamma)N_1 E \quad (\text{A.11})$$

$$A = (f-1)\gamma N_2 E \quad (\text{A.12})$$

The functions N_0 , N_1 , N_2 , C , D , E are listed below in terms of γ , τ , and N , for the cases $f = 2, 3, 4, 6$.

(i) the case $f = 2$:

$$1/N_0 = (1-\gamma)^2 + 2\gamma(1-\gamma+2\gamma\tau N^2) + \gamma^2 N^2 \quad (\text{A.13})$$

$$1/N_1 = 1 - \gamma + (\gamma + \tau)N^2 \quad (\text{A.14})$$

$$N_2 = 1 \quad (\text{A.15})$$

$$C = 1 \quad (\text{A.16})$$

$$D = 1 \quad (\text{A.17})$$

$$E = 1 \quad (\text{A.18})$$

(ii) the case $f = 3$:

$$1/N_0 = (1-\gamma)^3 + 3\gamma(1-\gamma)^2 + 3\gamma(1-\gamma)(\gamma + 2\tau)N^2 + \gamma(\gamma^2 + 6\gamma\tau + 3\tau^2)N^6 \quad (\text{A.19})$$

$$1/N_1 = (1-\gamma)^2 + 2(1-\gamma)(\gamma + \tau)N^2 + (\gamma^2 + 4\gamma\tau + \tau^2)N^6 \quad (\text{A.20})$$

$$1/N_2 = (1-\gamma)^2 + 2\gamma(1-\gamma) + \gamma(\gamma + 2\tau)N^2 \quad (\text{A.21})$$

$$C = 1 - \gamma + (\gamma + \tau)N^2 \quad (\text{A.22})$$

$$D = 1 - \gamma + (\gamma + 2\tau)N^2 \quad (\text{A.23})$$

$$E = 1 - \gamma + (\gamma + \tau)N^2 \quad (\text{A.24})$$

(iii) the case $f = 4$:

$$1/N_0 = (1-\gamma)^4 + 4\gamma(1-\gamma)^3 + 6\gamma(1-\gamma)^2(\gamma + 2\tau)N^2 + 4\gamma(1-\gamma)(\gamma^2 + 6\gamma\tau + 3\tau^2)N^6 + \gamma(\gamma^3 + 12\gamma^2\tau + 24\gamma\tau^2 + 4\tau^3)N^{12} \quad (\text{A.25})$$

$$1/N_1 = (1-\gamma)^3 + 3(1-\gamma)^2(\gamma + \tau)N^2 + 3(1-\gamma)(\gamma^2 + 4\gamma\tau + \tau^2)N^6 + (\gamma^3 + 9\gamma^2\tau + 12\gamma\tau^2 + \tau^3)N^{12} \quad (\text{A.26})$$

$$1/N_2 = (1-y)^3 + 3y(1-y)^2 + 3y(1-y)(y+2\tau)N^2 + y(y^2 + 6y\tau + 3\tau^2)N^6 \quad (A.27)$$

$$C = (1-y)^2 + 2(1-y)(y+\tau)N^4 + (y^2 + 4y\tau + \tau^2)N^{10} \quad (A.28)$$

$$D = (1-y)^2 + 2(1-y)(y+2\tau)N^4 + (y^2 + 6y\tau + 4\tau^2)N^{10} \quad (A.29)$$

$$E = (1-y)^2 + 2(1-y)(y+\tau)N^2 + (y^2 + 4y\tau + \tau^2)N^6 \quad (A.30)$$

(iv) the case $f = 6$:

$$\begin{aligned} 1/N_0 &= (1-y)^6 + 6y(1-y)^5 + 15y(1-y)^4(y+2\tau)N^2 \\ &+ 20y(1-y)^3(y^2 + 6y\tau + 3\tau^2)N^6 + 15y(1-y)^2(y^3 + 12y^2\tau + 24y\tau^2 + 4\tau^3)N^{12} \\ &+ 6y(1-y)(y^4 + 20y^3\tau + 90y^2\tau^2 + 80y\tau^3 + 5\tau^4)N^{20} \\ &+ y(y^5 + 30y^4\tau + 240y^3\tau^2 + 540y^2\tau^3 + 240y\tau^4 + 6\tau^5)N^{30} \end{aligned} \quad (A.31)$$

$$\begin{aligned} 1/N_1 &= (1-y)^5 + 5(1-y)^4(y+\tau)N^2 + 10(1-y)^3(y^2 + 4y\tau + \tau^2)N^6 \\ &+ 10(1-y)^2(y^3 + 9y^2\tau + 12y\tau^2 + \tau^3)N^{12} \\ &+ 5(1-y)(y^4 + 16y^3\tau + 54y^2\tau^2 + 32y\tau^3 + \tau^4)N^{20} \\ &+ (y^5 + 25y^4\tau + 160y^3\tau^2 + 270y^2\tau^3 + 80y\tau^4 + \tau^5)N^{30} \end{aligned} \quad (A.32)$$

$$\begin{aligned} 1/N_2 &= (1-y)^5 + 5y(1-y)^4 + 10y(1-y)^3(y+2\tau)N^2 \\ &+ 10y(1-y)^2(y^2 + 6y\tau + 3\tau^2)N^6 + 5y(y^3 + 12y^2\tau + 24y\tau^2 + 4\tau^3)N^{12}(1-y) \\ &+ y(y^4 + 20y^3\tau + 90y^2\tau^2 + 80y\tau^3 + 5\tau^4)N^{20} \end{aligned} \quad (A.33)$$

$$\begin{aligned} C &= (1-y)^4 + 4(1-y)^3(y+\tau)N^4 + 6(1-y)^2(y^2 + 4y\tau + \tau^2)N^{10} \\ &+ 4(1-y)(y^3 + 9y^2\tau + 12y\tau^2 + \tau^3)N^{18} + (y^4 + 16y^3\tau + 54y^2\tau^2 + 32y\tau^3 + \tau^4)N^{28} \end{aligned} \quad (A.34)$$

$$\begin{aligned} D &= (1-y)^4 + 4(1-y)^3(y+2\tau)N^4 + 6(1-y)^2(y^2 + 6y\tau + 4\tau^2)N^{10} \\ &+ 4(1-y)(y^3 + 12y^2\tau + 27y\tau^2 + 8\tau^3)N^{18} + (y^4 + 20y^3\tau + 96y^2\tau^2 + 108y\tau^3 + 16\tau^4)N^{28} \end{aligned} \quad (A.35)$$

$$\begin{aligned} E &= (1-y)^4 + 4(1-y)(y+\tau)N^2 + 6(1-y)(y^2 + 4y\tau + \tau^2)N^6 \\ &+ 4(1-y)(y^3 + 9y^2\tau + 12y\tau^2 + \tau^3)N^{12} + (y^4 + 16y^3\tau + 54y^2\tau^2 + 32y\tau^3 + \tau^4)N^{20} \end{aligned} \quad (A.36)$$

Appendix B Comparison of Kinetic Rate Equations (4.55)
with Equilibrium Equations (4.21), (4.23)

The kinetic rate equation for systems with a linear FSSE and a cyclization component (eq. 4.55) is

$$-\frac{d P_{i,j}}{dt} = k_a^* C_o \left[kN^{i+j} P_{i,j} - (k+1)N^{i+j-1} P_{i,j-1} \right] \langle kN^{i+j} \rangle + k_o^* i \left[kN^{i+j} P_{i,j} - (k+1)N^{i+j-1} P_{i,j-1} \right] \langle ikN^{i+j} \rangle \sum_{x \neq x_o} m_x (x_o)^{-3/2} / \langle ik \rangle \quad (B.1)$$

Differentiating eq. (4.49):

$$\begin{aligned} f \frac{d\alpha}{dt} &= \langle i dP_{i,j} / dt \rangle \\ &= -k_a^* C_o \langle kN^{i+j} \rangle \\ &\times \left\{ \begin{aligned} &[(f-1)NP_{1,0} - fP_{0,0} + (f-2)N^2 P_{1,1} + (f-3)N^3 P_{1,2} + \dots + N^{f-1} P_{1,f-2}] \\ &+ 2[(f-2)N^2 P_{2,0} - (f-1)NP_{1,0} + (f-3)N^3 P_{2,1} - (f-2)N^2 P_{1,1} + \dots - N^{f-1} P_{1,f-2}] \\ &+ 3[(f-3)N^3 P_{3,0} - (f-2)N^2 P_{2,0} + (f-4)N^4 P_{3,1} - (f-3)N^3 P_{2,1} + \dots - N^{f-1} P_{2,f-3}] \\ &+ [\dots] \\ &+ [-N^{f-1} P_{f-1,0}] \end{aligned} \right\} \\ &- k_o^* \sum m_x (x_o)^{-3/2} \langle ikN^{i+j} \rangle (\langle ik \rangle)^{-1} \\ &\times \left\{ \begin{aligned} &[(f-1)N P_{1,0} + (f-2)N^2 P_{1,1} - (f-1)N P_{1,0} + \dots - N^{f-1} P_{1,f-2}] \\ &+ 4[(f-2)N^2 P_{2,0} + (f-3)N^3 P_{2,1} - (f-2)N^2 P_{2,0} + \dots - N^{f-1} P_{2,f-3}] \\ &+ 9[(f-3)N^3 P_{3,0} + (f-4)N^4 P_{3,1} - (f-3)N^3 P_{3,0} + \dots - N^{f-1} P_{3,f-4}] \\ &+ [\dots] \\ &+ (f-1)^2 [-N^{f-1} P_{f-1,0}] \end{aligned} \right\} \quad (B.2) \end{aligned}$$

$$f \frac{d\alpha}{dt} = -k_a^* C_o \langle kN^{i+j} \rangle [-fP_{0,0} - (f-1)NP_{1,0} - (f-2)N^2 P_{2,0} - \dots] - k_o^* \sum m_x (x_o)^{-3/2} \langle ikN^{i+j} \rangle (\langle ik \rangle)^{-1} [0] \quad (B.3)$$

$$= k_a^* C_o (\langle kN^{i+j} \rangle)^2 \quad (B.4)$$

which, using eq. (4.49), (4.50), (4.59) can be written

$$d\alpha / dt = k^* C_o f(1-\alpha-o)^2 S_\alpha \quad (B.5)$$

The identity between the equilibrium and kinetic rate equations for cross-linking can be seen by comparing the left hand side of eq. (4.21) with eq. (B.5).

Similarly differentiating eq. (4.5)

$$\begin{aligned}
 f \cdot \frac{d\sigma}{dt} &= \langle j \, dP_{i,j} / dt \rangle \\
 &= -k_x^* C_o \langle kN^{i+j} \rangle \\
 &\quad \times \left\{ \begin{aligned} &[(f-2)N^2 P_{1,1} + (f-3)N^3 P_{2,1} - (f-2)N^2 P_{1,1} + (f-4)N^4 P_{3,1} - \dots - N^{f+1} P_{f-2,1}] \\ &+ 2[(f-3)N^3 P_{1,2} + (f-4)N^4 P_{2,2} - (f-3)N^3 P_{1,2} + (f-5)N^5 P_{3,2} - \dots - N^{f+1} P_{f-3,2}] \\ &+ [\dots] \\ &+ (f-2)[\dots - N^{f+1} P_{f-2,2}] \end{aligned} \right\} \\
 &\quad - k_x^* \sum m_x (x\nu)^{-3/2} \langle ikN^{i+j} \rangle (\langle ik \rangle)^{-1} \\
 &\quad \left\{ \begin{aligned} &[(f-2)N^2 P_{1,1} - (f-1)N P_{1,0} + 2((f-3)N^3 P_{2,1} - (f-2)N^2 P_{2,0}) \\ &\quad + \dots - (f-1)N^{f+1} P_{f-1,0}] \\ &+ 2[(f-3)N^3 P_{1,2} - (f-2)N^2 P_{1,1} + 2((f-4)N^4 P_{2,2} - (f-3)N^3 P_{2,1}) \\ &\quad + \dots - (f-2)N^{f+1} P_{f-2,1}] \\ &+ [\dots] \\ &+ (f-2)[\dots - N^{f+1} P_{f-2,2}] \end{aligned} \right\} \quad (B.6)
 \end{aligned}$$

$$\begin{aligned}
 f \cdot \frac{d\sigma}{dt} &= -k_x^* C_o \langle kN^{i+j} \rangle [0] \\
 &\quad - k_x^* \sum m_x (x\nu)^{-3/2} \langle ikN^{i+j} \rangle (\langle ik \rangle)^{-1} \\
 &\quad [- (f-1)N P_{1,0} - (f-2)N^2 P_{1,1} - 2(f-3)N^3 P_{2,1} - \dots] \quad (B.7)
 \end{aligned}$$

$$= k_x^* \sum m_x (x\nu)^{3/2} \langle ikN^{i+j} \rangle (\langle ik \rangle)^{-1} \langle ikN^{i+j} \rangle \quad (B.8)$$

which, using eq. (4.49), (4.50), (4.61), (4.62) can be written

$$d\sigma / dt = k_x^* (1 - \alpha - \sigma) A S_o \sum_{x=x_0}^{\infty} m_x (x\nu)^{-3/2} \quad (B.9)$$

which, using eq. (4.54), (4.18) gives

$$d\sigma / dt = k_x^* (1 - \alpha - \sigma) S_o \sum_{x=x_0}^{\infty} n_x (x\nu)^{-3/2} \quad (B.10)$$

The kinetic cyclization rate equation (B.10) is to be compared with the left hand side of eq. (4.23) which, when summed over all x , is the forward rate of cyclization.

Appendix C

Transformation of the (σ_c, α_c) to the (λ, N) plane for functionalities $f = 3, 4, 6$ in equilibrium controlled systems and to the $(\lambda, N^{1/2})$ plane for the same functionalities in kinetically controlled systems. N and λ are the fundamental parameters for non-random polycondensations. Deviations of N from unity measure the intensity of the linear first shell substitution effect; deviations of λ from zero measure the tendency to ring formation. The total critical conversion of functionalities, $\alpha_c + \sigma_c$, is directly measurable. The applicability of the model is most firmly established in the region $4\sigma_c < \alpha_c$.

TABLE	CONTROL	FUNCTIONALITY
C.1	Equilibrium	3
C.2	Equilibrium	4
C.3	Equilibrium	6
C.4	Kinetic	3
C.5	Kinetic	4
C.6	Kinetic	6

Fig. C.1 Equilibrium control; $f = 3$.

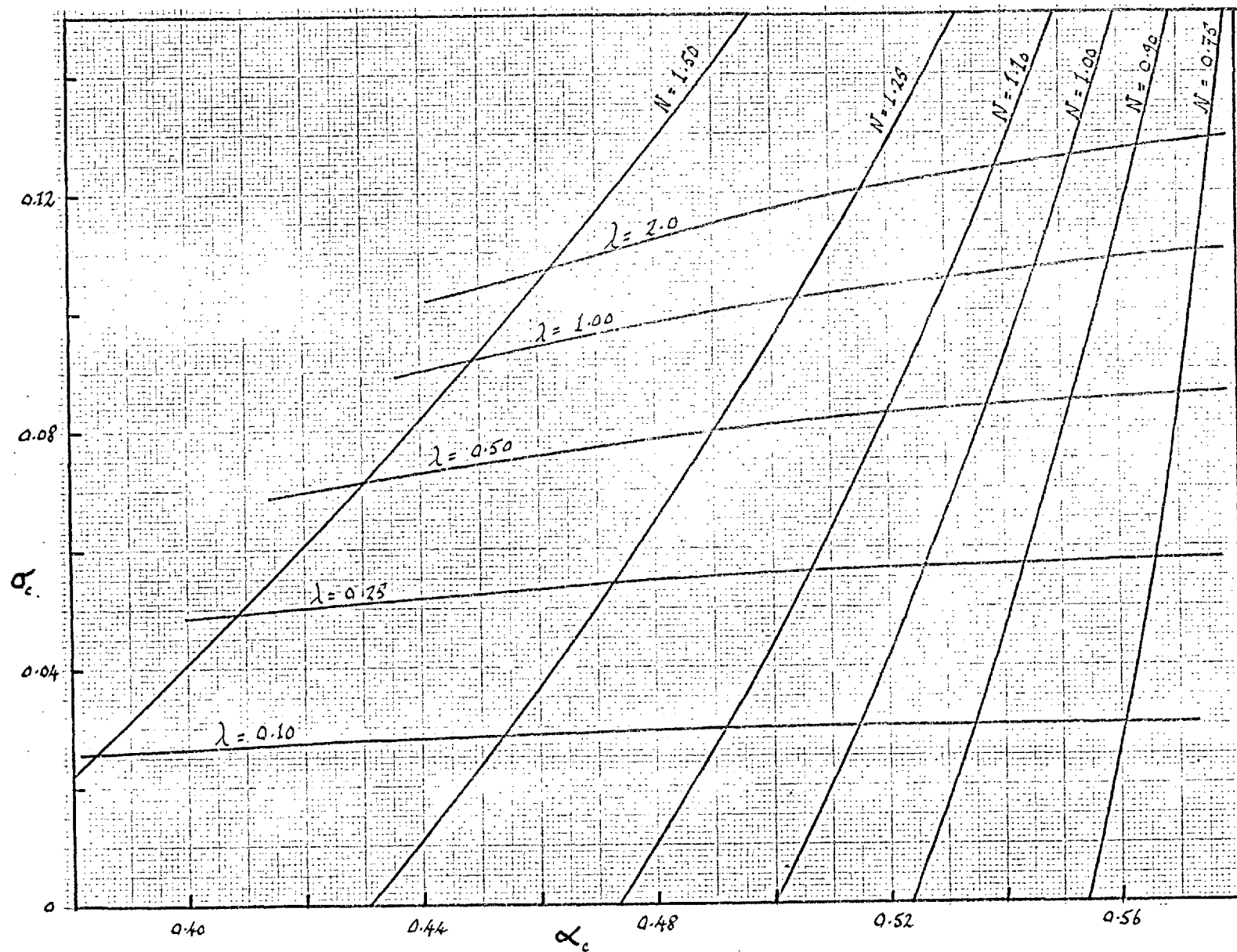


Fig. C.2 Equilibrium control; $f = 4$.

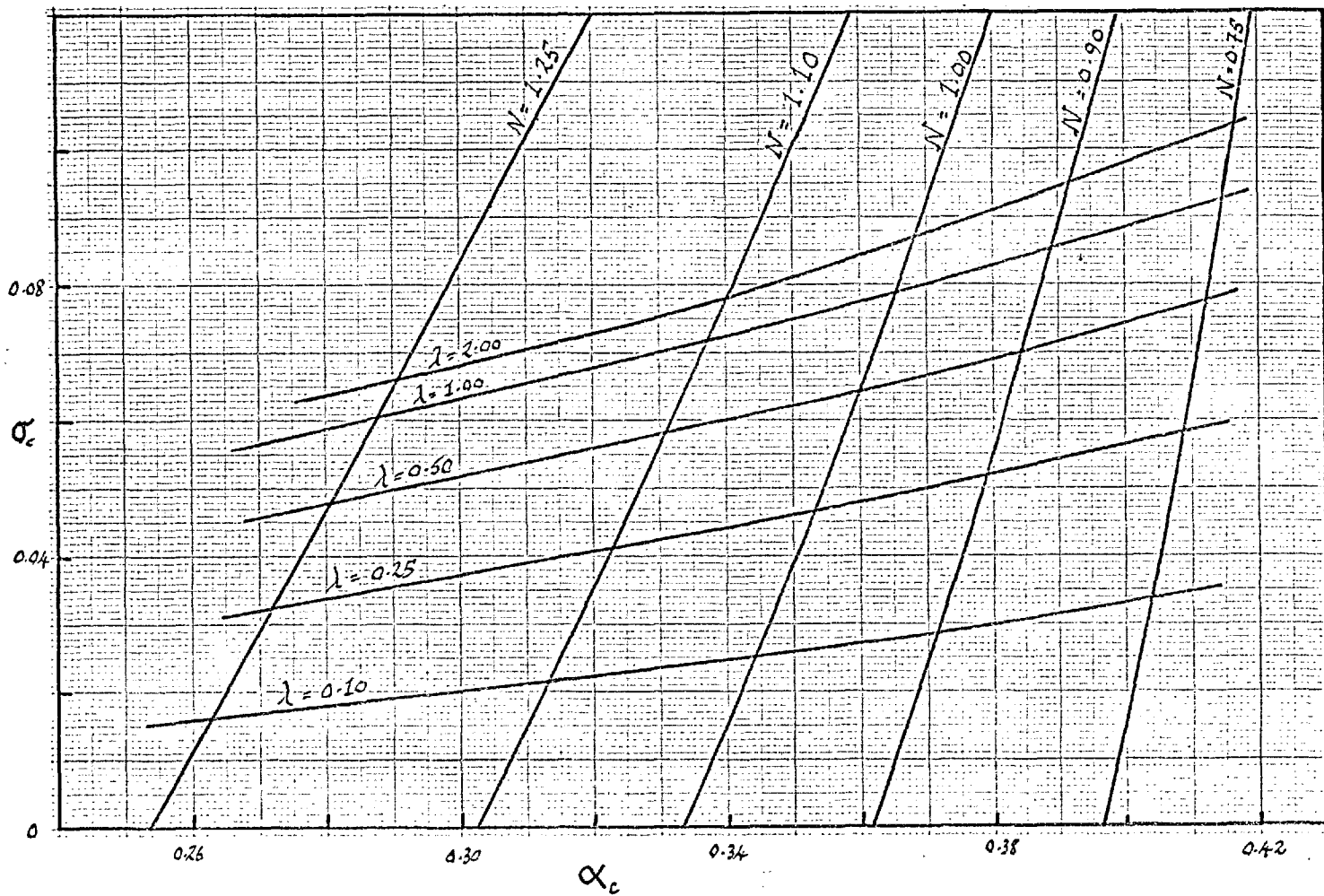


Fig. C.3 Equilibrium control; $f = 6$.

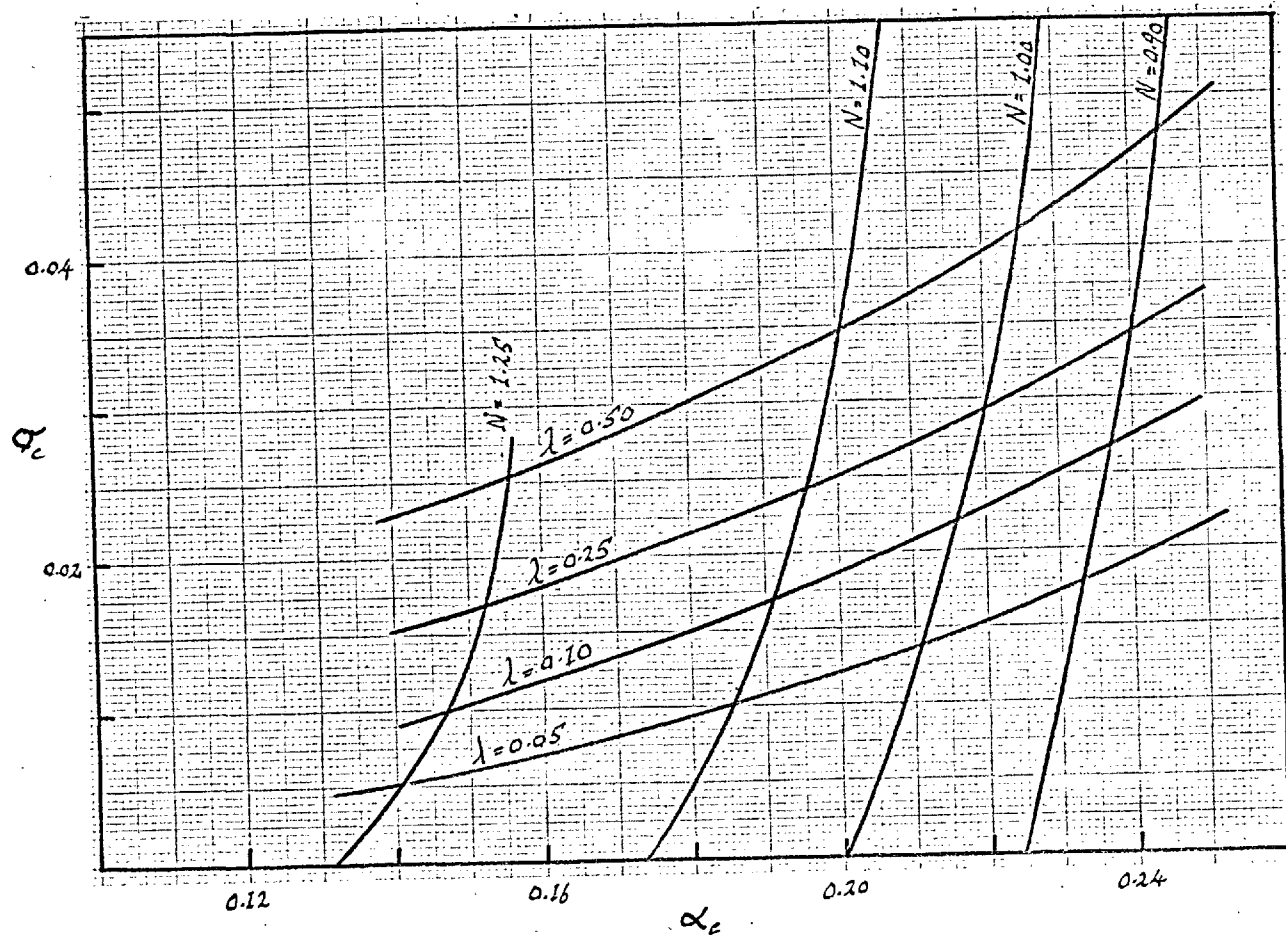


Fig. C.4 Kinetic control; $f = 3$.

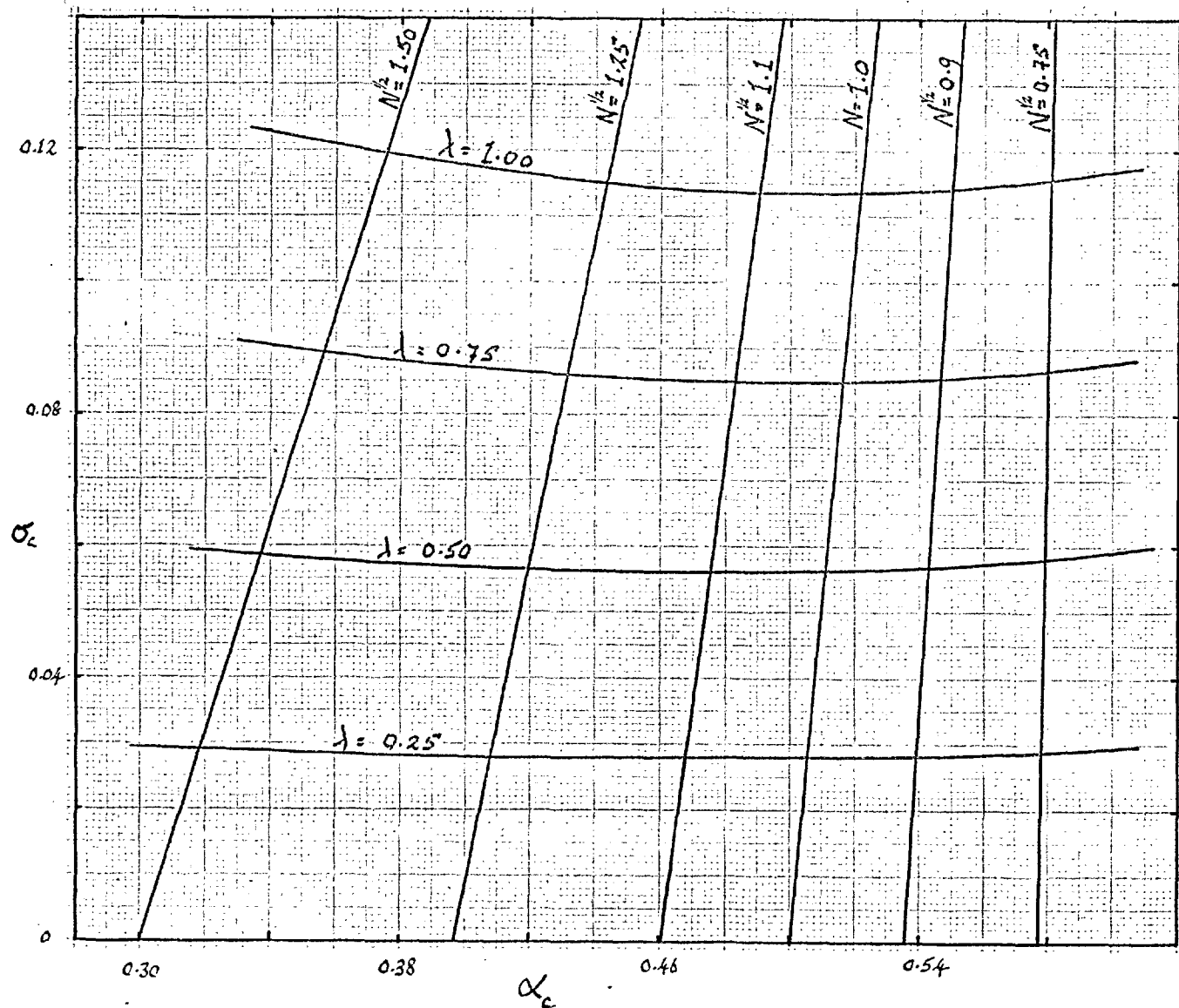


Fig. C.5 Kinetic control; $f = 4$.

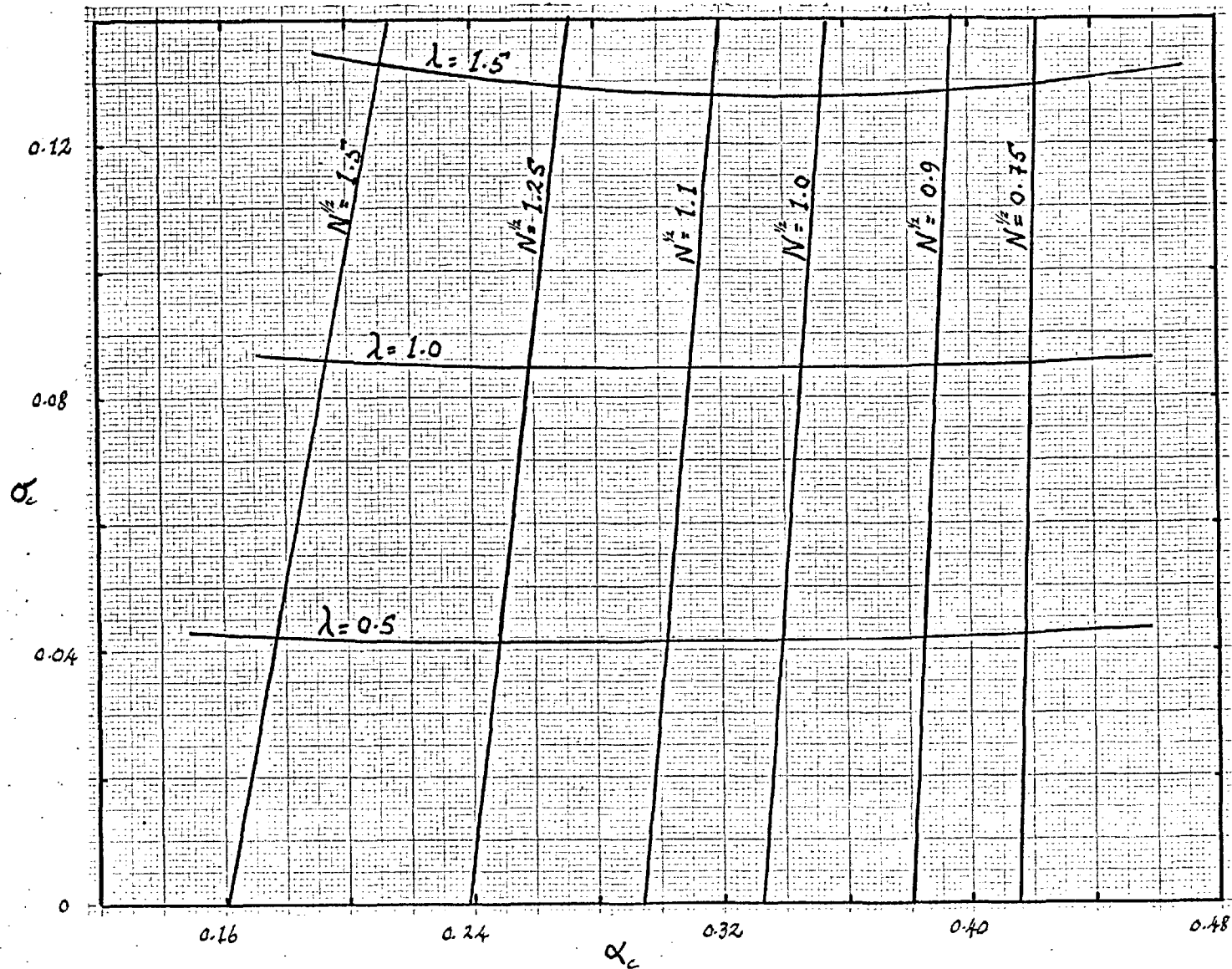
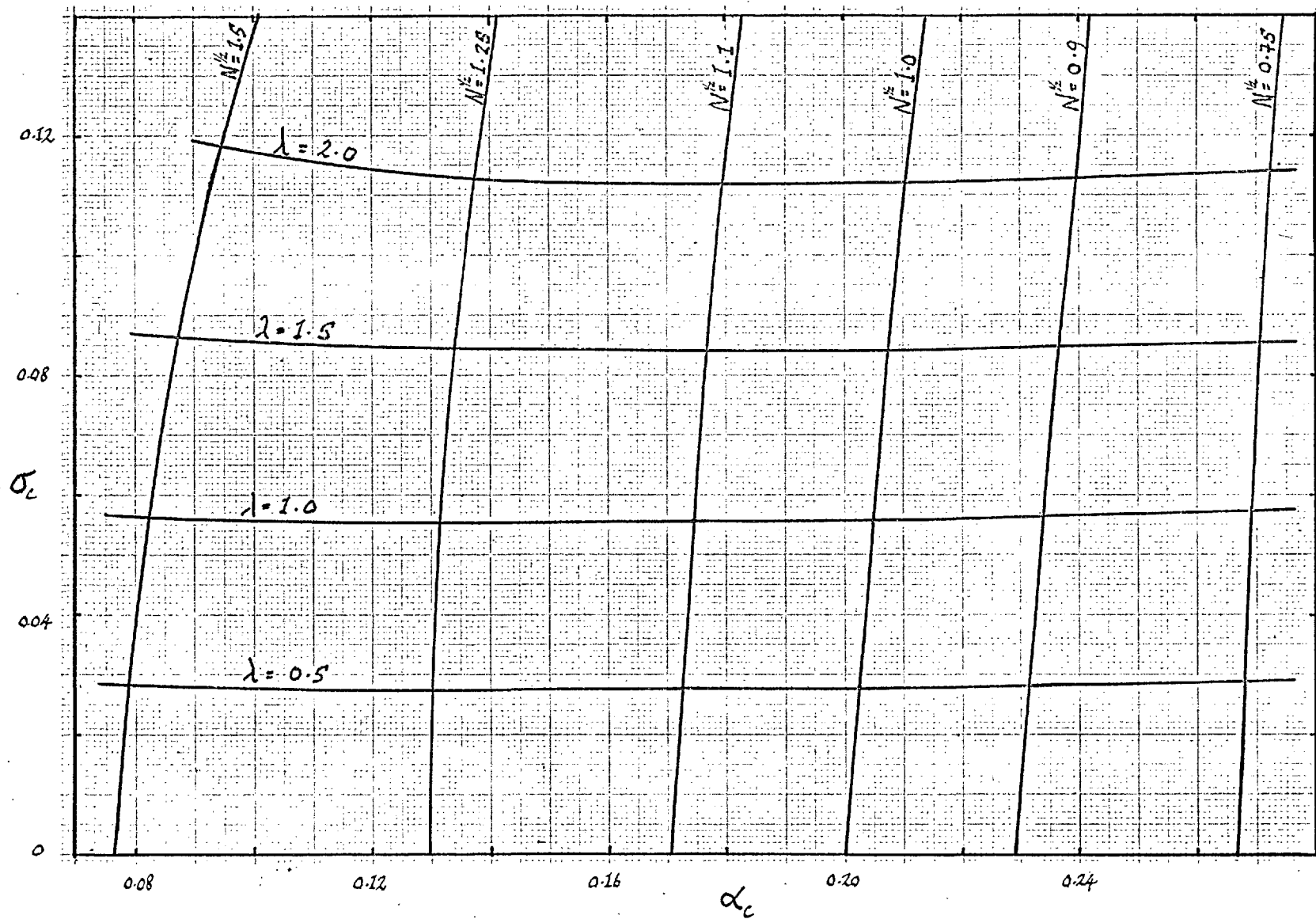


Fig. C.6 Kinetic control; $f = 6$.



Appendix DTables of critical parameters

Tables of the critical parameters α_c and σ_c for the kinetically controlled co-polymerization of f_1 -functional polyols ($f_1 = 3, 4$) with bi-functional acids ($f_2 = 2$) are presented as functions of the cyclization parameter λ^c , the two linear substitution parameters N_1 , N_2 referring to the f_1 -functional and bi-functional unit respectively, and the equivalence (E) of the mixture. The gel times for both second (t_{2c}) and third (t_{3c}) order reactions are recorded. The volume shrinkage factor (k') (see eq. (8.20)) is taken to be 0.45 except in Tables (D.4), (D.9) in which it is set to zero. These tables are based on eq. (8.22); the procedure for solving these rate equations is outlined in Appendix F.

In the range of N_1 , N_2 , and λ^c presented, σ_c is (to the third decimal place) independent of N_1 and N_2 and solely a function of λ^c and hence only values of α_c are presented in full.

TABLE	f_1	f_2	E	k'
D.1	4	2	0.50	0.45
D.2	4	2	0.75	0.45
D.3	4	2	1.00	0.45
D.4	4	2	1.00	0.00
D.5	4	2	1.50	0.45
D.6	4	2	2.00	0.45
D.7	3	2	0.67	0.45
D.8	3	2	1.00	0.45
D.9	3	2	1.00	0.00
D.10	3	2	1.50	0.45

TABLE D.1

$f_1 = 4, f_2 = 2, E = 0.50; k_{2x}^* C_o = 1.024 \text{ min}^{-1}, k_{3x}^* C_o^2 = 1.292 \text{ min}^{-1}, k' = 0.45$

N_1	N_2	$\lambda^s = 0.000, \alpha_c = 0.000$			$\lambda^s = 0.133, \alpha_c = 0.041$			$\lambda^s = 0.267, \alpha_c = 0.083$		
		t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c
0.81	0.81	1.749	4.479	0.859	2.049	6.711	0.863	2.558	12.80	0.867
0.81	1.00	1.500	3.664	0.855	1.742	5.489	0.860	2.181	10.48	0.865
0.81	1.44	1.171	2.646	0.843	1.377	3.937	0.852	1.715	7.566	0.861
1.00	0.81	1.241	2.641	0.823	1.403	3.597	0.829	1.650	5.595	0.834
1.00	1.00	1.070	2.180	0.817	1.213	2.945	0.824	1.419	4.629	0.831
1.00	1.44	0.842	1.588	0.801	0.964	2.170	0.812	1.140	3.391	0.823
1.44	0.81	0.698	1.140	0.746	0.767	1.409	0.755	0.854	1.846	0.764
1.44	1.00	0.610	0.947	0.734	0.673	1.176	0.745	0.753	1.554	0.757
1.44	1.44	0.494	0.704	0.708	0.537	0.886	0.723	0.608	1.168	0.740

TABLE D.2

$f_1 = 4, f_2 = 2, E = 0.75; k_{2c}^* C_a = 1.230 \text{ min}^{-1}, k_{3c}^* C_c^2 = 1.864 \text{ min}^{-1}, k^1 = 0.45$

N_1	N_2	$\lambda^{75} = 0.000, \sigma_c = 0.000$			$\lambda^{75} = 0.111, \sigma_c = 0.035$			$\lambda^{75} = 0.222, \sigma_c = 0.069$		
		t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c
0.81	0.81	1.473	1.951	0.703	1.608	2.320	0.708	1.789	2.838	0.713
0.81	1.00	1.259	1.598	0.690	1.382	1.908	0.697	1.534	2.335	0.703
0.81	1.44	0.979	1.165	0.665	1.080	1.392	0.674	1.204	1.709	0.682
1.00	0.81	1.080	1.328	0.681	1.173	1.556	0.688	1.287	1.874	0.694
1.00	1.00	0.931	1.102	0.667	1.015	1.294	0.675	1.113	1.553	0.683
1.00	1.44	0.732	0.815	0.639	0.803	0.955	0.649	0.886	1.155	0.660
1.44	0.31	0.643	0.697	0.629	0.694	0.802	0.639	0.755	0.941	0.649
1.44	1.00	0.561	0.587	0.610	0.607	0.673	0.622	0.662	0.792	0.634
1.44	1.44	0.451	0.444	0.576	0.491	0.510	0.590	0.540	0.606	0.606

TABLE D.3

$f_1 = 4, f_2 = 2, E = 1.00; k_{2c}^* C_o = 1.366 \text{ min}^{-1}, k_{3c}^* C_o^2 = 2.300 \text{ min}^{-1}; k^1 = 0.45$

$\lambda^1 = 0.000, \sigma_c = 0.000$

$\lambda^1 = 0.100, \sigma_c = 0.031$

$\lambda^1 = 0.200, \sigma_c = 0.062$

N_1	N_2	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c
0.81	0.81	1.521	1.543	0.609	1.667	1.791	0.614	1.846	2.116	0.620
0.81	1.00	1.289	1.261	0.593	1.414	1.463	0.599	1.566	1.728	0.605
0.81	1.44	0.985	0.910	0.563	1.085	1.057	0.570	1.207	1.250	0.578
1.00	0.81	1.101	1.066	0.595	1.194	1.223	0.602	1.313	1.429	0.609
1.00	1.00	0.944	0.882	0.577	1.027	1.012	0.585	1.129	1.179	0.593
1.00	1.44	0.735	0.650	0.544	0.804	0.745	0.554	0.886	0.871	0.564
1.44	0.81	0.653	0.579	0.558	0.706	0.660	0.569	0.772	0.766	0.579
1.44	1.00	0.569	0.488	0.537	0.616	0.553	0.549	0.673	0.644	0.561
1.44	1.44	0.454	0.369	0.498	0.494	0.420	0.513	0.542	0.489	0.528

TABLE D.4

$f_1 = 4, f_2 = 2, E = 1.00; k_{2c}^* C_o = 1.366 \text{ min}^{-1}, k_{3c}^* C_o^2 = 2.300 \text{ min}^{-1}; k^1 = 0.00$

N_1	N_2	$\lambda^1 = 0.000, \sigma_c = 0.000$			$\lambda^1 = 0.100, \sigma_c = 0.033$			$\lambda^1 = 0.200, \sigma_c = 0.067$		
		t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c
0.81	0.81	1.623	1.778	0.609	1.799	2.108	0.615	2.019	2.558	0.620
0.81	1.00	1.371	1.444	0.593	1.521	1.710	0.599	1.708	2.074	0.606
0.81	1.44	1.043	1.029	0.563	1.159	1.219	0.571	1.306	1.478	0.579
1.00	0.81	1.169	1.217	0.595	1.285	1.425	0.602	1.426	1.709	0.610
1.00	1.00	1.000	1.000	0.577	1.099	1.168	0.586	1.221	1.401	0.594
1.00	1.44	0.774	0.727	0.544	0.854	0.852	0.555	0.952	1.020	0.565
1.44	0.81	0.688	0.650	0.558	0.750	0.753	0.570	0.829	0.896	0.581
1.44	1.00	0.596	0.542	0.537	0.653	0.628	0.549	0.723	0.747	0.562
1.44	1.44	0.472	0.406	0.498	0.521	0.469	0.513	0.578	0.561	0.529

TABLE D.5

$f_1 = 4, f_2 = 2, E = 1.50; k_{2\alpha}^* C_0 = 1.536 \text{ min}^{-1}, k_{3\alpha}^* C_0^2 = 2.908 \text{ min}^{-1}, k^* = 0.45$

N_1	N_2	$\lambda^s = 0.000, \sigma_c = 0.000$			$\lambda^s = 0.133, \sigma_c = 0.042$			$\lambda^s = 0.267, \sigma_c = 0.084$		
		t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c
0.81	0.81	1.890	1.485	0.747	2.157	1.777	0.754	2.526	2.192	0.762
0.81	1.00	1.550	1.181	0.718	1.755	1.395	0.726	2.035	1.703	0.735
0.81	1.44	1.131	0.820	0.668	1.275	0.962	0.678	1.461	1.156	0.688
1.00	0.81	1.308	1.001	0.738	1.467	1.174	0.748	1.687	1.424	0.758
1.00	1.00	1.091	0.809	0.707	1.222	0.941	0.718	1.392	1.129	0.729
1.00	1.44	0.821	0.578	0.654	0.915	0.669	0.667	1.035	0.791	0.680
1.44	0.81	0.745	0.539	0.711	0.833	0.630	0.726	0.953	0.762	0.742
1.44	1.00	0.636	0.443	0.675	0.710	0.518	0.692	0.805	0.619	0.710
1.44	1.44	0.493	0.329	0.615	0.551	0.379	0.634	0.620	0.453	0.655

TABLE D.6

$f_1 = 4, f_2 = 2, E = 2.00; k_{2\kappa}'' C_o = 1.640 \text{ min}^{-1}, k_{3\kappa}'' C_o^2 = 3.312 \text{ min}^{-1}, k' = 0.45$

$\lambda^z = 0.000, \sigma_c = 0.000$

$\lambda^z = 0.167, \sigma_c = 0.053$

$\lambda^z = 0.333, \sigma_c = 0.105$

N_1	N_2	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c
0.81	0.81	2.624	1.827	0.863	3.410	2.497	0.873	6.097	4.876	0.883
0.81	1.00	2.019	1.360	0.822	2.486	1.756	0.833	3.446	2.585	0.845
0.81	1.44	1.369	0.879	0.755	1.622	1.085	0.767	2.031	1.418	0.781
1.00	0.81	1.712	1.170	0.859	2.157	1.549	0.871	3.639	2.883	0.884
1.00	1.00	1.356	0.892	0.817	1.628	1.123	0.830	2.176	1.600	0.844
1.00	1.44	0.962	0.606	0.745	1.116	0.730	0.762	1.361	0.930	0.778
1.44	0.81	0.926	0.609	0.844	1.144	0.792	0.864	1.835	1.425	0.885
1.44	1.00	0.755	0.482	0.796	0.900	0.588	0.818	1.175	0.828	0.841
1.44	1.44	0.561	0.335	0.714	0.643	0.400	0.741	0.785	0.512	0.768

TABLE D.-7

$f_1 = 3, f_2 = 2, E = 0.67; k_{2x}^* C_o = 2.012 \text{ min}^{-1}, k_{3x}^* C_o = 3.704 \text{ min}^{-1}, k^t = 0.45$

		$\lambda^{dt} = 0.000, \sigma_c = 0.000$			$\lambda^{dt} = 0.120, \sigma_c = 0.036$			$\lambda^{dt} = 0.240, \sigma_c = 0.073$		
N_1	N_2	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c
0.81	0.81	1.678	3.598	0.894	2.036	5.967	0.897	2.757	15.19	0.900
0.81	1.00	1.420	2.923	0.891	1.718	4.858	0.895	2.332	12.35	0.899
0.81	1.44	1.095	2.076	0.883	1.333	3.452	0.890	1.805	8.788	0.897
1.00	0.81	1.213	2.195	0.870	1.423	3.309	0.875	1.787	6.350	0.879
1.00	1.00	1.034	1.787	0.866	1.216	2.705	0.872	1.527	5.204	0.878
1.00	1.44	0.802	1.277	0.855	0.945	1.936	0.864	1.203	3.760	0.874
1.44	0.81	0.725	1.005	0.819	0.821	1.366	0.827	0.971	2.073	0.835
1.44	1.00	0.622	0.824	0.811	0.706	1.123	0.822	0.842	1.714	0.832
1.44	1.44	0.491	0.590	0.793	0.562	0.813	0.808	0.672	1.261	0.822

TABLE D.8

$f_1 = 3, f_2 = 2, E = 1.00; k_{2x}^* C_o = 2.414 \text{ min}^{-1}, k_{3x}^* C_o^2 = 5.328 \text{ min}^{-1}; k^1 = 0.45$

N_1	N_2	$\lambda^1 = 0.000, \sigma_c = 0.000$			$\lambda^1 = 0.100, \sigma_c = 0.030$			$\lambda^1 = 0.200, \sigma_c = 0.061$		
		t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c
0.81	0.81	1.427	1.397	0.730	1.606	1.720	0.734	1.840	2.194	0.737
0.81	1.00	1.194	1.127	0.719	1.348	1.383	0.723	1.544	1.761	0.728
0.81	1.44	0.903	0.791	0.696	1.019	0.971	0.703	1.166	1.231	0.710
1.00	0.81	1.076	1.004	0.720	1.207	1.225	0.725	1.375	1.553	0.730
1.00	1.00	0.910	0.813	0.707	1.020	0.991	0.714	1.161	1.256	0.721
1.00	1.44	0.695	0.577	0.682	0.780	0.703	0.691	0.891	0.890	0.700
1.44	0.81	0.691	0.586	0.694	0.772	0.712	0.703	0.876	0.899	0.712
1.44	1.00	0.588	0.476	0.679	0.659	0.581	0.689	0.749	0.734	0.700
1.44	1.44	0.456	0.342	0.648	0.510	0.417	0.662	0.583	0.528	0.676

TABLE D.9

$f_1 = 3, f_2 = 2, E = 1.00; k_{2\alpha}^* C_o = 2.414 \text{ min}^{-1}, k_{3\alpha}^* C_o^2 = 5.328 \text{ min}^{-1}; k^i = 0.00$

N_1	N_2	$\lambda^i = 0.000, \sigma_c = 0.000$			$\lambda^i = 0.100, \sigma_c = 0.034$			$\lambda^i = 0.200, \sigma_c = 0.067$		
		t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c
0.81	0.81	1.581	1.748	0.730	1.812	2.236	0.734	2.133	3.007	0.738
0.81	1.00	1.322	1.398	0.719	1.515	1.784	0.724	1.781	2.393	0.729
0.81	1.44	0.990	0.970	0.696	1.137	1.233	0.703	1.337	1.649	0.711
1.00	0.81	1.184	1.244	0.720	1.353	1.580	0.725	1.582	2.106	0.731
1.00	1.00	0.998	1.000	0.707	1.140	1.267	0.714	1.332	1.685	0.722
1.00	1.44	0.755	0.699	0.632	0.864	0.885	0.692	1.013	1.173	0.702
1.44	0.81	0.753	0.713	0.694	0.858	0.901	0.704	0.997	1.190	0.713
1.44	1.00	0.641	0.577	0.679	0.730	0.729	0.690	0.850	0.966	0.702
1.44	1.44	0.492	0.408	0.648	0.562	0.512	0.663	0.657	0.683	0.678

TABLE D.10

$f_1 = 3, f_2 = 2, E = 1.50; k_{2x}^* C_o = 3.786 \text{ min}^{-1}, k_{3x}^* C_o^2 = 7.096 \text{ min}^{-1}, k^i = 0.45$

		$\lambda^{15} = 0.000, \sigma_c = 0.000$			$\lambda^{15} = 0.133, \sigma_c = 0.040$			$\lambda^{15} = 0.267, \sigma_c = 0.079$		
N_1	N_2	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c	t_{2c}	t_{3c}	α_c
0.81	0.81	1.955	1.342	0.896	2.493	1.854	0.902	4.071	3.460	0.908
0.81	1.00	1.523	1.002	0.870	1.869	1.316	0.877	2.570	1.991	0.885
0.81	1.44	1.042	0.638	0.824	1.233	0.804	0.832	1.538	1.082	0.842
1.00	0.81	1.429	0.960	0.893	1.803	1.309	0.901	2.882	2.383	0.908
1.00	1.00	1.129	0.723	0.866	1.372	0.940	0.875	1.860	1.413	0.884
1.00	1.44	0.788	0.471	0.817	0.927	0.585	0.828	1.150	0.785	0.840
1.44	0.81	0.893	0.575	0.384	1.121	0.780	0.896	1.750	1.410	0.907
1.44	1.00	0.719	0.436	0.853	0.870	0.532	0.868	1.172	0.860	0.882
1.44	1.44	0.516	0.285	0.796	0.607	0.366	0.815	0.753	0.488	0.833

Appendix EPolyesterification Data

The following tables give the conversion/time results for all the polyesterification experiments performed with PE/AA and TME/AA at 175°C. The experimental conditions have been given in Table (7.3) and the method by which these figures are obtained has been discussed in section (7.6). The time is scaled to a time of unity at the gel point. The second column lists the mean of the observed conversions at the 50 time intervals which were used in the analysis of the polyesterification data in chapter 8. The mean gel time and mean gel conversion have been given in Table (7.4). The value of the standard deviation of each run from the mean,

$$\text{STD. DEV. \%} = \sqrt{\left(\sum_{i=1}^{50} (\beta_i - \beta_{\text{mean},i})^2 / 50 \right)} \times 100 \quad (\text{E.1})$$

is listed under each run (cf. eq. (8.29)).

TABLE	SYSTEM	EQUIVALENCE
E.1	PE/AA	1.00
E.2	PE/AA	0.50
E.3	PE/AA	0.75
E.4	PE/AA	1.50
E.5	PE/AA	2.00
E.6	TME/AA	1.00
E.7	TME/AA	0.67
E.8	TME/AA	1.50

TABLE E.1

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PE/AA, E = 1.0

TIME	MEAN	PE/1	PE/2	PE/3	PE/4	PE/5	PE/6
0.00	0.0000	0.0000	0.0001	0.0001	0.0002	0.0004	0.0002
0.01	0.0140	0.0086	0.0146	0.0126	0.0225	0.0123	0.0136
0.02	0.0281	0.0211	0.0284	0.0256	0.0432	0.0246	0.0257
0.03	0.0420	0.0341	0.0420	0.0388	0.0626	0.0369	0.0375
0.04	0.0555	0.0464	0.0554	0.0519	0.0806	0.0492	0.0494
0.05	0.0687	0.0580	0.0688	0.0649	0.0975	0.0613	0.0617
0.06	0.0817	0.0691	0.0822	0.0778	0.1132	0.0734	0.0744
0.07	0.0945	0.0800	0.0955	0.0906	0.1278	0.0855	0.0873
0.08	0.1072	0.0911	0.1087	0.1034	0.1417	0.0978	0.1004
0.09	0.1198	0.1025	0.1218	0.1161	0.1549	0.1102	0.1136
0.10	0.1324	0.1141	0.1346	0.1288	0.1676	0.1228	0.1266
0.11	0.1449	0.1261	0.1473	0.1415	0.1798	0.1354	0.1394
0.12	0.1572	0.1381	0.1597	0.1541	0.1918	0.1481	0.1519
0.13	0.1694	0.1501	0.1718	0.1665	0.2034	0.1606	0.1641
0.14	0.1814	0.1621	0.1838	0.1788	0.2148	0.1730	0.1759
0.15	0.1931	0.1738	0.1956	0.1908	0.2259	0.1852	0.1875
0.16	0.2046	0.1853	0.2071	0.2026	0.2367	0.1970	0.1987
0.17	0.2157	0.1966	0.2185	0.2140	0.2471	0.2085	0.2097
0.18	0.2266	0.2076	0.2296	0.2251	0.2573	0.2196	0.2204
0.19	0.2372	0.2184	0.2406	0.2359	0.2670	0.2303	0.2309
0.20	0.2475	0.2290	0.2513	0.2464	0.2764	0.2407	0.2412
0.22	0.2673	0.2500	0.2721	0.2662	0.2942	0.2601	0.2613
0.24	0.2862	0.2705	0.2919	0.2849	0.3107	0.2783	0.2807
0.26	0.3042	0.2908	0.3105	0.3027	0.3264	0.2954	0.2993
0.28	0.3214	0.3105	0.3280	0.3197	0.3414	0.3116	0.3171
0.30	0.3379	0.3294	0.3443	0.3362	0.3561	0.3272	0.3340
0.32	0.3536	0.3473	0.3596	0.3521	0.3704	0.3422	0.3500
0.34	0.3686	0.3640	0.3741	0.3676	0.3844	0.3566	0.3650
0.36	0.3829	0.3796	0.3878	0.3825	0.3978	0.3704	0.3793
0.38	0.3964	0.3942	0.4009	0.3967	0.4104	0.3836	0.3927
0.40	0.4092	0.4080	0.4135	0.4101	0.4222	0.3961	0.4055
0.42	0.4214	0.4212	0.4256	0.4228	0.4332	0.4081	0.4176
0.44	0.4330	0.4338	0.4371	0.4346	0.4435	0.4196	0.4291
0.46	0.4439	0.4459	0.4480	0.4458	0.4531	0.4307	0.4401
0.48	0.4544	0.4574	0.4584	0.4563	0.4625	0.4415	0.4505
0.50	0.4644	0.4682	0.4681	0.4663	0.4716	0.4519	0.4604
0.53	0.4787	0.4833	0.4817	0.4806	0.4850	0.4669	0.4745
0.56	0.4921	0.4971	0.4945	0.4941	0.4981	0.4810	0.4877
0.59	0.5048	0.5101	0.5068	0.5070	0.5104	0.4941	0.5003
0.62	0.5168	0.5227	0.5188	0.5191	0.5218	0.5063	0.5122
0.65	0.5281	0.5348	0.5304	0.5302	0.5322	0.5177	0.5233
0.68	0.5387	0.5462	0.5413	0.5403	0.5420	0.5288	0.5335
0.71	0.5486	0.5565	0.5514	0.5498	0.5516	0.5395	0.5430
0.74	0.5580	0.5658	0.5606	0.5588	0.5611	0.5499	0.5520
0.77	0.5670	0.5746	0.5693	0.5676	0.5701	0.5595	0.5608
0.80	0.5756	0.5834	0.5778	0.5763	0.5783	0.5683	0.5696
0.84	0.5866	0.5953	0.5886	0.5875	0.5881	0.5794	0.5806
0.88	0.5969	0.6058	0.5984	0.5977	0.5983	0.5904	0.5905
0.92	0.6065	0.6156	0.6072	0.6073	0.6083	0.6005	0.6001
0.96	0.6156	0.6268	0.6159	0.6166	0.6161	0.6100	0.6082
1.00	0.6234	0.6339	0.6236	0.6225	0.6246	0.6188	0.6168
STD. DEV. %		1.194	0.332	0.219	2.128	0.933	0.537

TABLE E.2
PE/AA, E =0.5

TIME	MEAN	PE/7	PE/8	PE/9
0.00	0.0000	0.0005	-0.0019	0.0012
0.01	0.0471	0.0453	0.0517	0.0443
0.02	0.0938	0.0926	0.0990	0.0897
0.03	0.1382	0.1384	0.1413	0.1347
0.04	0.1795	0.1810	0.1797	0.1778
0.05	0.2175	0.2198	0.2146	0.2180
0.06	0.2523	0.2551	0.2467	0.2551
0.07	0.2841	0.2872	0.2761	0.2891
0.08	0.3133	0.3165	0.3034	0.3200
0.09	0.3401	0.3435	0.3287	0.3481
0.10	0.3649	0.3685	0.3524	0.3737
0.11	0.3878	0.3917	0.3746	0.3970
0.12	0.4091	0.4133	0.3956	0.4184
0.13	0.4290	0.4334	0.4154	0.4381
0.14	0.4476	0.4522	0.4343	0.4563
0.15	0.4650	0.4696	0.4522	0.4733
0.16	0.4814	0.4858	0.4693	0.4891
0.17	0.4967	0.5008	0.4855	0.5039
0.18	0.5112	0.5147	0.5009	0.5179
0.19	0.5248	0.5277	0.5156	0.5312
0.20	0.5376	0.5398	0.5294	0.5437
0.22	0.5611	0.5618	0.5548	0.5668
0.24	0.5820	0.5813	0.5771	0.5876
0.26	0.6006	0.5989	0.5966	0.6063
0.28	0.6172	0.6150	0.6138	0.6228
0.30	0.6320	0.6296	0.6288	0.6375
0.32	0.6452	0.6429	0.6422	0.6504
0.34	0.6570	0.6550	0.6542	0.6619
0.36	0.6678	0.6660	0.6652	0.6721
0.38	0.6775	0.6759	0.6752	0.6815
0.40	0.6865	0.6850	0.6844	0.6901
0.42	0.6949	0.6934	0.6929	0.6983
0.44	0.7027	0.7012	0.7008	0.7060
0.46	0.7100	0.7084	0.7081	0.7135
0.48	0.7169	0.7152	0.7149	0.7206
0.50	0.7234	0.7215	0.7212	0.7273
0.53	0.7323	0.7301	0.7302	0.7367
0.56	0.7404	0.7377	0.7384	0.7450
0.59	0.7476	0.7444	0.7459	0.7525
0.62	0.7541	0.7504	0.7525	0.7594
0.65	0.7601	0.7561	0.7583	0.7657
0.68	0.7655	0.7616	0.7634	0.7716
0.71	0.7706	0.7667	0.7681	0.7769
0.74	0.7754	0.7716	0.7729	0.7816
0.77	0.7798	0.7760	0.7776	0.7858
0.80	0.7839	0.7801	0.7819	0.7896
0.84	0.7885	0.7847	0.7864	0.7944
0.88	0.7923	0.7883	0.7898	0.7986
0.92	0.7959	0.7916	0.7942	0.8018
0.96	0.7994	0.7942	0.7975	0.8064
1.00	0.8024	0.7964	0.8014	0.8093
STD. DEV. %		0.318	0.657	0.587

TABLE E.3

PE/AA, E=0.75

TIME	MEAN	PE/10	PE/11	PE/12
0.00	0.0000	-0.0002	-0.0004	0.0004
0.01	0.0190	0.0213	0.0162	0.0195
0.02	0.0377	0.0420	0.0315	0.0395
0.03	0.0562	0.0624	0.0462	0.0599
0.04	0.0744	0.0825	0.0607	0.0800
0.05	0.0924	0.1024	0.0753	0.0995
0.06	0.1101	0.1218	0.0902	0.1182
0.07	0.1272	0.1405	0.1053	0.1359
0.08	0.1439	0.1585	0.1205	0.1526
0.09	0.1600	0.1757	0.1358	0.1683
0.10	0.1755	0.1921	0.1511	0.1833
0.11	0.1905	0.2077	0.1662	0.1975
0.12	0.2049	0.2225	0.1811	0.2111
0.13	0.2189	0.2367	0.1957	0.2243
0.14	0.2324	0.2503	0.2099	0.2370
0.15	0.2455	0.2634	0.2238	0.2494
0.16	0.2583	0.2760	0.2372	0.2616
0.17	0.2707	0.2881	0.2503	0.2735
0.18	0.2827	0.2999	0.2630	0.2852
0.19	0.2944	0.3112	0.2754	0.2966
0.20	0.3058	0.3221	0.2875	0.3078
0.22	0.3275	0.3426	0.3107	0.3293
0.24	0.3480	0.3617	0.3328	0.3496
0.26	0.3673	0.3792	0.3538	0.3688
0.28	0.3853	0.3953	0.3739	0.3868
0.30	0.4023	0.4103	0.3929	0.4037
0.32	0.4183	0.4243	0.4110	0.4197
0.34	0.4335	0.4375	0.4280	0.4349
0.36	0.4479	0.4502	0.4441	0.4494
0.38	0.4616	0.4624	0.4593	0.4631
0.40	0.4747	0.4742	0.4736	0.4762
0.42	0.4871	0.4857	0.4871	0.4885
0.44	0.4988	0.4969	0.4996	0.5000
0.46	0.5100	0.5077	0.5114	0.5108
0.48	0.5205	0.5183	0.5223	0.5210
0.50	0.5305	0.5286	0.5324	0.5305
0.53	0.5445	0.5436	0.5462	0.5438
0.56	0.5577	0.5580	0.5589	0.5563
0.59	0.5701	0.5715	0.5706	0.5682
0.62	0.5817	0.5839	0.5818	0.5795
0.65	0.5926	0.5952	0.5924	0.5902
0.68	0.6026	0.6054	0.6024	0.6000
0.71	0.6119	0.6149	0.6117	0.6091
0.74	0.6206	0.6241	0.6203	0.6175
0.77	0.6289	0.6330	0.6283	0.6254
0.80	0.6367	0.6413	0.6359	0.6327
0.84	0.6461	0.6508	0.6457	0.6417
0.88	0.6547	0.6590	0.6550	0.6502
0.92	0.6636	0.6679	0.6642	0.6587
0.96	0.6715	0.6754	0.6730	0.6662
1.00	0.6797	0.6834	0.6795	0.6762

STD. DEV. % 1.025 1.329 0.410

PE/AA, E = 1.5

TIME	MEAN	PE/13	PE/14	PE/15	PE/16	PE/17	PE/18
0.00	0.00000	-0.00001	-0.00004	0.00003	-0.00002	0.00004	-0.00002
0.01	0.00163	0.00135	0.00192	0.00170	0.00191	0.00138	0.00150
0.02	0.00322	0.00270	0.00369	0.00344	0.00374	0.00278	0.00298
0.03	0.00481	0.00403	0.00544	0.00518	0.00557	0.00417	0.00444
0.04	0.00639	0.00534	0.00721	0.00690	0.00743	0.00554	0.00590
0.05	0.00796	0.00663	0.00901	0.00857	0.00929	0.00689	0.00736
0.06	0.00952	0.00792	0.01080	0.01022	0.01110	0.00824	0.00883
0.07	0.01106	0.00920	0.01256	0.01183	0.01285	0.00960	0.01029
0.08	0.01257	0.01049	0.01427	0.01343	0.01451	0.01096	0.01176
0.09	0.01406	0.01180	0.01591	0.01501	0.01608	0.01233	0.01323
0.10	0.01551	0.01312	0.01747	0.01657	0.01755	0.01369	0.01469
0.11	0.01694	0.01445	0.01896	0.01810	0.01895	0.01505	0.01615
0.12	0.01834	0.01580	0.02038	0.01962	0.02028	0.01639	0.01760
0.13	0.01972	0.01716	0.02174	0.02111	0.02156	0.01771	0.01904
0.14	0.02107	0.01852	0.02304	0.02258	0.02280	0.01901	0.02047
0.15	0.02240	0.01987	0.02430	0.02402	0.02403	0.02028	0.02189
0.16	0.02370	0.02121	0.02551	0.02542	0.02523	0.02154	0.02330
0.17	0.02498	0.02252	0.02669	0.02680	0.02643	0.02278	0.02469
0.18	0.02625	0.02381	0.02783	0.02814	0.02761	0.02402	0.02607
0.19	0.02748	0.02506	0.02894	0.02945	0.02879	0.02525	0.02742
0.20	0.02870	0.02627	0.03001	0.03073	0.02995	0.02648	0.02874
0.22	0.03106	0.02860	0.03207	0.03320	0.03223	0.02896	0.03131
0.24	0.03333	0.03080	0.03400	0.03555	0.03443	0.03145	0.03375
0.26	0.03551	0.03290	0.03584	0.03778	0.03651	0.03395	0.03606
0.28	0.03759	0.03494	0.03760	0.03989	0.03849	0.03639	0.03822
0.30	0.03958	0.03695	0.03931	0.04187	0.04037	0.03873	0.04026
0.32	0.04149	0.03895	0.04099	0.04373	0.04215	0.04093	0.04218
0.34	0.04331	0.04093	0.04265	0.04546	0.04385	0.04296	0.04399
0.36	0.04504	0.04286	0.04428	0.04709	0.04547	0.04481	0.04572
0.38	0.04669	0.04474	0.04587	0.04862	0.04703	0.04649	0.04737
0.40	0.04825	0.04653	0.04740	0.05007	0.04852	0.04803	0.04894
0.42	0.04973	0.04821	0.04885	0.05145	0.04995	0.04947	0.05044
0.44	0.05112	0.04977	0.05021	0.05276	0.05130	0.05083	0.05185
0.46	0.05244	0.05123	0.05148	0.05402	0.05259	0.05214	0.05319
0.48	0.05369	0.05259	0.05267	0.05523	0.05381	0.05340	0.05445
0.50	0.05488	0.05388	0.05379	0.05638	0.05498	0.05462	0.05563
0.53	0.05657	0.05573	0.05538	0.05799	0.05664	0.05638	0.05728
0.56	0.05816	0.05751	0.05690	0.05947	0.05820	0.05804	0.05883
0.59	0.05967	0.05924	0.05838	0.06084	0.05966	0.05962	0.06030
0.62	0.06111	0.06085	0.05979	0.06213	0.06103	0.06115	0.06173
0.65	0.06247	0.06232	0.06109	0.06337	0.06231	0.06266	0.06309
0.68	0.06375	0.06362	0.06227	0.06457	0.06354	0.06414	0.06438
0.71	0.06495	0.06481	0.06335	0.06571	0.06471	0.06553	0.06558
0.74	0.06606	0.06595	0.06437	0.06676	0.06583	0.06677	0.06669
0.77	0.06711	0.06709	0.06537	0.06772	0.06689	0.06782	0.06776
0.80	0.06810	0.06823	0.06636	0.06859	0.06786	0.06874	0.06879
0.84	0.06936	0.06966	0.06765	0.06974	0.06906	0.06995	0.07008
0.88	0.07056	0.07093	0.06884	0.07091	0.07019	0.07124	0.07124
0.92	0.07166	0.07215	0.06990	0.07199	0.07120	0.07238	0.07234
0.96	0.07268	0.07320	0.07088	0.07296	0.07219	0.07346	0.07341
1.00	0.07367	0.07418	0.07194	0.07407	0.07303	0.07445	0.07435
STD. DEV. %		1.753	1.379	1.421	1.053	1.244	0.622

TABLE E.5
PE/AA, E = 2.0

TIME	MEAN	PE/19	PE/20	PE/21	PE/22	PE/23
0.00	0.0000	-0.0000	-0.0005	-0.0001	-0.0002	-0.0003
0.01	0.0254	0.0264	0.0226	0.0264	0.0236	0.0278
0.02	0.0503	0.0523	0.0451	0.0528	0.0468	0.0544
0.03	0.0748	0.0781	0.0674	0.0788	0.0692	0.0804
0.04	0.0993	0.1039	0.0900	0.1045	0.0913	0.1066
0.05	0.1237	0.1296	0.1129	0.1297	0.1134	0.1330
0.06	0.1482	0.1551	0.1362	0.1545	0.1355	0.1597
0.07	0.1726	0.1802	0.1597	0.1787	0.1578	0.1864
0.08	0.1967	0.2046	0.1832	0.2023	0.1802	0.2130
0.09	0.2204	0.2283	0.2066	0.2253	0.2026	0.2391
0.10	0.2435	0.2512	0.2296	0.2475	0.2248	0.2646
0.11	0.2660	0.2731	0.2521	0.2689	0.2467	0.2894
0.12	0.2878	0.2941	0.2738	0.2897	0.2681	0.3133
0.13	0.3088	0.3141	0.2948	0.3097	0.2890	0.3362
0.14	0.3290	0.3332	0.3149	0.3291	0.3094	0.3582
0.15	0.3484	0.3513	0.3343	0.3479	0.3291	0.3792
0.16	0.3670	0.3686	0.3528	0.3662	0.3482	0.3992
0.17	0.3850	0.3851	0.3706	0.3840	0.3668	0.4184
0.18	0.4023	0.4009	0.3877	0.4013	0.3849	0.4368
0.19	0.4190	0.4160	0.4041	0.4182	0.4025	0.4544
0.20	0.4352	0.4305	0.4199	0.4346	0.4196	0.4713
0.22	0.4660	0.4580	0.4499	0.4663	0.4526	0.5032
0.24	0.4949	0.4839	0.4779	0.4960	0.4838	0.5328
0.26	0.5219	0.5085	0.5040	0.5237	0.5131	0.5602
0.28	0.5470	0.5318	0.5283	0.5491	0.5401	0.5856
0.30	0.5702	0.5540	0.5510	0.5722	0.5648	0.6088
0.32	0.5915	0.5750	0.5722	0.5930	0.5872	0.6299
0.34	0.6111	0.5948	0.5921	0.6120	0.6075	0.6489
0.36	0.6291	0.6134	0.6110	0.6295	0.6259	0.6659
0.38	0.6458	0.6307	0.6289	0.6456	0.6429	0.6811
0.40	0.6614	0.6467	0.6460	0.6609	0.6587	0.6946
0.42	0.6759	0.6617	0.6622	0.6753	0.6735	0.7069
0.44	0.6896	0.6758	0.6775	0.6890	0.6874	0.7181
0.46	0.7024	0.6892	0.6916	0.7019	0.7005	0.7285
0.48	0.7143	0.7020	0.7046	0.7141	0.7126	0.7384
0.50	0.7256	0.7144	0.7165	0.7254	0.7239	0.7477
0.53	0.7411	0.7323	0.7324	0.7410	0.7390	0.7607
0.56	0.7553	0.7493	0.7466	0.7552	0.7526	0.7726
0.59	0.7683	0.7651	0.7598	0.7686	0.7650	0.7832
0.62	0.7804	0.7792	0.7722	0.7813	0.7766	0.7926
0.65	0.7914	0.7915	0.7838	0.7934	0.7875	0.8009
0.68	0.8014	0.8024	0.7942	0.8047	0.7973	0.8085
0.71	0.8103	0.8121	0.8033	0.8148	0.8059	0.8156
0.74	0.8185	0.8212	0.8115	0.8237	0.8137	0.8224
0.77	0.8262	0.8299	0.8195	0.8316	0.8211	0.8288
0.80	0.8334	0.8379	0.8274	0.8387	0.8282	0.8346
0.84	0.8419	0.8475	0.8372	0.8468	0.8366	0.8413
0.88	0.8490	0.8563	0.8444	0.8537	0.8434	0.8472
0.92	0.8564	0.8650	0.8518	0.8615	0.8516	0.8521
0.96	0.8624	0.8713	0.8602	0.8671	0.8575	0.8561
1.00	0.8675	0.8770	0.8664	0.8718	0.8622	0.8602
STD. DEV. %		0.891	1.237	0.318	1.075	2.446

TABLE E.6

TME/AA, E = 1.0

TIME	MEAN	TME/1	TME/2	TME/3	TME/4
0.00	0.0000	0.0001	0.0001	-0.0001	-0.0005
0.01	0.0195	0.0204	0.0167	0.0208	0.0202
0.02	0.0389	0.0412	0.0329	0.0421	0.0393
0.03	0.0581	0.0616	0.0490	0.0637	0.0583
0.04	0.0774	0.0814	0.0652	0.0853	0.0776
0.05	0.0965	0.1007	0.0815	0.1066	0.0974
0.06	0.1157	0.1201	0.0979	0.1275	0.1172
0.07	0.1347	0.1397	0.1143	0.1479	0.1370
0.08	0.1536	0.1595	0.1308	0.1678	0.1564
0.09	0.1723	0.1797	0.1472	0.1872	0.1754
0.10	0.1908	0.1999	0.1636	0.2059	0.1938
0.11	0.2089	0.2200	0.1800	0.2239	0.2116
0.12	0.2266	0.2398	0.1964	0.2414	0.2289
0.13	0.2439	0.2590	0.2127	0.2582	0.2457
0.14	0.2607	0.2774	0.2290	0.2744	0.2620
0.15	0.2770	0.2950	0.2451	0.2900	0.2779
0.16	0.2927	0.3115	0.2611	0.3049	0.2934
0.17	0.3079	0.3271	0.2768	0.3193	0.3084
0.18	0.3225	0.3416	0.2922	0.3331	0.3230
0.19	0.3365	0.3552	0.3073	0.3463	0.3372
0.20	0.3499	0.3680	0.3219	0.3589	0.3508
0.22	0.3752	0.3914	0.3500	0.3827	0.3767
0.24	0.3984	0.4125	0.3764	0.4046	0.4003
0.26	0.4200	0.4321	0.4011	0.4248	0.4218
0.28	0.4399	0.4506	0.4243	0.4437	0.4412
0.30	0.4586	0.4681	0.4460	0.4614	0.4589
0.32	0.4760	0.4847	0.4664	0.4781	0.4751
0.34	0.4924	0.5003	0.4853	0.4938	0.4901
0.36	0.5076	0.5150	0.5029	0.5086	0.5041
0.38	0.5219	0.5286	0.5189	0.5225	0.5174
0.40	0.5351	0.5413	0.5336	0.5355	0.5300
0.42	0.5475	0.5531	0.5471	0.5476	0.5421
0.44	0.5590	0.5641	0.5594	0.5587	0.5536
0.46	0.5697	0.5744	0.5709	0.5691	0.5646
0.48	0.5799	0.5840	0.5817	0.5787	0.5751
0.50	0.5894	0.5930	0.5919	0.5877	0.5852
0.53	0.6029	0.6054	0.6061	0.6003	0.5996
0.56	0.6153	0.6168	0.6190	0.6123	0.6130
0.59	0.6267	0.6274	0.6304	0.6237	0.6252
0.62	0.6371	0.6371	0.6405	0.6346	0.6362
0.65	0.6466	0.6463	0.6496	0.6448	0.6459
0.68	0.6554	0.6547	0.6583	0.6540	0.6547
0.71	0.6635	0.6624	0.6667	0.6623	0.6629
0.74	0.6712	0.6696	0.6747	0.6697	0.6707
0.77	0.6783	0.6764	0.6816	0.6767	0.6783
0.80	0.6848	0.6829	0.6871	0.6834	0.6855
0.84	0.6926	0.6910	0.6933	0.6918	0.6944
0.88	0.7000	0.6980	0.7000	0.6995	0.7025
0.92	0.7068	0.7049	0.7058	0.7069	0.7097
0.96	0.7127	0.7109	0.7103	0.7138	0.7159
1.00	0.7191	0.7167	0.7178	0.7191	0.7230
STD. DEV. %		0.940	1.704	0.764	0.254

TABLE E.7
TME/AA, E = 0.67

TIME	MEAN	TME/5	TME/6	TME/7	TME/8	TME/9	TME/10
0.00	0.0000	0.0001	-0.0014	-0.0002	-0.0009	0.0003	0.0005
0.01	0.00471	0.0419	0.0498	0.0493	0.0524	0.0424	0.0469
0.02	0.00935	0.0339	0.0967	0.0979	0.1041	0.0852	0.0932
0.03	0.01380	0.1254	0.1407	0.1436	0.1520	0.1282	0.1382
0.04	0.01802	0.1659	0.1824	0.1857	0.1955	0.1705	0.1810
0.05	0.02198	0.2050	0.2218	0.2246	0.2348	0.2113	0.2215
0.06	0.02571	0.2427	0.2589	0.2606	0.2706	0.2500	0.2595
0.07	0.02918	0.2786	0.2934	0.2943	0.3034	0.2862	0.2951
0.08	0.03243	0.3129	0.3255	0.3259	0.3337	0.3197	0.3282
0.09	0.03546	0.3455	0.3551	0.3555	0.3620	0.3506	0.3590
0.10	0.03827	0.3759	0.3823	0.3833	0.3884	0.3790	0.3875
0.11	0.04089	0.4047	0.4074	0.4091	0.4131	0.4053	0.4139
0.12	0.04332	0.4317	0.4307	0.4330	0.4362	0.4296	0.4382
0.13	0.04558	0.4569	0.4522	0.4551	0.4579	0.4523	0.4607
0.14	0.04768	0.4805	0.4722	0.4753	0.4780	0.4735	0.4814
0.15	0.04965	0.5019	0.4910	0.4939	0.4969	0.4934	0.5005
0.16	0.05144	0.5220	0.5086	0.5109	0.5144	0.5122	0.5181
0.17	0.05312	0.5404	0.5252	0.5265	0.5308	0.5300	0.5345
0.18	0.05470	0.5573	0.5409	0.5410	0.5461	0.5467	0.5498
0.19	0.05617	0.5728	0.5557	0.5544	0.5605	0.5625	0.5640
0.20	0.05754	0.5870	0.5697	0.5671	0.5741	0.5773	0.5774
0.22	0.06004	0.6120	0.5953	0.5903	0.5989	0.6041	0.6019
0.24	0.06225	0.6332	0.6178	0.6113	0.6214	0.6273	0.6237
0.26	0.06420	0.6516	0.6376	0.6305	0.6417	0.6473	0.6432
0.28	0.06593	0.6678	0.6549	0.6479	0.6600	0.6646	0.6607
0.30	0.06747	0.6825	0.6701	0.6633	0.6764	0.6796	0.6762
0.32	0.06884	0.6959	0.6839	0.6768	0.6910	0.6929	0.6899
0.34	0.07008	0.7084	0.6964	0.6886	0.7040	0.7050	0.7022
0.36	0.07120	0.7199	0.7081	0.6992	0.7157	0.7159	0.7133
0.38	0.07223	0.7305	0.7190	0.7088	0.7263	0.7259	0.7235
0.40	0.07319	0.7402	0.7291	0.7178	0.7361	0.7351	0.7329
0.42	0.07407	0.7490	0.7384	0.7265	0.7452	0.7436	0.7417
0.44	0.07489	0.7571	0.7468	0.7348	0.7536	0.7513	0.7500
0.46	0.07565	0.7645	0.7543	0.7427	0.7615	0.7585	0.7577
0.48	0.07635	0.7714	0.7610	0.7501	0.7687	0.7652	0.7649
0.50	0.07700	0.7780	0.7670	0.7568	0.7752	0.7715	0.7715
0.53	0.07789	0.7874	0.7753	0.7659	0.7838	0.7804	0.7805
0.56	0.07870	0.7962	0.7832	0.7741	0.7914	0.7888	0.7885
0.59	0.07947	0.8043	0.7911	0.7821	0.7984	0.7966	0.7959
0.62	0.08020	0.8116	0.7986	0.7901	0.8054	0.8037	0.8027
0.65	0.08087	0.8181	0.8053	0.7975	0.8122	0.8104	0.8088
0.68	0.08145	0.8238	0.8109	0.8036	0.8183	0.8168	0.8138
0.71	0.08195	0.8290	0.8158	0.8082	0.8234	0.8231	0.8177
0.74	0.08241	0.8342	0.8205	0.8119	0.8279	0.8291	0.8209
0.77	0.08287	0.8392	0.8256	0.8160	0.8325	0.8345	0.8245
0.80	0.08336	0.8440	0.8309	0.8210	0.8376	0.8390	0.8290
0.84	0.08399	0.8493	0.8371	0.8276	0.8443	0.8448	0.8362
0.88	0.08449	0.8530	0.8419	0.8320	0.8487	0.8518	0.8423
0.92	0.08497	0.8558	0.8478	0.8377	0.8523	0.8580	0.8469
0.96	0.08533	0.8602	0.8501	0.8396	0.8586	0.8594	0.8518
1.00	0.08579	0.8631	0.8543	0.8496	0.8619	0.8622	0.8561
STD. DEV. %		0.919	0.368	0.990	0.594	0.467	0.262

TABLE E.8

TME/AA, $E = 1.5$

TIME	MEAN	TME/11	TME/12	TME/13	TME/14	TME/15	TME/16
0.00	0.0000	0.0005	0.0002	-0.0003	-0.0001	-0.0003	0.0004
0.01	0.0381	0.0362	0.0394	0.0355	0.0435	0.0347	0.0391
0.02	0.0761	0.0729	0.0796	0.0705	0.0867	0.0680	0.0787
0.03	0.1129	0.1082	0.1184	0.1058	0.1264	0.1011	0.1174
0.04	0.1481	0.1413	0.1552	0.1415	0.1620	0.1341	0.1545
0.05	0.1816	0.1720	0.1897	0.1771	0.1944	0.1666	0.1898
0.06	0.2134	0.2003	0.2221	0.2121	0.2245	0.1980	0.2232
0.07	0.2436	0.2268	0.2526	0.2460	0.2533	0.2282	0.2549
0.08	0.2725	0.2519	0.2815	0.2785	0.2813	0.2568	0.2848
0.09	0.3000	0.2759	0.3090	0.3094	0.3089	0.2838	0.3131
0.10	0.3264	0.2991	0.3352	0.3386	0.3360	0.3094	0.3398
0.11	0.3516	0.3218	0.3603	0.3662	0.3624	0.3337	0.3651
0.12	0.3757	0.3439	0.3842	0.3922	0.3881	0.3567	0.3888
0.13	0.3986	0.3656	0.4069	0.4167	0.4126	0.3787	0.4111
0.14	0.4205	0.3866	0.4286	0.4399	0.4359	0.3998	0.4321
0.15	0.4413	0.4070	0.4492	0.4619	0.4579	0.4199	0.4517
0.16	0.4610	0.4267	0.4686	0.4827	0.4786	0.4393	0.4701
0.17	0.4797	0.4456	0.4871	0.5024	0.4978	0.4577	0.4873
0.18	0.4973	0.4635	0.5045	0.5211	0.5159	0.4754	0.5035
0.19	0.5140	0.4806	0.5210	0.5388	0.5328	0.4922	0.5188
0.20	0.5298	0.4967	0.5366	0.5554	0.5488	0.5082	0.5332
0.22	0.5589	0.5262	0.5653	0.5859	0.5782	0.5377	0.5599
0.24	0.5849	0.5522	0.5910	0.6126	0.6049	0.5643	0.5844
0.26	0.6085	0.5761	0.6143	0.6359	0.6293	0.5884	0.6069
0.28	0.6299	0.5978	0.6354	0.6563	0.6513	0.6104	0.6279
0.30	0.6493	0.6181	0.6546	0.6743	0.6710	0.6308	0.6473
0.32	0.6671	0.6372	0.6721	0.6903	0.6882	0.6497	0.6651
0.34	0.6833	0.6552	0.6881	0.7049	0.7031	0.6672	0.6814
0.36	0.6981	0.6722	0.7027	0.7182	0.7162	0.6832	0.6962
0.38	0.7117	0.6880	0.7162	0.7306	0.7280	0.6977	0.7096
0.40	0.7241	0.7025	0.7285	0.7420	0.7390	0.7107	0.7219
0.42	0.7355	0.7157	0.7397	0.7526	0.7493	0.7226	0.7332
0.44	0.7461	0.7275	0.7499	0.7623	0.7593	0.7336	0.7438
0.46	0.7559	0.7381	0.7591	0.7712	0.7688	0.7443	0.7539
0.48	0.7650	0.7478	0.7673	0.7793	0.7775	0.7548	0.7636
0.50	0.7736	0.7566	0.7747	0.7867	0.7854	0.7654	0.7729
0.53	0.7854	0.7687	0.7843	0.7965	0.7955	0.7810	0.7862
0.56	0.7959	0.7799	0.7928	0.8052	0.8039	0.7952	0.7983
0.59	0.8051	0.7902	0.8005	0.8129	0.8114	0.8068	0.8088
0.62	0.8132	0.7997	0.8080	0.8197	0.8188	0.8152	0.8177
0.65	0.8202	0.8084	0.8150	0.8257	0.8260	0.8212	0.8250
0.68	0.8265	0.8164	0.8213	0.8312	0.8326	0.8262	0.8311
0.71	0.8321	0.8239	0.8268	0.8362	0.8378	0.8315	0.8365
0.74	0.8373	0.8314	0.8315	0.8406	0.8418	0.8372	0.8415
0.77	0.8421	0.8378	0.8358	0.8444	0.8456	0.8428	0.8463
0.80	0.8466	0.8440	0.8400	0.8477	0.8498	0.8475	0.8506
0.84	0.8521	0.8510	0.8454	0.8520	0.8554	0.8537	0.8553
0.88	0.8570	0.8571	0.8493	0.8567	0.8587	0.8608	0.8592
0.92	0.8609	0.8627	0.8525	0.8602	0.8630	0.8633	0.8638
0.96	0.8646	0.8681	0.8567	0.8621	0.8666	0.8654	0.8683
1.00	0.8682	0.8716	0.8597	0.8665	0.8694	0.8702	0.8719
STD. DEV. %		2.234	0.643	1.555	1.329	1.421	0.650

Appendix FComputer Programs

A problem for which a computer was used is the evaluation of the function $\beta(x,s)$ defined by the series

$$\beta(x,s) = \sum_{n=1}^{\infty} x^n n^{-s} \quad (\text{F.1})$$

which arises in the expression (eq. (4.19)) for the rate of cyclization. Truesdell (1945) studied this function and worked out practical methods for its evaluation. The series (F.1) is rapidly convergent when x is near 0, near 1 it is so slowly convergent as to be quite useless for computation. Fortunately another series, first given by Lindelöf (1905):

$$\beta(x,s) = \Gamma(1-s)(-\log x)^{s-1} + \sum_{n=1}^{\infty} \zeta(s-n)(\log x)^n \quad (\text{F.2})$$

is admirably suited for computing values of $\beta(x,s)$ when x is near 1 and s is not an integer; the more unsuited for numerical work is the series (F.1), the better suited is Lindelöf's expansion (F.2). If the terms are grouped in pairs, it is an alternating series when s and x are real and $-2\pi < \log x < 0$. In eq. (F.2) the function $\zeta(s)$ is Riemann's Zeta function and $\Gamma(1-s)$ is a Gamma function, and we have that

$$\beta(1,s) = \zeta(s) \quad (\text{F.3})$$

The entries in table (F.1) were computed by means of the series (F.1) for values of $x < 0.99$ and the series (F.2) for values of x in the range $0.99 < x < 1$.

In the kinetic rate equation for the post-gel model (eq. (5.9)), a similar series arises for a polycondensation between f -functional

TABLE F.1

A Table of the Functions $\beta(x, 3/2)$, $\beta(x, 5/2)$

x	$\beta(x, 3/2)$	$\beta(x, 5/2)$
0.050	0.0509	0.0504
0.100	0.1037	0.1018
0.150	0.1587	0.1542
0.200	0.2159	0.2076
0.250	0.2757	0.2622
0.300	0.3383	0.3179
0.350	0.4041	0.3750
0.400	0.4734	0.4334
0.450	0.5468	0.4934
0.500	0.6248	0.5550
0.550	0.7083	0.6184
0.600	0.7982	0.6838
0.650	0.8959	0.7515
0.700	1.0031	0.8218
0.750	1.1226	0.8950
0.800	1.2586	0.9717
0.850	1.4179	1.0526
0.900	1.6144	1.1390
0.910	1.6605	1.1571
0.920	1.7098	1.1755
0.930	1.7628	1.1943
0.940	1.8205	1.2134
0.950	1.8842	1.2330
0.960	1.9556	1.2531
0.970	2.0381	1.2738
0.980	2.1380	1.2952
0.990	2.2715	1.3175
0.991	2.2882	1.3198
0.992	2.3060	1.3222
0.993	2.3251	1.3245
0.994	2.3458	1.3268

TABLE F.1 (cont.)

x	$\beta(x, 3/2)$	$\beta(x, 5/2)$
0.995	2.3683	1.3292
0.996	2.3934	1.3316
0.997	2.4221	1.3340
0.998	2.4563	1.3364
0.999	2.5013	1.3389
1.000	2.6120	1.3414

TABLE F.2

A table of the function $\phi(x, t, m)$
for $f = 4, m = 12$

t	x	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9
0.00		.9235									
0.05		.8598									
0.10		.8334	13.98								
0.15		.8131	2.359								
0.20		.7961	1.500	11.04							
0.25		.7811	1.235	3.795	30.77						
0.30		.7676	1.105	2.304	8.419	51.70					
0.35		.7552	1.024	1.748	4.184	14.15	62.74				
0.40		.7437	.9675	1.467	2.761	6.547	18.85	62.78			
0.45		.7329	.9243	1.299	2.108	4.006	8.757	21.33	56.27		
0.50		.7227	.8897	1.186	1.747	2.873	5.223	10.32	21.66	47.49	
0.55		.7130	.8608	1.103	1.521	2.266	3.634	6.201	11.09	20.52	38.88
0.60		.7037	.8360	1.040	1.366	1.898	2.784	4.277	6.817	11.16	18.65
0.65		.6948	.8142	.9895	1.252	1.653	2.272	3.234	4.734	7.077	10.74
0.70		.6863	.7949	.9476	1.166	1.480	1.937	2.603	3.574	4.989	7.048
0.75		.6781	.7773	.9120	1.097	1.351	1.703	2.189	2.862	3.790	5.065
0.80		.6702	.7614	.8813	1.040	1.251	1.530	1.901	2.392	3.040	3.890
0.85		.6626	.7467	.8545	.9929	1.171	1.399	1.691	2.064	2.538	3.138
0.90		.6556	.7336	.8312	.9535	1.106	1.297	1.534	1.827	2.189	2.632
0.95		.6495	.7226	.8125	.9226	1.057	1.221	1.420	1.661	1.949	2.295
1.00		.6465	.7172	.8033	.9078	1.034	1.186	1.368	1.585	1.843	2.147

TABLE F.2 (cont.)

t	x	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0
0.55		75.00										
0.60		31.44	53.56	91.77								
0.65		16.46	25.38	39.26	60.81	94.22						
0.70		10.03	14.35	24.57	29.49	42.26	60.45	86.27				
0.75		6.812	9.193	12.43	16.80	22.68	30.56	41.07	55.05	75.54	97.92	
0.80		5.002	6.449	8.324	10.74	13.85	17.81	22.86	29.25	37.31	47.43	60.11
0.85		3.893	4.840	6.021	7.488	9.302	11.53	14.27	17.60	21.65	26.55	32.46
0.90		3.173	3.831	4.627	5.585	6.733	8.102	9.730	11.66	13.93	16.59	19.71
0.95		2.706	3.194	3.769	4.443	5.232	6.150	7.213	8.442	9.855	11.47	13.32
1.00		2.505	2.923	3.409	3.972	4.621	5.366	6.219	7.189	8.291	9.537	10.94

TABLE F.3

A Table of the Function $\phi(x, t, m)$
for $f = 4$, $m = 6$

x	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9
t										
0.00	.9235									
0.05	.8343									
0.10	.7975	1.845								
0.15	.7693	1.174	4.124							
0.20	.7456	1.001	1.785	2.936	66.21					
0.25	.7248	.9120	1.314	1.713	6.559	31.33				
0.30	.7060	.8531	1.113	1.634	2.842	6.188	17.84	73.78		
0.35	.6888	.8091	.9973	1.313	1.884	3.012	5.470	11.49	28.54	86.98
0.40	.6729	.7738	.9188	1.136	1.475	2.029	2.983	4.716	8.059	14.98
0.45	.6579	.7442	.8605	1.021	1.249	1.580	2.075	2.837	4.041	6.009
0.50	.6439	.7185	.8143	.9392	1.104	1.326	1.629	2.047	2.635	3.473
0.55	.6305	.6957	.7762	.8766	1.003	1.163	1.367	1.630	1.971	2.417
0.60	.6178	.6752	.7438	.8264	.9261	1.047	1.194	1.374	1.595	1.867
0.65	.6057	.6565	.7156	.7847	.8655	.9602	1.071	1.202	1.356	1.538
0.70	.5942	.6393	.6907	.7493	.8161	.8922	.9790	1.078	1.191	1.320
0.75	.5832	.6235	.6685	.7187	.7747	.8371	.9066	.9840	1.070	1.165
0.80	.5729	.6090	.6487	.6922	.7397	.7917	.8485	.9104	.9778	1.051
0.85	.5634	.5960	.6313	.6693	.7102	.7542	.8014	.8521	.9063	.9643
0.90	.5553	.5850	.6167	.6504	.6862	.7242	.7644	.8068	.8517	.8989
0.95	.5492	.5768	.6060	.6367	.6690	.7028	.7383	.7754	.8141	.8545
1.00	.5466	.5734	.6015	.6310	.6619	.6941	.7277	.7627	.7990	.8367

TABLE F.3 (cont.)

t	x	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0
0.40		30.52	69.23									
0.45		9.336	15.18	25.93	46.68	89.30						
0.50		4.688	6.481	9.175	13.30	19.77	30.16	47.30	76.47			
0.55		3.005	3.786	4.833	6.248	8.178	10.84	14.53	19.74	27.15	37.84	53.49
0.60		2.204	2.621	3.140	3.789	4.604	5.629	6.926	8.572	10.67	13.36	16.83
0.65		1.752	2.005	2.305	2.660	3.082	3.582	4.178	4.888	5.735	6.747	7.957
0.70		1.467	1.634	1.825	2.043	2.292	2.576	2.900	3.269	3.690	4.172	4.721
0.75		1.272	1.389	1.520	1.665	1.825	2.003	2.200	2.417	2.658	2.923	3.217
0.80		1.131	1.217	1.311	1.413	1.524	1.643	1.772	1.912	2.063	2.225	2.401
0.85		1.026	1.092	1.163	1.238	1.317	1.402	1.492	1.588	1.689	1.797	1.910
0.90		.9487	1.001	1.056	1.114	1.174	1.237	1.304	1.373	1.446	1.521	1.600
0.95		.8965	.9402	.9856	1.033	1.081	1.132	1.184	1.239	1.295	1.352	1.412
1.00		.8757	.9161	.9579	1.001	1.045	1.091	1.138	1.187	1.237	1.288	1.341

and bi-functional monomers reacting pairwise and it may be written

as:

$$\rho(x, t, m) = \sum_{n=2,4,6,\dots}^{\infty} \left\{ x^{(n-2)/2} \left[\sum_{j=0}^m \binom{(f-1)n/2}{j} t^j (1-t)^{(f-1)n/2-j} \right] n^{-3/2} \right\} \quad (F.4)$$

where the parameters x , t , m have been defined in section (5.2). The function $\rho(x, t, m)$ has been computed using eq. (F.4) for the cases $f = 4$ and $m = 6$ and 12, and the results are shown in tables (F.2), (F.3).

The majority of the computer programs incorporated a section to solve the kinetic differential equations of the type eq. (4.55). A basic Ferranti autocode instruction INTSTEP was used to solve these simultaneous differential equations. By means of this instruction a single step in a set of $n \gg 1$ simultaneous first-order differential equations of the form

$$f_i = D_x(y_i) = f_i(x, y_1, y_2, \dots, y_n) \quad (F.5)$$

where $i = 1, 2, \dots, n$, may be carried out. Given a value x_r of x and the corresponding values of $y_{i,r}$ of the y_i , the given equations determine values $f_{i,r}$ of the first derivatives. Starting from this combined set of initial values at $x = x_r$, the INTSTEP instruction computes values $y_{i,r+1}$ of the y_i at $x = x_{r+1} = x_r + h_r$, where h_r is the specified step-length of the step, and leaves these in place of the $y_{i,r}$. Assuming that these initial $y_{i,r}$ from which the step starts are accurate, the computed values $y_{i,r+1}$ left at the end of the step are approximate, being subject to a truncation error which depends partly on $h_r(O(h_r)^5)$ and partly on the local behaviour of the higher derivatives.

This step-by-step integration therefore consists of a series of repetitions of the procedure of a single step, taking the computed values for one step as the initial values of the next step. The fourth-order Runge-Kutta procedure followed by INTSTEP is given by the formulae:

$$x_{r+1} = x_r + h_r \quad (F.6)$$

$$y_{i,r+1} = y_{i,r} + h_r (f_{i,a_r} + 2f_{i,b_r} + 2f_{i,c_r} + f_{i,d_r})/6 \quad (F.7)$$

where

$$f_{i,a_r} = f_i(x_r, \sum y_{i,r}) \quad (F.8)$$

$$f_{i,b_r} = f_i(x_r + h_r/2, \sum (y_{i,r} + hf_{i,a_r}/2)) \quad (F.9)$$

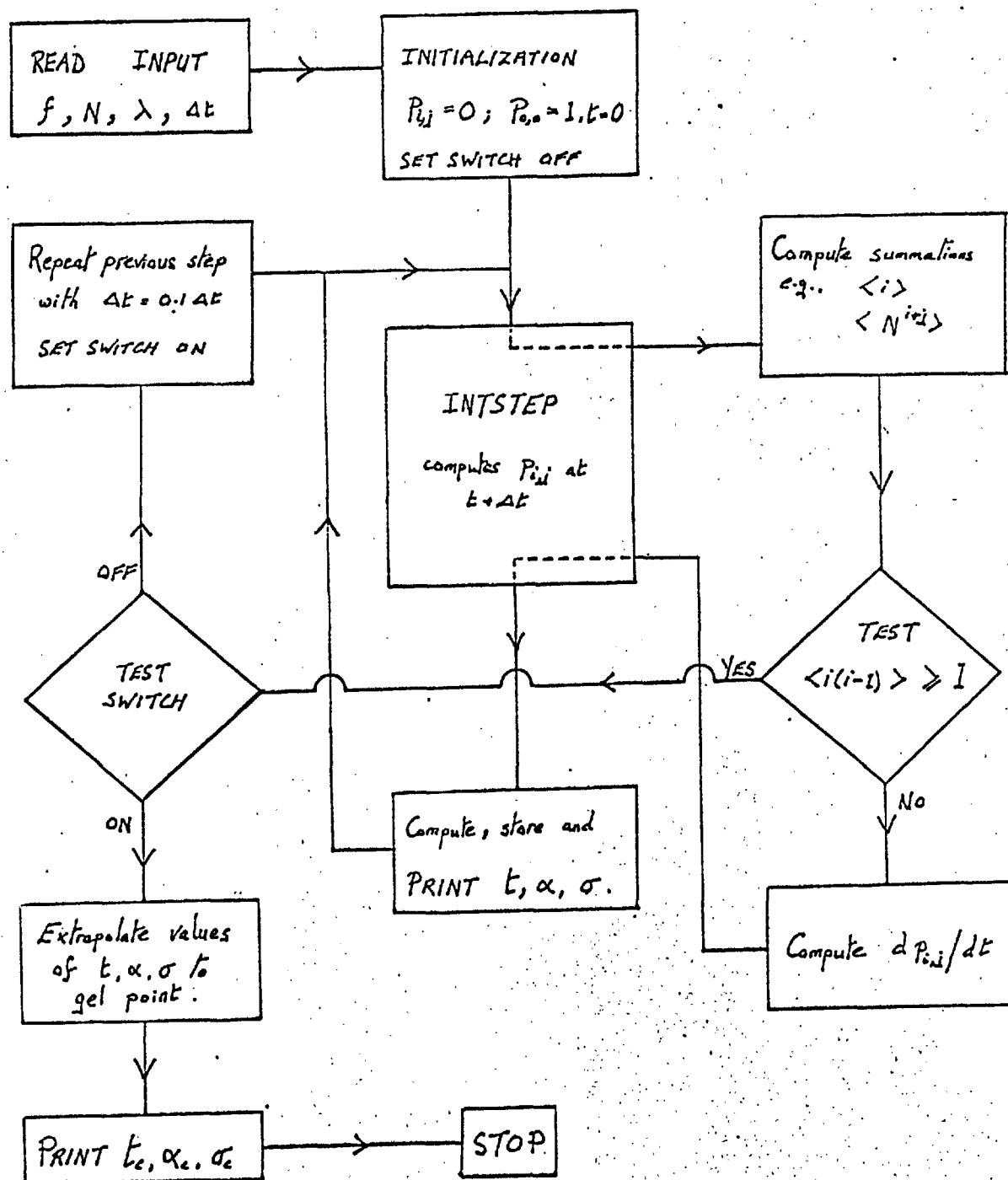
$$f_{i,c_r} = f_i(x_r + h_r/2, \sum (y_{i,r} + hf_{i,b_r}/2)) \quad (F.10)$$

$$f_{i,d_r} = f_i(x_r + h_r, \sum (y_{i,r} + hf_{i,c_r})) \quad (F.11)$$

and the range of the summations is $i = 1, 2, \dots$, i.e. four successive evaluations of the derivative function $f_i(x, y_i)$ have to be performed for each step.

The auxiliary sequence that is used to evaluate the derivative values $dP_{i,j}/dt$ at time t incorporates a routine to evaluate the function $\rho(x, s)$. INTSTEP then computes $P_{i,j}$ at time $t + \Delta t$. A flow diagram for a program to compute the critical parameters of a f -functional polycondensation is shown in figure (F.1). As a check on this integration method of solving the differential rate equations and to find the optimum step-length, the program was run with the parameter λ set to zero. This corresponds to a ring free system with FSSE, whose solution was obtained analytically using Laplace Transforms in section (3.6). The values of α_c as a function of N were computed by both methods and found to agree to five decimal places. The optimum step-

Fig. F.1 Flow diagram for calculation of $P_{i,j}$ as functions of time, and for the calculation of the critical parameters (t_c , α_c , σ_c).



length used corresponded to taking ~ 50 time intervals up to the gel time. In practice for the post-gel calculations this step-length was progressively increased after the gel point as the 'reaction' slowed down. The flow diagram (fig. (F.1)) shows that for the evaluation of the critical parameters, the step before the gel point was repeated at a tenth of the original step-length, and the value of the parameters in this interval extrapolated to the gel point. This procedure is necessary since it is not possible to set the step-length to be an exact fraction of the gel time, and also unless a post-gel model is incorporated into the program, the cyclization series diverges after the gel point.