

CORRIGENDA.

p.8 Bottom line; add $\neq 0$ between $k_{t_{xx}}$, $X \cdot X \cdot$ and (2).

p.12 Line 4; for "form" read "from".

p.69 Fig. 15; in legend, for "Styrene" read "Methyl
Methacrylate in Feed".

p.126 line 8; for "vinylidene chloride" read "poly(vinylidene
chloride)".

p.141 line 21; "that this" should read "which indicates
that this etc.".

SOME ASPECTS OF COPOLYMERISATION
UNDER HIGH PRESSURE

A thesis presented for the Degree of
DOCTOR OF PHILOSOPHY
in Engineering
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by

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Abstract

The free radicle bulk copolymerisations of some typical vinyl monomers have been studied at pressures up to 4,000 atm. using benzoyl peroxide as initiator. In general the systems have been found to behave in a manner similar to homopolymer systems. Increase in pressure produces an increase in polymerisation rate and in the molecular weight of the polymers together with increase in their melting points.

The monomer pair studied in greatest detail was styrene - methyl methacrylate. This system showed little variation of monomer reactivity ratios with pressure, the variation being within the limits of experimental error. The cross termination rate constant was found to be greater than the geometric mean of the rate constants for termination between like radicles, and to be dependent on the composition of the monomer mixture. The behaviour of the copolymer systems has been explained in terms of the accepted kinetic processes of vinyl copolymerisation where account has been taken of the possibility of polarisation and electron transfer in some of the reactions.

The system styrene - perchlorethylene was found to

be exceptional and it is shown that copolymerisation does not occur between these monomers. The behaviour of the system is explained by the suggestion that the styrene homopolymerises and the perchlorethylene acts as a diluent and chain transfer agent with a transfer constant of about 600×10^{-5} at 60°C .

The graft copolymerisation of styrene and methyl methacrylate onto irradiated polyethylene was accelerated by pressure, but chloroethylenes could not be grafted onto this substrate. Vinyl acetate was successfully grafted onto irradiated polystyrene by the application of high pressure.

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SECTION ONE

Part I. Introduction.

A. General Review of Free Radicle Polymerisation.

Development of studies.

Staudinger⁽¹⁾ was one of the earliest protagonists of the theory that vinyl polymerisation is a chain reaction involving the break-down of the ethylenic linkage. Since the nineteen thirties a very large volume of work has been published on this subject and the early development of the theory of polymerisation has been traced in some detail by Mark and Raff.⁽²⁾ The result of this early work is that it is now generally accepted that vinyl polymerisation, (a term loosely used to describe the polymerisation of substituted ethylenes), is a chain reaction which takes place in three distinct stages;

a) Initiation

b) Propagation

and c) Termination.

The polymerisation may take place by an ionic or a free radicle mechanism in many cases, depending on the nature of the initiation process. In this thesis interest lies only in the free radicle reaction and so ionic reaction will not be considered further.

One of the characteristics of chain reactions is their marked sensitivity to certain impurities. The use of impure reagents has been one of the greatest hindrances to the elucidation of free radical polymerisation kinetics and it is only with the use of rigorous purification techniques that useful experimental data may be obtained.

There is ample evidence for the free radical nature of polymerisation. Direct introduction of triphenyl methyl radicals to styrene (a typical vinyl monomer) has been shown to initiate polymerisation, and under conditions where they are known to decompose to give free radicals many substances prove to be effective vinyl polymerisation initiators. Fragments of these initiators have been shown to be incorporated in the resulting polymer molecules by the use of initiators labeled chemically or isotopically. The actions of inhibitors such as the free radical diphenyl picryl hydrazyl which "mops up" free radicals in a polymerising system and the quinones which produce stable free radicals on reacting with other radicals provide further evidence of a free radical mechanism.

Reactions in free radicle vinyl polymerisation.

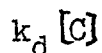
The reaction steps by which a vinyl polymerisation proceeds are described in detail by several authors⁽³⁻⁶⁾ and they are outlined below:

a) Initiation.

The initiation of chain growth arises from the reaction of a primary radicle, $X\cdot$, with the olefinic linkage of a monomer molecule, M , to produce a larger particle



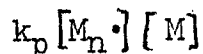
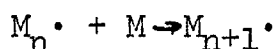
These primary radicles may be produced by several agencies; heat, irradiation or the decomposition of an initiator. Thermal initiation is not a universal property of vinyl monomers and when it does occur it may be by any one of a variety of mechanisms such as disproportionation of two monomer molecules to give a pair of mono-radicles, or opening of a double bond to give a di-radicle. Even ter-molecular initiation reactions have been postulated to explain the kinetic behaviour of some polymer systems. Ionising radiation produces pairs of free radicles by "knocking off" labile groups from monomer molecules. Photochemical or thermal decomposition of initiators, C , (often loosely termed catalysts) produces radicles by a reaction of the type



or by more complicated processes if complex formation or solvation producing a "cage effect" is involved.

b) Propagation.

This reaction consists of the opening of a monomeric double bond by addition to a polymer radicle producing a larger, but similar, radicle capable of further growth.

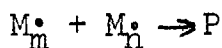


(Note: It is usual to make the simplifying assumption that the value of k_p is independent of the magnitude of n .)

c) Termination.

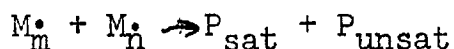
There are two forms of mutual chain termination which may take place;

i) Combination, in which two chains unite to give one dead polymer molecule, P;



(k_t is also assumed independent of m and n .)

ii) Disproportionation, in which a hydrogen atom or other small radicle is transferred between two growing chains to give two dead polymer radicles, one of which is unsaturated;



Two further termination reactions, involving primary radicles, may also take place;



d) Transfer.

These reactions involve the transfer of a labile radicle between some molecule in the system and a growing chain, thus terminating the chain and producing another free radicle.

i) Monomer transfer



ii) Solvent transfer



iii) Initiator transfer



iv) Polymer transfer



e) Other reactions.

i) Degradation; this reaction consists of chain fracture producing two smaller units, one of which is unsaturated.

ii) Depolymerisation; the reverse of the propagation reaction.

iii) Re-initiation, i.e. the attacking of a dead

polymer chain by a primary radicle which extracts a small radicle group leaving a centre on the polymer molecule which is capable of propagation, leading to chain branching and cross-linking.

Simplifications in the Reaction Scheme.

A full kinetic analysis by experimental methods of the system described above would be extremely difficult because of its complexity. Fortunately, however, it is frequently possible to adjust the experimental conditions so that some reactions take place only to a limited extent so that they may justifiably be ignored. A few examples illustrating this remark are listed below;

a) Initiation.

In the bulk polymerisation of styrene at 60°C., the presence of 0.1 mole % benzoyl peroxide gives an overall rate of polymerisation twenty times greater than the thermal rate⁽⁴⁾, showing that, even for low initiator concentrations, thermal initiation is relatively insignificant.

Initiation via complex and initiation with "cage effect" both give an initiation rate equation of the form

$$R_i = k_c [C] \left[\frac{K [M]}{1 + K[M]} \right] \quad (1)$$

and the established values of K are such that the term

in the large brackets is nearly unity except for very low values of $[M]$.⁽⁷⁾

b) Termination.

The question of whether, in a given system, mutual termination takes place by combination or disproportionation has been a stumbling block in the elucidation of polymerisation kinetics. Experimental accuracy in many cases is not high enough to lead to unambiguous conclusions. It seems to be agreed, nevertheless, that polystyrene radicals mutually terminate almost exclusively by combination but it has been shown that poly(methyl methacrylate) radicals terminate mutually both by combination and by disproportionation.

Study of termination by primary radicals suggests that this type of termination does not take place to any significant extent unless the initiation rate is very high or the monomer concentration is very low.

c) Degradation and de-polymerisation do not occur under normal experimental conditions and need not be considered further.

Kinetic Equations.

In polymerisation studies it is usual to allow the reaction to proceed only to a low degree of conversion

so that the concentrations of reactants remain effectively constant and effects caused by the increase in the bulk viscosity of the medium due to the presence of large amounts of polymer are kept to a minimum.

In kinetic studies much use is made of the fact that after a very short time a quasi-stationary state obtains in the system (unless polymer is precipitated) so that the rate of change of free radicle concentration with time may be assumed to be zero. A further assumption made in many cases is that the polymer molecules produced are of high molecular weight, so that it is a good approximation to say that monomer is consumed only in the propagation reaction. These assumptions are shown to be reasonable by the relative values of the various reaction rate constants.

As has been mentioned earlier, to obtain tractable kinetic equations it is necessary also to assume that the rates of reactions involving macroradicles are independent of the chain size of the radicles.

a) Steady state free radicle concentration.

Applying the steady state assumption to the concentration of free radicles ($\Sigma[M_n] = [M\cdot]$) we obtain

$$\frac{d[M\cdot]}{dt} = I - 2(k_t + k_{t'})[M\cdot]^2 - k_{tx}[M\cdot][X\cdot] - k_{t'xx'}[X\cdot][X\cdot'] \quad (2)$$

where I is the initiation rate.

Under conditions where primary radicle termination is negligible.

$$[M\cdot] = [I/2(k_t + k_{t'})]^{1/2} \quad (3)$$

b) Polymerisation rate.

Using the assumption that the kinetic chain length is large, i.e. monomer is consumed predominantly in the propagation process

$$\begin{aligned} -\frac{d[M]}{dt} &= k_p [M\cdot] [M] \\ &= k_p [I/2(k_t + k_{t'})]^{1/2} [M] = (I/2)^{1/2} \delta^{-1} [M] \end{aligned} \quad (4)$$

where $\delta = (k_t + k_{t'})^{1/2}/k_p$

c) Molecular weight.

The mean degree of polymerisation, DP, is given by the ratio (rate of consumption of monomer molecules)/ (rate of production of polymer molecules)

$$\begin{aligned} \text{so } \frac{1}{DP} &= \frac{k_t [M\cdot]^2 + 2k_{t'} [M\cdot]^2 + k_{fm} [M\cdot] [M] + k_{fc} [M\cdot] [C] + k_{fs} [M\cdot] [SY]}{k_p [M\cdot] [M]} \\ &= \frac{(I/2)^{1/2} \delta (k_t + 2k_{t'})}{[M]} + \frac{k_{fm}}{k_p} + \frac{k_{fc} [C]}{k_p [M]} + \frac{k_{fs} [SY]}{k_p [M]} \\ &\approx \frac{(I/2)^{1/2} (k_t + 2k_{t'})}{[M]} + C_m + C_c \frac{[C]}{[M]} + C_s \frac{[SY]}{[M]} \end{aligned} \quad (5)$$

when transfer to polymer is neglected.

Absolute values of rate constants.

From study of such quantities as polymerisation rate, molecular weight and the life times of growing radicals it is possible to determine the values of the reaction rate constants in a polymerising system. The chief difficulty lies in obtaining sufficiently accurate molecular weight measurements which can be used to evaluate the various terms of equation 5.

Probably the most studied monomers are styrene and methyl methacrylate and approximate values for the rate constants at 60°C. are:

Rate Const. (l., mole, sec.units)	Styrene	Methyl Methacrylate
k_p	200	600
k_{fm}	10^{-2}	4×10^{-4}
k_t	10^7	3×10^7
$k_{t'}$	0	4×10^7
k_{f, Bz_2O_2}	10	0

In such systems very high molecular weight products are formed and the various assumptions made in deriving the kinetic equations are therefore justified. For example, in the bulk polymerisation of styrene at 60°C. initiated with 0.1 mole % benzoyl peroxide $I \approx 3 \times 10^{-8}$

mole/l.sec. and it follows from eqn. 5 that

$$DP \simeq 4,000$$

so the average polymer molecule contains 4,000 monomer units.

B. Copolymerisation.

The phenomenon of copolymerisation, where two different monomers enter the same polymer chain has been known and made use of for some considerable time. Small quantities of a second monomer in a polymer can modify the polymer's properties considerably. The classic example of this is the use of traces of divinyl benzene in styrene polymerisation to produce a cross-linked polymer. Only a few cross-links per polystyrene chain are necessary to produce a polymer which is insoluble in aromatic solvents and which has very different properties from polystyrene. A styrene-butadiene copolymer is the basis of many synthetic rubbers. The mechanical properties of poly(vinylidene chloride) are improved by copolymerising with small amounts of vinyl chloride. Ion exchange resins are made by copolymerising monomers, one of which contains reactive side groups. There is a large number of patents describing the production of copolymers for synthetic rubbers, resins, fibres, insulators etc.

This great use of copolymers has aroused interest in the chemistry of their production and much early work was carried out with a view to predicting the composition of polymers arising from a given feed. On the theoretical side, interest in the behaviour of free radicals has led to study of copolymerisation as a useful tool in elucidating the effects of radical structures on their behaviour. Homopolymerisation studies lead to a knowledge of the behaviour of a radical towards molecules or similar radicals, but study of reactions between dissimilar radicals must be carried out in a copolymer system. Much of the work on copolymerisation carried out before 1952 is reported by Alfrey, Bohrer and Mark⁽⁸⁾.

It can be seen from the next section, however, that the introduction of a second monomer to a polymerising system produces a very complicated situation in which a great many reactions take place so that a full kinetic analysis is extremely difficult to carry out. It is for this reason that most copolymerisation studies have been confined to the measurement of the ratios of radical reactivities towards different monomer molecules and only in a few cases have radical-radical reactions been studied.

C. Theory of Copolymerisation.

Reactions.

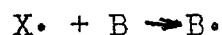
The reactions taking place in a two-monomer system are similar to those for a single monomer described in section A. The situation is complicated, however, by the possibility of various cross-reactions where dissimilar monomer units react. For some monomers, e.g. many 1:2 di-substituted ethylenes, homopolymerisation is impossible due to the large steric effects of the substituents, so that the propagation step $B\cdot + B \rightarrow B\cdot$ and other $B - B$ reactions do not occur, and yet the monomer may still be capable of copolymerisation. An interesting extension of this case occurs in the maleic anhydride - stilbene system where neither of the monomers homopolymerises and the resulting copolymer is always of the structure $\sim ABABABA \sim$.

In more normal copolymer systems most, or all, of the following reactions take place.

a) Initiation.



$$k_{xa} [X\cdot] [A]$$



$$k_{xb} [X\cdot] [B]$$

b) Propagation.

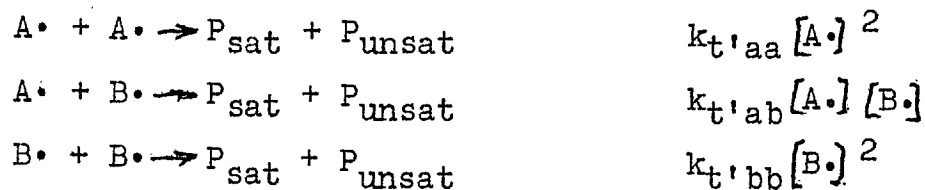


c) Termination

i) Combination



ii) Disproportionation



iii) Primary Radicle



d) Transfer.

i) with monomer



ii) with solvent



iii) with initiator



iv) with polymer



Copolymerisation kinetics.

By restricting studies to low degrees of conversion where the reactant concentrations remain sensibly constant and the resulting copolymer composition does not change greatly during the course of the reaction, the assumptions used in the treatment of homopolymerisation may be employed. As well as the assumption that a quasi-stationary state obtains and that radicle reactivities are independent of radicle size, it is assumed that radicle reactivities are independent of the nature of the penultimate unit of a growing chain.

Employing these assumptions the following relations may be deduced;

a) Steady state free radicle concentrations.

For steady state conditions

$$\begin{aligned} \frac{d[A\cdot]}{dt} = & k_{xa}[X\cdot][A] + k_{pba}[B\cdot][A] - k_{pab}[A\cdot][B] - 2T_{aa}[A\cdot]^2 - T_{ab}[A\cdot][B\cdot] \\ & - k_{tax}[A\cdot][X\cdot] + k_{fba}[B\cdot][A] - k_{fab}[A\cdot][B] \\ & - k_{fac}[A\cdot][C] - k_{fas}[A\cdot][SY] \\ = & 0 \end{aligned} \quad (7)$$

Replacing all the symbols A by B and vice versa gives the expression for

$$\frac{d[B\cdot]}{dt} = 0 = \dots \quad (8)$$

where $T_{aa} = k_{taa} + k_{t'aa}$; $T_{ab} = k_{tab} + k_{t'ab}$ and $T_{bb} = k_{tbb} + k_{t'bb}$.

From equations 7 and 8 explicit expressions for $[A\cdot]$ and $[B\cdot]$ may be obtained but they are very unwieldy. Under conditions where solvent and catalyst transfer are negligible, addition of eqns 7 and 8 gives

$$\begin{aligned} \frac{d[A\cdot] + [B\cdot]}{dt} = & I - 2(T_{aa}[A\cdot]^2 + T_{ab}[A\cdot][B\cdot] + T_{bb}[B\cdot]^2) \\ = & 0 \end{aligned} \quad (9)$$

if primary radicle termination is ignored.

For processes producing high molecular weight polymers the propagation terms in eqns. 7 and 8 are far larger than the others, in which case

$$k_{pab}[A\cdot][B] = k_{pba}[B\cdot][A] \quad (10)$$

From relations 9 and 10 it follows that

$$[A\cdot] = \left[\frac{1}{2} \frac{1}{\{T_{aa}k_{pba}^2[A]^2 + T_{ab}k_{pab}k_{pba}[A][B] + T_{bb}k_{pab}^2[B]^2\}} \right]^{\frac{1}{2}} k_{pba} [A] \quad (11)$$

$$\text{and } [B\cdot] = \left[\frac{1}{2} \cdot \frac{1}{Z} \right]^{\frac{1}{2}} k_{pab} [B] \quad (12)$$

where Z is the term in curly brackets in eqn. 11.

b) Polymerisation Rates.

The assumptions leading to eqn. 10 may also be employed to give a good approximation to the rates of monomer consumption;

$$-\frac{d[A]}{dt} = k_{paa} [A\cdot][A] + k_{pba} [B\cdot][A] \quad (13)$$

$$-\frac{d[B]}{dt} = k_{pbb} [B\cdot][B] + k_{pab} [A\cdot][B] \quad (14)$$

Substituting for A· and B· from eqns. 11 and 12

$$-\frac{d[A]}{dt} = \left[\frac{1}{2} \cdot \frac{1}{Z} \right]^{\frac{1}{2}} (k_{paa}k_{pba}[A]^2 + k_{pab}k_{pba}[A][B]) \quad (15)$$

$$-\frac{d[B]}{dt} = \left[\frac{1}{2} \cdot \frac{1}{Z} \right]^{\frac{1}{2}} (k_{pbb}k_{pab}[B]^2 + k_{pab}k_{pba}[A][B]) \quad (16)$$

writing $\frac{k_{paa}}{k_{pab}} = r_a$, $\frac{k_{pbb}}{k_{pba}} = r_b$, $\frac{T_{aa}^{\frac{1}{2}}}{k_{paa}} = \delta_a$, $\frac{T_{bb}^{\frac{1}{2}}}{k_{pbb}} = \delta_b$ and $\frac{T_{ab}}{T_{aa}T_{bb}^{\frac{1}{2}}} = \phi$

the overall polymerisation rate is

$$-\frac{d([A]+[B])}{dt} = \frac{(r_a[A]^2 + [A][B] + r_b[B]^2)(\frac{1}{2})^{\frac{1}{2}}}{(r_a^2\delta_a^2[A]^2 + r_ar_b\delta_a\delta_b\phi[A][B] + r_b^2\delta_b^2[B]^2)^{\frac{1}{2}}} \quad (17)$$

c) Copolymer composition.

The instantaneous copolymer composition produced

by monomer concentrations $[A]$ and $[B]$ is given by the ratio of the rates of disappearance of the monomers. From eqns. 15 and 16, then the molar ratio of monomer units entering the polymer is

$$\begin{aligned} \frac{a}{b} = \frac{d[A]}{d[B]} &= \frac{k_{paa}k_{pba}[A]^2 + k_{pab}k_{pba}[A][B]}{k_{pbb}k_{pab}[B]^2 + k_{pab}k_{pba}[A][B]} \\ &= \frac{[A]}{[B]} \cdot \frac{(r_a[A] + [B])}{(r_b[B] + [A])} \end{aligned} \quad (18)$$

d) Molecular Weight.

The mean degree of polymerisation, DP , is given by the ratio (rate of consumption of monomer molecules/ rate of production of polymer molecules). It follows that DP^{-1} is the sum of the following terms divided by $(r_a[A]^2 + [A][B] + r_b[B]^2)$

i) Termination

$$\left[\frac{I \cdot \eta^{\frac{1}{2}}}{2Z} \right] \left[(T_{aa} + k_{t'aa})(k_{pba}/k_{pab})[A]^2 + (T_{ab} + k_{t'ab})[A][B] + (T_{bb} + k_{t'bb})(k_{pab}/k_{pba})[B]^2 \right] \quad (19)$$

ii) Monomer Transfer.

$$\left[C_{am}[A] + (k_{fab}/k_{paa})[B] \right] r_a[A] + \left[C_{bm}[B] + (k_{fba}/k_{pbb})[A] \right] r_b[B] \quad (20)$$

iii) Catalyst Transfer.

$$[C_{ac}r_a[C][A] + C_{bc}r_b[C][B]] \quad (21)$$

iv) Solvent Transfer.

$$[C_{as}r_a[SY][A] + C_{bs}r_b[SY][B]] \quad (22)$$

where symbols C_{tm} are the transfer constants in homopolymerisation for radicles type 't' with molecules type 'm'.

From these expressions it is seen that the additional information concerning free radicle reactivities provided by copolymerisation studies is implicit in the parameters r_a , r_b , ϕ , k_{fab} and k_{fba} . All other reaction constants are obtainable from homopolymerisation studies, provided the change in properties of the reaction medium does not affect the various rate constants.

Of the five parameters listed above, the reactivity ratios r_a and r_b have received the most attention due to the ease with which they may be determined. All that is necessary for their determination is a knowledge of the monomer and copolymer compositions.

D. The Effect of Pressure in Liquid Phase Reactions.

It is evident from the kinetic relationships considered above, that any effect of pressure in a polymerising system on properties which are easily measured experimentally, such as molecular weight and polymerisation rate, is difficult to interpret in terms of the individual reactions and their mechanisms. Some of the physical and chemical effects of high pressure are

outlined below, as they have a direct bearing on the systems considered and can provide explanations for some of the phenomena noted in the course of this work.

a) Concentration Changes.

The effect of pressure upon the thermodynamic properties of a condensed phase system are far less pronounced than in the gaseous phase. In an ideal gas system a tenfold isothermal increase in pressure produces a tenfold increase in concentration. Liquids are far less compressible and compressibilities of the order of 10^{-4}atm^{-1} which decrease with increasing pressure are usual.

Most liquids contract on freezing and increase of pressure therefore favours the production of the solid phase. In a mixture of reagents, then, pressure freezing of one component from the liquid phase will alter the composition of the reacting mixture.

It is not unusual to find that superpressing occurs, especially if the pressure is increased rapidly. Large degrees of superpressing can reduce the mobility of the liquid components to such an extent that crystallisation becomes kinetically very difficult.

b) Reaction Rate Changes.

According to the transition state theory of Glasstone, Laidler and Eyring⁽⁹⁾, one form of the

Arrhenius equation is

$$k = \frac{kT}{h} \cdot \exp(\Delta S^\ddagger/R) \cdot \exp(-\Delta H^\ddagger/RT) = \frac{kT}{h} \cdot \exp(-\Delta G^\ddagger/RT) \quad (23)$$

This equation is similar to the rate equation derived from the kinetic theory of gases;

$$k = PZ \cdot \exp(-E/RT) \quad (24)$$

$\Delta H^\ddagger$ and E are roughly equivalent as are the collision number Z and the quantity $\frac{kT}{h}$, the probability factor

being related to the exponential entropy term.

From the Maxwell relationship

$$\frac{\partial G}{\partial P} = V$$

it follows that

$$\frac{\partial \ln k}{\partial P} = -\frac{\Delta V^\ddagger}{RT} \quad (25)$$

In general, the volume of activation, $\Delta V^\ddagger$, tends to increase or decrease in the same direction as the entropy of activation, $\Delta S^\ddagger$. Bimolecular reactions involving large molecules which have single active centres obviously have a large steric factor and are thus associated with large negative values of $\Delta S^\ddagger$. All the reactions in copolymerisation involve macro-radicals, (except the unimolecular dissociation of initiator, primary radicle termination and the first few steps of the propagation reaction), and should thus

exhibit marked acceleration with increasing pressure according to equation 25.

c) Steric Effects.

Reactions which take place at low pressure to give only low molecular weight polymers (tetramers and lower), due to steric hindrance may in some cases, at high hydrostatic pressures, yield high polymer products. Pressure does not, however, overcome high degrees of steric hindrance⁽¹⁰⁾ Low molecular weight polymers may also be produced where the monomer transfer is an important reaction.

d) Viscosity Changes.

It is found for the majority of liquids not containing -OH groups that

$$\frac{\partial \ln \eta}{\partial P} \approx \text{const.}$$

For a diffusion controlled rate process, the rate constant k_d is dependent on the diffusivity, D , of the reacting species. The diffusivity, according to the Stokes-Einstein relation, which applies to the ideal case of spherical molecules, is inversely proportional to the viscosity of the medium so $k_d \propto \eta^{-1}$.

So k_d is approximately proportional to e^{-P} and the effect of pressure is to retard a diffusion controlled process.

From the above considerations it is seen that, although the chemical reaction rate may be increased by increase in pressure, the physical rate process of diffusion is reduced so that a transition may occur in the rate controlling process. Such a transition from reaction to diffusion control has been found experimentally in work carried out by Hamann.⁽¹¹⁾ on the alkaline etherification of ethyl bromide. Diffusion control in the low pressure polymerisation of methyl methacrylate has been shown to occur in the termination reaction whose rate was found to be inversely proportional to the bulk viscosity by Benson and North.⁽¹²⁾

E. Pressure Effect on Polymerisation.

It was first noted by Bridgman and Conant that high pressures increase the rate of polymerisation of olefins.⁽¹³⁾ Since this work, papers have been published on the ^hthermal homopolymerisation of styrene, substituted styrenes and methyl methacrylate.⁽¹⁴⁻¹⁸⁾ Studies have also been carried out on the polymerisation of styrene, methyl methacrylate, allyl acetate and several 1:2 di-substituted ethylenes in systems initiated "catalytically" or photochemically.⁽¹⁹⁻²²⁾

Much of the earlier work is only qualitative or

semi-quantitative due to poor purification techniques or non-isothermal conditions and it is only in the more recent papers of Merrett and Norrish,⁽¹⁹⁾ Walling and Pellon,⁽²¹⁾ Nicholson and Norrish⁽²⁰⁾ and Melekhina and Kuvshinski⁽²²⁾ that accurate work seems to have been carried out. The results of these workers show that the overall rate of polymerisation increases exponentially with pressure as would be suggested by eqn. 25. In styrene polymerisation, the molecular weight increases with pressure up to about 3,000atm. above which pressure it remains fairly constant. This indicates that the transfer constants are not greatly affected by pressure although the termination reaction is retarded. Styrene and methyl methacrylate polymerisation rates are both found to be proportional to $[C]^{\frac{1}{2}}$ as predicted by eqn. 4 although the exponent does decrease slightly with increasing pressure.

F. Scope of this Work.

Although a considerable number of copolymer systems have been studied at low pressures, little attention has been given to the effect of high pressure on copolymerisation reactions. The monomer ethylene has been copolymerised at pressures up to around 1,000atm. with many vinyl

monomers and the methods employed are described under several patents. (Many of these patents are mentioned in "Polyethylene" by Raff and Allison⁽⁹⁶⁾) Two papers published in 1952^(97,98) describe a systematic study of the copolymerisation of ethylene with carbon monoxide at pressures up to 1,000 atm and the properties of the resulting copolymers. Little other systematic work has been done and it was therefore decided that it would be of interest to study the behaviour of some other copolymer systems at high pressures.

The object of the work described in this thesis was to investigate the effect of pressure on copolymerisability, polymerisation rates and the composition and structure of the resulting polymers. Where sufficient data are available, the monomer reactivity ratios have been determined and the ϕ factors for cross-termination. Some copolymer melting points have been determined in the hope that some indication of the copolymer structures would result.

The systems styrene-methyl methacrylate, styrene-diethyl fumarate, methyl methacrylate-maleic anhydride and styrene-perchloroethylene have been studied at pressures up to 4,000atm. (9,000atm. in the case of the styrene-perchloroethylene system where it was suspected

that steric hindrance was preventing copolymerisation.)

PART 2 APPARATUS AND EXPERIMENTAL PROCEDURE

A.1. Pressure vessels and ancillary equipment.

Two high pressure vessels have been used in this work, both are basically of the same design with similar ancillary equipment. Details of the construction of the pressure vessels are indicated in fig. 1. The pressure seals employed are shown in fig. 2.

Vessel A has a large internal volume and is designed for working pressures up to 5,000atm. The high pressure chamber is a duplex shrunk cylinder of "Vibrac V45" steel originally designed to be sealed at the top with a lens ring. Since the vessel was made "Neoprene" Poulter packings have been brought into use by the simple expedient of backing up the packing with a mushroom head. These seals have been used successfully and are less prone to leaks than lens rings. In recent years rubber "O" rings have found widespread application as pressure seals and were found to be satisfactory up to pressures of 3,000atm. above which pressure they tend to be extruded with consequent leakage from the high pressure system. Their advantage over Poulter packings lies in the ease with which the seal

can be made and broken. Forcing the Poulter packing into the high pressure cylinder is a slow and laborious process because of the large volume of oil which has to be expelled through the 0.016" dia. side injection hole, and removal of the packing involves pumping a similar volume of oil back into the vessel to expel it.

Pressure up to 1,000atm. may be applied direct to the high pressure chamber through the side inlet. Higher pressures are obtained by use of the intensifier which has an area ratio of 13.3:1. Pressure is applied to the bottom of the low pressure piston which is sealed with a Bridgman packing, and the force is transmitted through a thrust block to the high pressure piston sealed with a Poulter packing. The high pressure piston travels up into the high pressure chamber isolating the side injection hole and further compressing the contents of the high pressure chamber.

Vessel B is shown diagrammatically in fig. 1 with the intensifier attached. The high pressure chamber is of a smaller bore than vessel A and is an autofrettaged monobloc of "Vibrac V45" steel. It is capable of withstanding internal pressures up to 20,000atm. and is sealed, top and bottom, with Poulter packings. The intensifier for this vessel has an area

ratio of 16:1.

A line diagram of the arrangement of the apparatus is shown in fig. 3. Liquid paraffin B.P. is used as the hydraulic fluid and is transmitted through $\frac{3}{8}$ "x $\frac{1}{8}$ " stainless steel tubing. The pressure is generated in a hand operated, two stage ram pump P capable of delivering 2,000atm. pressure. The pressure is applied to the high pressure chamber through valve H and to the low pressure piston via valve L. The pressure in the low pressure system is measured by a Bourdon tube test gauge G. Oil is released from the apparatus through valve V to the Reservoir R.

Temperature control.

The two vessels are each surrounded by an electrical heating jacket J, and the intensifiers are lagged. In vessel A temperature control to $\pm 0.1^{\circ}\text{C}$. in the high pressure chamber was achieved by the use of a variable mercury contact thermometer situated between the jacket and the vessel in conjunction with a hot wire vacuum relay switch. There was a temperature gradient at the lower end of the vessel due to heat loss through the intensifier and the supports of the vessel, so that it was found necessary to situate reagent samples in the upper part of the reaction

chamber where the temperature profile was less effected by these losses.

Vessel B had a heater which provided more heating at the lower end of the vessel to compensate for the heat losses at the intensifier. Temperature control was achieved by the use of an energy input regulator in the power supply and the temperature was therefore affected by ambient temperature fluctuations. As runs in this vessel were of relatively short duration, this was not a great drawback. A temperature gradient also existed along the length of this vessel so the same precautions were taken in carrying out runs as with vessel A.

Reaction Vessels.

The types of reaction vessel used are shown in fig. 4. Glass reaction tubes with ground glass stoppers were used in vessel A sealed from the hydraulic fluid by mercury and floated in mercury in a stainless steel bucket shown at (a). Because of the smaller volume of the high pressure chamber of vessel B, a more compact reaction vessel of mild steel was used for work using vessel B. This reaction vessel was closed at the top by a screwed plug with a copper washer and

at the bottom by a mercury seal, as shown at (b).

For the determination of freezing pressures it was desirable to introduce a large volume of the test liquid into vessel B. This was done using a "Fluon" capsule as shown at (c), fitted with a brass sleeve at each end to prevent the tube belling out. These capsules were not used for polymerisation experiments as the stoppers were sometimes blown out, presumably when the apparatus was de-pressurised.

2. Atmospheric bath.

The bath used for reactions at atmospheric pressure was filled with liquid paraffin, well lagged and equipped with an efficient stirrer. A blackened 100 watt light bulb was used as an immersion heater. Temperature control was effected by a mercury-toluene thermoregulator operating a hot wire vacuum relay switch, Temperature control to $\pm 0.1^{\circ}\text{C}$. was achieved.

3. Viscometers.

For viscosity determinations micro-viscometers sizes M1 and M2 as specified in B.S. 188 were used. Determinations were made in a water-filled glass thermostat bath whose temperature was maintained at

$30 \pm 0.1^\circ\text{C}$. by a mercury-toluene thermoregulator operating a vacuum relay switch. The bath was efficiently stirred.

4. Dilatometer.

The dilatometer used for melting point determinations consisted of a small pyrex glass bottle of about 1.5 cc capacity. This was attached by a standard B7 cone and socket joint to a 25 cm. length of precision bore capillary tubing of 0.5 mm. bore. In use, the bottle of the dilatometer was immersed in a small, lagged bath filled with "tetra aryl silicate" which was well stirred. The bath could be heated at a controlled rate by regulating the power input to the hotplate on which it stood.

B. Experimental Procedure.

1) Purification of materials.

a) Benzoyl Peroxide was obtained as a water wet paste from B.D.H. It was dried in vacuo at room temperature for 48 hrs. after which it was twice taken up in chloroform, filtered and precipitated in dry methanol. It was then dried and stored under vacuum at room temperature. The purified product had a

melting point of 105°C.

b) Styrene was obtained from two sources. In each case it was the middle cut of a crude styrene distillation and contained benzoquinone as inhibitor. It was washed three times with 10% sodium hydroxide solution and three times with distilled water to remove the inhibitor after which it was dried over anhydrous calcium chloride for at least 24 hrs. Distillation under an atmosphere of oxygen free nitrogen at 10mm. Hg was carried out collecting the middle 60% of the distillate which came over at 32°C. This fraction, having a refractive index $n_D^{20} = 1.5462$ was stored under vacuum at 0°C. until required. Distilled styrene was not stored for longer than 48 hrs. before use.

c) Methyl Methacrylate inhibited with quinol was obtained from B.D.H. It was purified in the same manner as the styrene in (b) above. The fraction collected boiled at 25°C. (45mm.Hg.) and had a refractive index $n_D^{20} = 1.4145$. The purified product was stored at 0°C. under vacuum and was used within two days of being distilled.

d) Maleic Anhydride, 99.5% pure was obtained from B.D.H. It was vacuum distilled and recrystallised twice from chloroform after which it was dried for 48 hrs. under vacuum at room temperature. The product had a melting point of 58.2°C.

e) Diethyl Fumarate, supplied by L. Light & Co., was vacuum distilled at 24mm. Hg. The middle 70% cut boiling at 32°C. was collected and had a refractive index $n_D^{20} = 1.4420$.

f) Perchlorethylene, obtained from B.D.H. was distilled and the middle fraction boiling at 120.8°C. was collected. ($n_D^{20} = 1.5068$).

g) Benzene, 'Analar' quality was used without further purification after drying over anhydrous calcium chloride.

h) Methanol of 'Analar' quality was used without further purification.

j) 1:2 Epoxy Propane from B.D.H. was not further purified.

2) Preparation of Copolymers.

a) General remarks.

Studies of a great number of two-monomer systems at low pressures have been carried out by Mayo, Lewis, Walling and co-workers whose findings are reported extensively in the Journal of the American Chemical Society. The greater part of their work was carried out at 60°C. using 0,1 mole% benzoyl peroxide as initiator and, for the purposes of comparison, it was decided to conduct experiments at the same temperature and catalyst concentration.

The rate of decomposition of benzoyl peroxide at 60°C. is such that the concentration is not greatly reduced during the course of the reactions carried out in this work. The use of benzoyl peroxide as initiator is convenient as it does not undergo chain transfer to any marked extent and the concentration used is low enough for primary radicle termination to be discounted as insignificant at 60°C. Some workers have found that mercury reacts with benzoyl peroxide to give a dense precipitate of phenyl mercuric benzoate, (21), (94) but there was no evidence of this in the work described here, possibly due to the low

concentrations used.

To develop an experimental technique and check the repeatability of results, several runs were carried out using styrene initiated with benzoyl peroxide under experimental conditions similar to those described by Merrett and Norrish.⁽¹⁹⁾ Benzene, Methyl ethyl ketone and 1:2 epoxy propane were each used as solvent in the precipitation of the polymer in methanol. It was found that use of the third solvent led to the production of the most easily handled precipitate and its use was adopted for all subsequent work. The results of these runs are given in table 1.

In an attempt to detect acceleration of polymerisation rate due to heating of the reacting monomer through poor heat dissipation from the reaction tube two different sized tubes were used, having internal diameters of 15 and 5 mm. and volumes of 26 and 6 ml. respectively. The different tube diameters were found to have no measurable effect on a reaction rate of 20%/hr for styrene at 3,000atm (Gillham⁽¹⁶⁾ found that styrene reaction rate of 30%/hr in a 4 mm. diameter tube is essentially isothermal).

b) Reagents.

Monomer mixtures were made up by weight and the requisite quantity of catalyst was added. Monomer pairs styrene-methyl methacrylate, styrene-diethyl fumarate and styrene-perchloroethylene were used in bulk. The pair methyl methacrylate-maleic anhydride had, in most cases, to be diluted with an equimolar quantity of benzene to ensure that all the maleic anhydride remained in solution. Bulk polymerisation of methyl methacrylate was carried out at 40°C. as the rate of reaction at 60°C. was so high that reactions went almost to 100% conversion in a few minutes at the higher pressures. The compositions of the reaction mixtures are indicated in table 2.

c) The Reaction.

In high pressure runs a small quantity of mercury was placed in an inverted reaction tube which was then flushed with nitrogen. The tube was then filled with the reagents and inverted into the bucket containing the mercury seal. The reaction mixtures were held under pressure long enough for about 8% by weight of the monomers to be polymerised. Care was taken in pressurising the system that at no time did the gauge

pressure exceed the required value as this would have rendered pressure reading inaccurate due to the friction in the packings of the intensifier.

Atmospheric pressure runs were carried out in sealed 10ml. glass ampoules which had been flushed out with nitrogen. The thermostat bath was shielded from bright light during the course of the reaction.

d) Separation of High Polymers.

On removal from the reaction vessel, a sample of the product was weighed, dissolved in 1:2 epoxy propane and precipitated in 150ml. of methanol. The precipitate was left for a short time to coagulate after which it was filtered in a sintered glass crucible of porosity 3 washed with 30ml. of methanol, dried at 60°C. for 24hrs., cooled and weighed.

3. Viscosity Determinations.

Toluene was found to be a suitable solvent for all the polymers produced which contained styrene. Solution viscosities of these polymers were determined at 30°C. using M2 viscometers, except for polymers from the styrene-perchloroethylene system, where flow times were so low in some cases that M1 viscometers

were used. Huggins constants, k' , were determined for each copolymer composition by finding the values of specific viscosity, η_{sp} , over a range of concentration, c , from 0.45 to 0.10g./100ml. and plotting η_{sp}/c against η_{sp} . k' was then obtained as the ratio of the slope of the plot to the intercept at $\eta_{sp} = 0$, as

$$[\eta] = \frac{\eta_{sp}/c}{1 + k'\eta_{sp}}, \quad \text{where } [\eta] \text{ is the limiting}$$

viscosity number defined by $[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c$.

It was assumed that the value of k' was not affected by the pressure at which the polymer had been prepared, but only by the composition of the polymer.

Employing this assumption, limiting viscosity numbers of copolymers of a given composition were calculated from specific viscosities determined at a concentration of 0.35g./100ml. using the Huggins equation.

Poly(methyl methacrylate) prepared at 40°C. was not soluble in toluene and limiting viscosity numbers were therefore determined in chloroform solution.

Methyl methacrylate-maleic anhydride copolymer solutions in chloroform showed a decrease in viscosity with time, possibly due to a depolymerisation reaction taking place in the solvent. Solution viscosities of these copolymers were therefore determined in

dry acetone. The Huggins constant for these copolymers was found to be very nearly zero, so specific viscosities were measured at 0.23g./100ml. concentration and not extrapolated to infinite dilution.

4) Copolymer Composition.

The ratio of monomer units present in copolymer samples was deduced from carbon analyses carried out in the Organic Micro-analytical Laboratory of this college. 10mg. samples were used and results were subject to an error of 0.3% carbon by weight. Several analyses of polystyrene and poly(methyl methacrylate) samples were made and the measured carbon contents were found to be 0.4 to 0.8% lower than the theoretical values. Values given in the results have been corrected for this disparity.

5) Tests for Copolymerisation.

Under conditions similar to those employed in this work, it has been shown that diethyl fumarate and maleic anhydride do not homopolymerise to give high molecular weight products.⁽¹⁰⁾ The fact that these monomers are shown to be present in the polymer product in quantities up to, but not exceeding 50% is

considered sufficient evidence that they have copolymerised.

As a test for copolymerisation in the styrene-methyl methacrylate system a procedure similar to that employed by Lewis and Mayo⁽²³⁾ was adopted. A solution of 1g. of (co)polymer prepared at 2,000atm. and containing about 50% each of the two monomers was made up in 50ml. chloroform. Different volumes of dry methanol were added to samples of this solution and the weight of precipitate produced in each case was found. Carbon analyses as indicated in the footnotes to table 3 were carried out. From the smoothness of the precipitation curve (see fig. 5) compared with curves found for mixtures of homopolymers of styrene and methyl methacrylate, and the much less marked variation in carbon content of the precipitates it is inferred that the solute was a copolymer and not a polymer mixture.

Experimental evidence showing that perchlorethylene does not copolymerise with styrene will be discussed in a later section.

6) Melting Points.

For melting point determinations a sample of copolymer was packed into the pyrex bottle of the

dilatometer, covered with liquid paraffin and degassed by holding under a high vacuum for two hours. The bottle was then filled with a further volume of liquid paraffin and the capillary stem was fitted.

The dilatometer was heated at $0.5^{\circ}\text{C./min.}$ and the height of the liquid paraffin in the capillary was measured at 0.5° intervals using a cathetometer. Heating was discontinued when the melting point, observed as a discontinuity in the temperature-height plot, had been exceeded by about 5° .

7) Freezing Pressures.

To try to find an explanation for some of the phenomena observed in work on the styrene-perchloroethylene system it was decided to investigate the possibility of pressure freezing in this system. Two liquids were examined; pure perchlorethylene and a styrene-perchlorethylene mixture.

Samples were examined by enclosing in a "Fluon" capsule in vessel B at 60°C. Small increments of pressure were applied to the sample by pumping up the intensifier. Sufficient time was allowed to elapse for the heat of compression to be dissipated at each pressure before the pressure was noted. The

corresponding heights of a fiducial mark on the intensifier thrust block were observed through a cathetometer. Freezing was detected as a discontinuity in the plot of pressure v. intensifier displacement. The pressure was increased to about 50atm. above the freezing pressure thus found, and then reduced in small stages to find the pressure at which melting occurred.

To prevent thermal polymerisation of the styrene mixture during the freezing test 0.2 mole% of quinol was added to the test sample.

FIG.1 PRESSURE VESSELS.

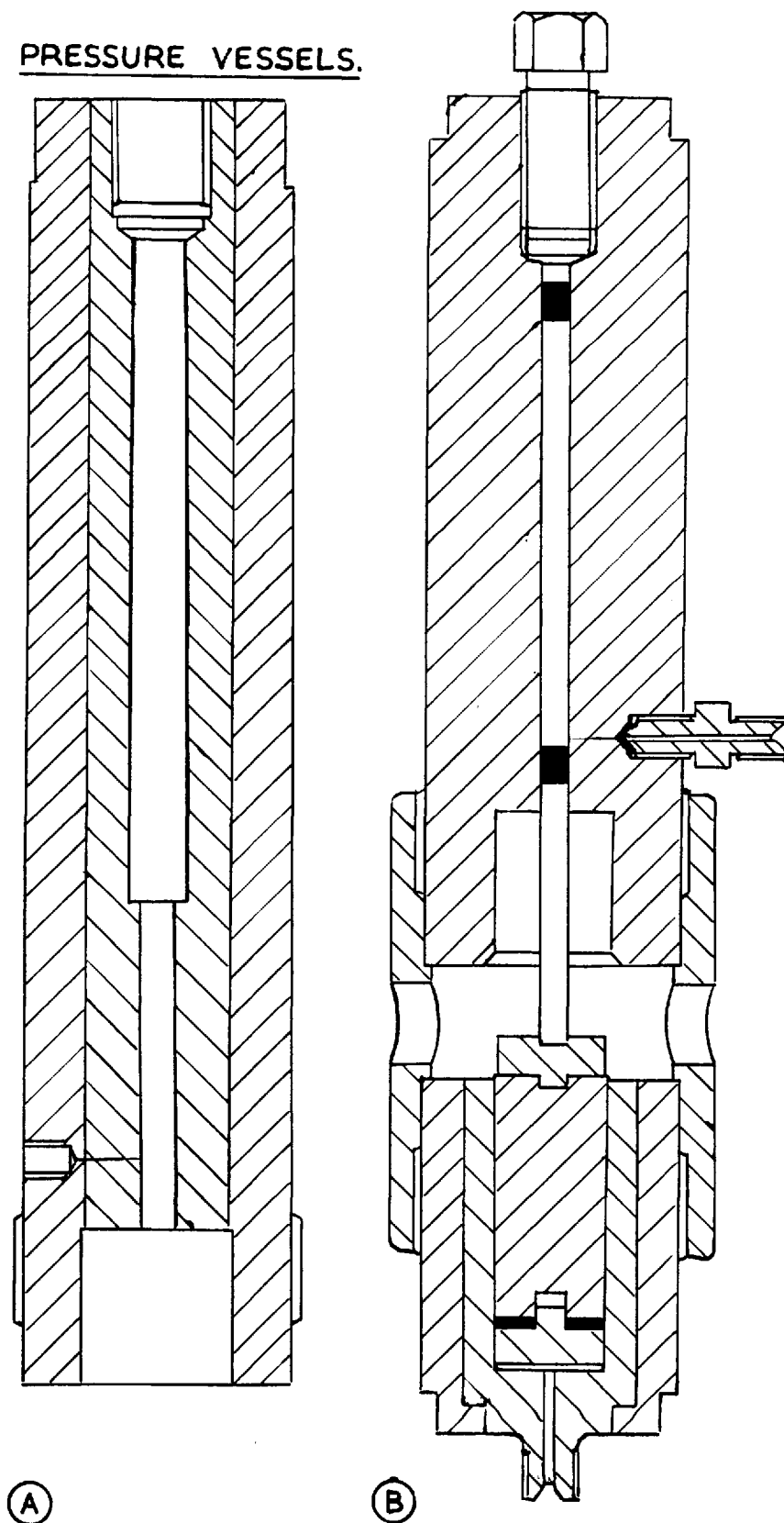


FIG.2

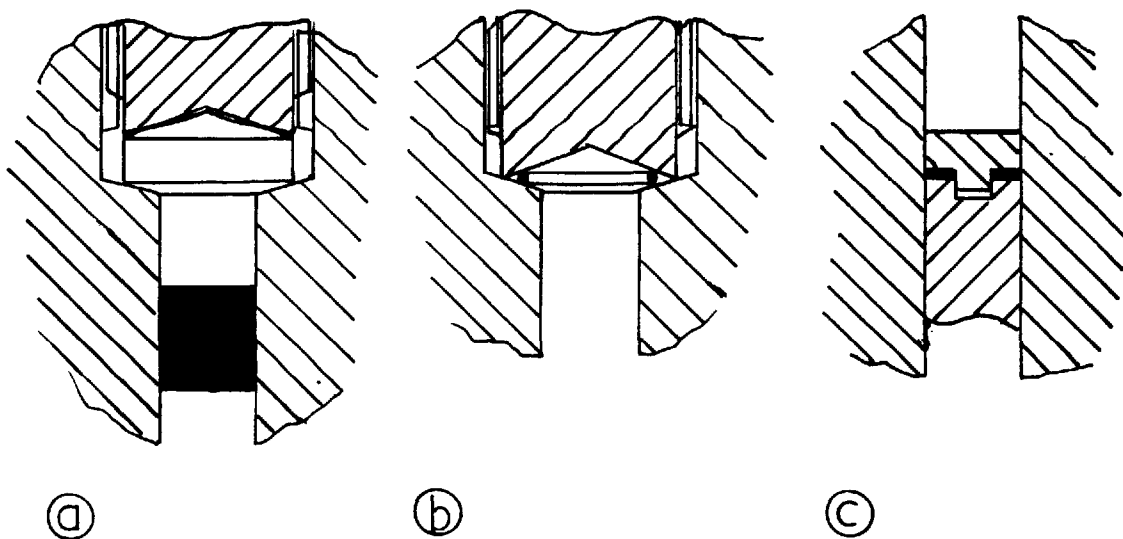
PRESSURE SEAL DETAILS

FIG. 3

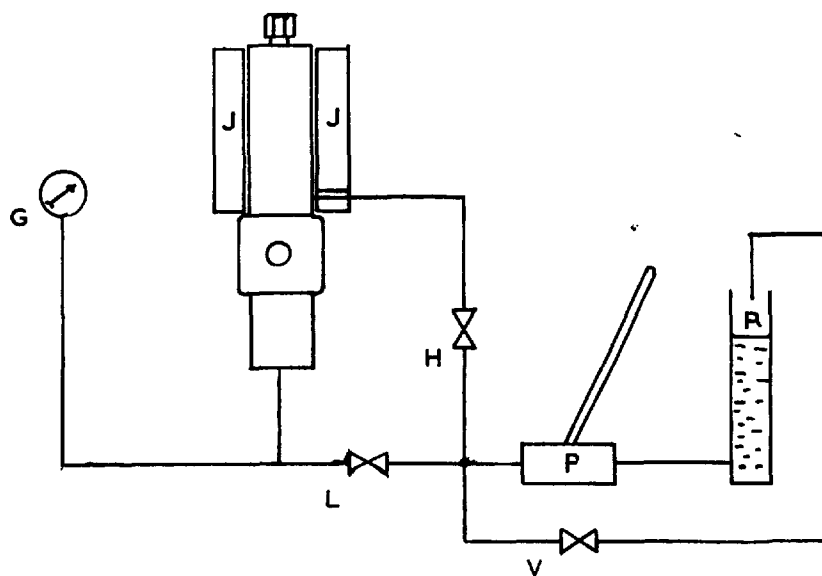
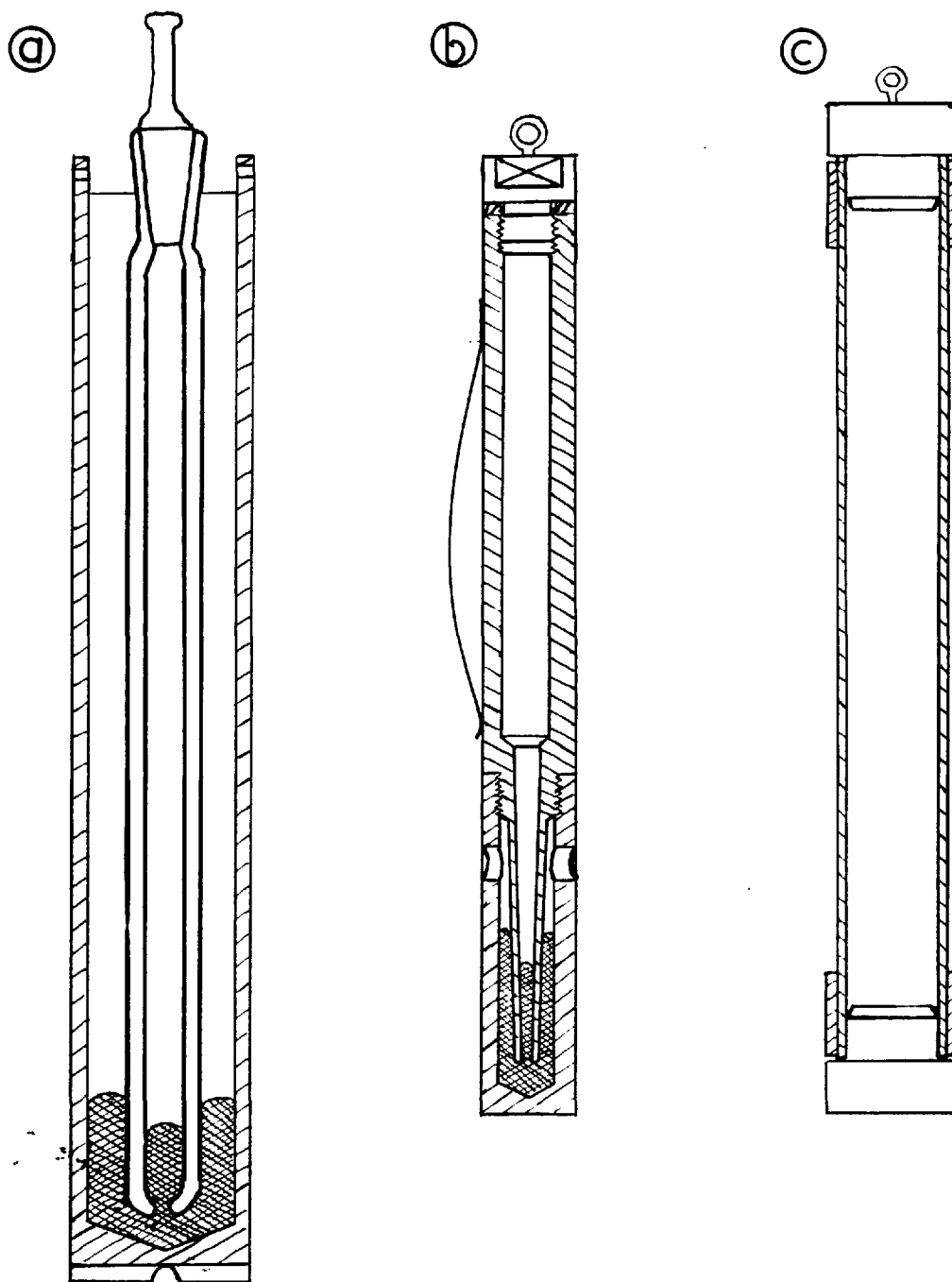
LINE DIAGRAM OF HIGH PRESSURE EQUIPMENT.

FIG. 4. REACTION VESSELS.



PART 3. EXPERIMENTAL RESULTS.

The experimental results are given in tabular form in Part 5 (p 19) and are summarised graphically in figures 5 to 20.

A. Monomer Reactivity Ratios.

Monomer reactivity ratios may be deduced from the carbon analyses of the copolymer products and the compositions of the monomer mixtures from which they arise by the use of the differential copolymer composition equation (eqn. 13) as the degrees of conversion are low enough for this procedure to be justified.

The method of Lewis and Mayo⁽²³⁾ has been used where the expression is set in the form

$$r_b = \frac{[A]_m}{[B]_m} \left[\frac{b}{a} \left(\frac{[A]_m}{[B]_m} \cdot r_a + 1 \right) - 1 \right] \quad (26)$$

where the suffix _m indicates mean values.

Values of r_b corresponding to various values of r_a are plotted for several monomer ratios at each reaction pressure and the centre of the polygon of error at the intersection of these plots is taken for the values of r_a and r_b . (See example given in fig. 6) The values of monomer reactivity ratios found are given in table 5. From the error polygons it seems that for

the systems Styrene - Methyl Methacrylate and Styrene - Diethyl Fumarate the confidence limits on r values are ± 0.04 . For the Methyl Methacrylate - Maleic Anhydride and Styrene - Perchloroethylene systems these limits are far wider due to the difficulty in obtaining sufficiently accurate carbon analyses.

The Styrene - Methyl Methacrylate system has been studied in greatest detail and from the results it appears that pressure has little if any influence on the reactivity ratios in the pressure range studied. There does appear to be some slight increase with increasing pressure, (see fig. 7), but this variation is within the limits of experimental accuracy. This indicates that the volumes of activation for the styryl - Styrene and Styryl - Methyl Methacrylate propagation reactions must be similar as

$$\frac{\partial \ln r_a}{\partial P} = \frac{\Delta V_{pab}^\ddagger - \Delta V_{paa}^\ddagger}{RT} \quad \text{from eqn. 25.} \quad (27)$$

and similarly that $\Delta V_{pba}^\ddagger \approx \Delta V_{pbb}^\ddagger$ for the propagation of radicals having a Methyl Methacrylate radicle end group.

The values of monomer reactivity ratios found in the Styrene - Methyl Methacrylate and Styrene - Diethyl Fumarate systems agree with the results published for

low pressure by Mayo and Walling⁽²⁴⁾ and by Lewis and Mayo⁽²³⁾. The results of the pair Methyl Methacrylate - Maleic Anhydride differ considerably from the values found by de Wilde and Smets⁽²⁵⁾ and Blackley and Melville⁽²⁶⁾ probably due to the unsatisfactory use of carbon analyses as a method of deducing copolymer composition.

Table 6 shows some results for the styrene - Perchloroethylene system where copolymer compositions are calculated from molecular weights on the assumption that only one Perchloroethylene unit is present in each polymer molecule. These values are compared with the compositions deduced from carbon analyses. Allowing for the possible errors involved in the method of determining the molecular weights and the analyses, the comparison of these results suggests that perchloroethylene groups enter the polymer molecules only through transfer reactions. This would also explain why 'reactivity ratios' calculated for this system using the not unreasonable assumption that $r_b = 0$ are found to be dependent on the monomer compositions. In deducing a value of 185 for r_a , Doak⁽²⁷⁾ had presumably overlooked the possibility of transfer.

B. Reaction Rates.

From figs. 8 to 11 it is apparent that increase in pressure in all cases produces an increase in the overall rate of reaction. In most cases the increase is roughly exponential with pressure as has been found in studies of homopolymerisation reaction mentioned in part 1. However, whereas the effect of pressure on the overall rate constant for catalysed homopolymerisation, k_o , defined by the equation

$$-\frac{d[M]}{dt} = k_o [M][C]^{\frac{1}{2}} \quad (28)$$

$$\begin{aligned} \text{is } \frac{\partial \ln k_o}{\partial P} &= (-\Delta V_p^* - \Delta V_i^* + \frac{1}{2}\Delta V_T^*)/RT \\ &= \Delta V_o^*/RT \end{aligned} \quad (29)$$

the situation is more complicated in the case of copolymerisation. In fact, examination of eqn. 17 shows that the equivalent expression to (29) for copolymerisation would involve twelve different activation volumes and would also be dependent on the monomer concentrations. In contrast to the results of Merrett and Norrish⁽¹⁹⁾ and Walling and Pellon⁽²¹⁾ who find that the slope of the $\ln(\text{rate})$ v pressure plot has a decreasing slope with increasing pressure, the systems studied here, except styrene - perchlorethylene, show a positive change of slope at around 2,000atm. The experimental accuracy

for reactions whose rates exceed about 30%/hr. is not very high due to the short reaction time and the appreciable increase in viscosity of the reaction medium. Under such conditions, which are generally at high reaction pressures, a certain amount of adiabatic heating must take place on pressurisation and this will be dissipated only slowly due to the high viscosity of the hydraulic oil at such pressures. With the relatively rapid evolution of heat in the polymerisation itself and the slow rate of heat loss, isothermal conditions may not even be approached under such conditions.

C. The ϕ Factor.

For the system styrene - methyl methacrylate values of ξ_a and ξ_b for various pressures may be estimated from the data available by eqn. 4 using the relation

$$\delta \left[\frac{I}{2} \right]^{-\frac{1}{2}} = \left(\frac{1}{[M]} \frac{d[M]}{dt} \right)^{-1} \quad (30)$$

1) Values at Low Pressure.

There are several values of ξ_a and ξ_b quoted in the literature and nearly all the data published up to 1953 has been assessed by Tobolsky and Mesrobian.⁽²⁹⁾ Using the values 0 and 5.75 for k_t/k_p with styrene and methyl methacrylate respectively at 60°C. the values

$\delta_a = 33.5 \pm 15\%$ and $\delta_b = 6.2 \pm 15\%$ M.l.s. units at 1 atm. are obtained.

ii) The Effect of Pressure on δ Values.

Results of various workers for the ratios $(\delta(\frac{1}{2}I)^{-\frac{1}{2}})_P / (\delta(\frac{1}{2}I)^{-\frac{1}{2}})_1 = (\text{Rate})_1 / (\text{Rate})_P$ are given in the table below for styrene catalysed with benzoyl peroxide. at 60°C.

	$(\text{Rate})_1 / (\text{Rate})_P$			
Mole% Bz_2O_2	0.043	0.429	0.043	0.100
Pressure (atm)	ref.19	ref.19	ref.21	table 1(iv)
940	0.397	0.490		0.564
1880	0.216	0.254		0.314
1930			0.278	0.304
2810	0.130	0.176		0.175
3750	0.092	0.117		
3820			0.100	
4690	0.065	0.083		

From a graph of these points the following values are obtained;

Pressure (atm)	1	1000	1500	2000	2500	3000
$\delta_a(\frac{1}{2}I)^{-\frac{1}{2}}_P$		0.38	0.27	0.20	0.16	0.12
$\delta_a(\frac{1}{2}I)^{-\frac{1}{2}}_1$		-0.46	-0.32	-0.24	-0.20	-0.17

and mean values are used in the calculations which follow.

There are only two sets of results for the effect of pressure on the benzoyl peroxide catalysed polymerisation of methyl methacrylate; those of ref.22 and the results reported here. The data of the Russian workers does not compare at all well with the results found in this work or with the pressure effect found for the thermal polymerisation reaction reported in ref. 18. The values for $(\text{Rate})_{2000}/(\text{Rate})_1$ quoted below give some idea of how contradictory the results are;

Source	ref.22	table 1(iv)	table1(iii)	ref. 18
Temp ($^{\circ}\text{C}.$)	45	45	40	100
$\frac{(\text{Rate})_{2000}}{(\text{Rate})_1}$	19	4.7	4.9	3 ^x

^xEstimated.

$(\zeta_b)_p/(\zeta_b)_1$ values given below are therefore calculated from the results given in table 1 (iii). The extrapolation from 40 to 60 $^{\circ}\text{C}.$ has been carried out using the data of Bevington et al.(28) who give $k_t/k_t = 5.75$ at 60 $^{\circ}\text{C}.$ and 3.1 at 40 $^{\circ}\text{C}.$ A value of 4.7 k.cal/mole given by Tobolsky and Mesrobian(29) for ζ_b is used. Pressure is assumed to have little effect on k_t/k_t as the two termination reactions probably proceed through similar transition states and will therefore have similar activation volumes.

Press. (atm)	1	1000	1500	2000	2500	3000
$\frac{\delta_p (\frac{1}{2}I)^{-\frac{1}{2}}_p}{\delta_p (\frac{1}{2}I)^{-\frac{1}{2}}_1}$	1	0.468	0.295	0.192	0.166	0.065

iii) Initiation Rate.

Tobolsky and Mesrobian show that the rate of decomposition differs in different solvents. For 0.001 molar Bz_2O_2 at $60^\circ C$. they give $I_a = 4.24 \times 10^{-8}$ and $I_b = 2.99 \times 10^{-8}$ moles/l.sec.

iv) Monomer reactivity ratios.

It is seen from fig. 7 that the monomer reactivity ratios are essentially independent of pressure and the values $r_a = 0.52$ and $r_b = 0.46$ are therefore used in the calculation of ϕ .

From these data and the rates of reaction given in table 1 (v) it is possible to calculate ϕ values by eqn. 17 using mean concentrations of reactants if the following assumptions are made;

a) That there is a linear variation of initiation rate with monomer composition from that in pure styrene to that in pure methyl methacrylate.

b) That the values of δ_a and δ_b are unaffected by change in the nature of the environment.

c) That the variation of initiation rate with pressure is independent of environment.

and d) That the pressure effect on ϕ values is independent of environment.

Values of ϕ calculated on these premises are given in table 6 and are shown graphically in fig. 12.

The values of ϕ are sensitive to errors in the assumed values of δ_a and δ_b . For example, an error of $\pm 15\%$ in δ_a and δ_b produces a 50% error in ϕ at 3000atm. ϕ is not very sensitive to errors in r_a or r_b and rate measurements, which are probably accurate to $\pm 5\%$, produce a variation of $\pm 10\%$ in ϕ .

It seems unlikely, however, that the marked increase in ϕ with pressure at high styrene concentrations is entirely attributable to experimental error as this could be the case only for a full range of variation of the true δ values from -15% to $+15\%$ of their assumed values.

The variation of ϕ with monomer concentration at 1 atm. found here is essentially in agreement with that obtained from the results of Mayo and Lewis.⁽³⁰⁾

D) Molecular Weights.

Molecular weights of the copolymers prepared

have not been measured directly and it should be borne in mind that limiting viscosity numbers only give an indication of any variation of molecular weight with experimental conditions.

From figures 13 to 15 it appears that the variation of copolymer molecular weight with pressure of reaction has the same characteristics as found in single monomer systems; the intrinsic viscosity increasing steadily with pressure up to about 3,000atm. above which pressure the increase is far less pronounced.

The system styrene - perchlorethylene shows quite different characteristics as can be seen from fig. 16. The effect of increasing reaction pressure is far less pronounced up to about 3,000atm. where the limiting viscosity number is only increased to about 1.3 of its atmospheric value. Between 3,000 and 6,000atm. the molecular weight increases much more rapidly with reaction pressure and above 6,000 atm. the increase falls off. The curves of fig. 16 give molecular weights calculated from the relation $MW = 0.236 \times 10^6 [\eta]^{1.4}$. This relation may not be completely accurate in the present case as chain termination by transfer may give a different molecular weight distribution from that of the fractionated polystyrenes used in the determination

of this relationship. On the curves of fig. 16 are marked the freezing pressures of perchlorethylene and styrene. The value for perchlorethylene at 60°C. is that found in this work, the value at 50°C. is estimated. Styrene freezing pressures are estimated from the data of Bridgman. (31)

E. Freezing Pressures.

The freezing pressures at 60°C. of perchlorethylene and of a styrene - perchlorethylene mixture inhibited with 0.2 mole % quinol are given in table 4. together with the readings taken in the determinations. The freezing of the pure liquid is an isobaric process as can be seen from fig. 17. Freezing of the mixture occurs over a pressure range but it is not possible from the simple measurements made hereto decide whether the mixture behaves ideally or not and thus to deduce the compositions of the two phases. A certain amount of superpressing is evident with both liquids.

F. Melting Points.

The melting points of some styrene - methyl methacrylate and styrene - diethyl fumarate copolymers have

been determined and are given in table 2 and figs. 19 and 20. A typical expansion curve observed with the dilatometer is shown in fig. 18. The curve AB is the expansion of the solid polymer and covering fluid. From B to D melting occurs and DE is the expansion curve for the liquid polymer and paraffin oil. The melting range of the polymers was found to be between 5 and 9°C. and the temperature at the mid-range point, C, is reported as the copolymer melting "point".

For one of the styrene - diethyl fumarate copolymers a second discontinuity in the expansion curve was noted at a temperature some 20°C. below the melting point. This discontinuity indicates a second order transition or "internal melting".

Certain of the styrene - methyl methacrylate copolymers decomposed with the evolution of gas at temperatures below the melting point. Copolymers with high methyl methacrylate content showed the greatest tendency to decompose.

FIG. 5

PRECIPITATION CURVE FOR STYRENE - METHYL
METHACRYLATE.

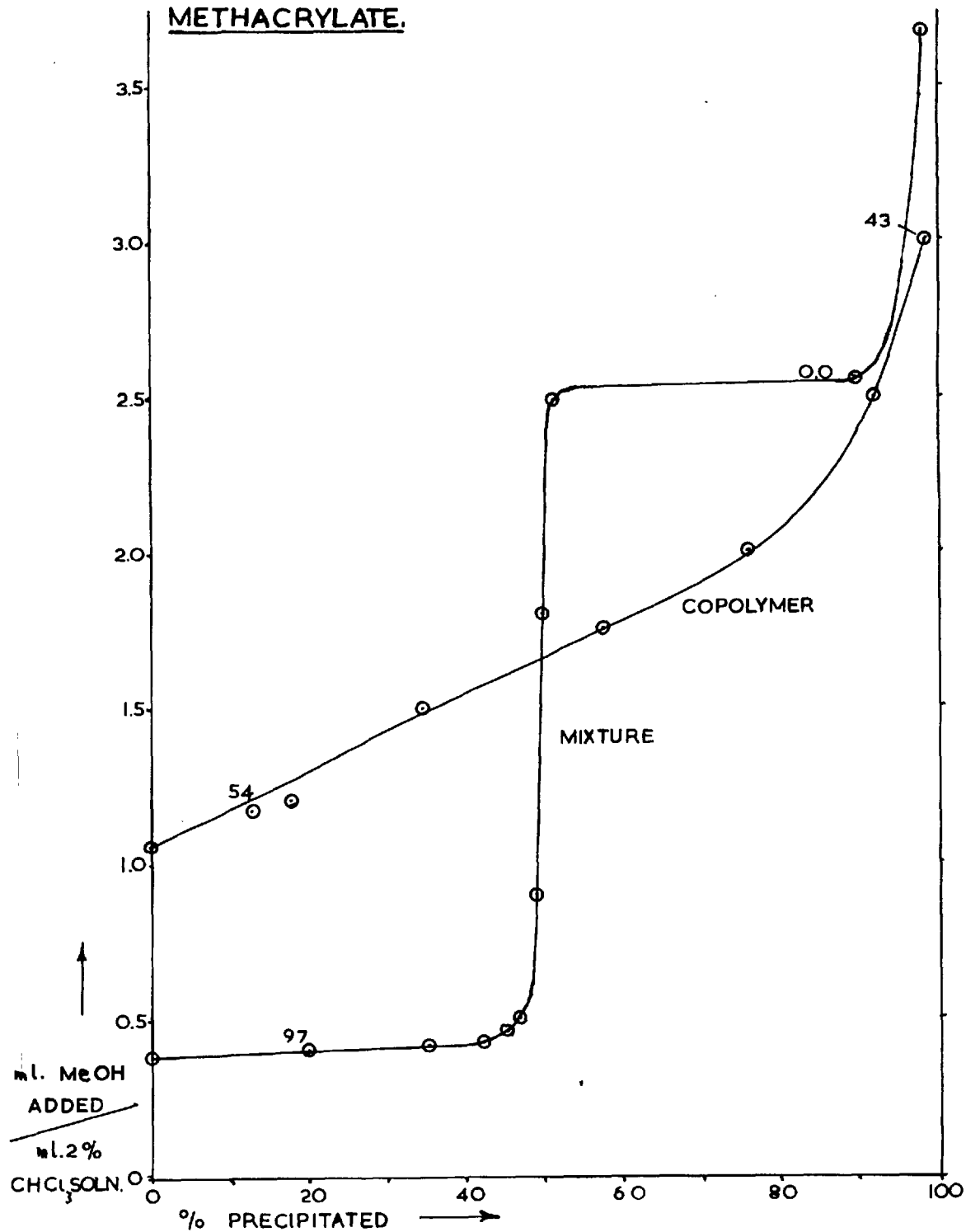


FIG.6. MONOMER REACTIVITY RATIOS;
STYRENE (1) WITH METHYL
METHACRYLATE(2) AT 60°C. AND 3,500 ATM.

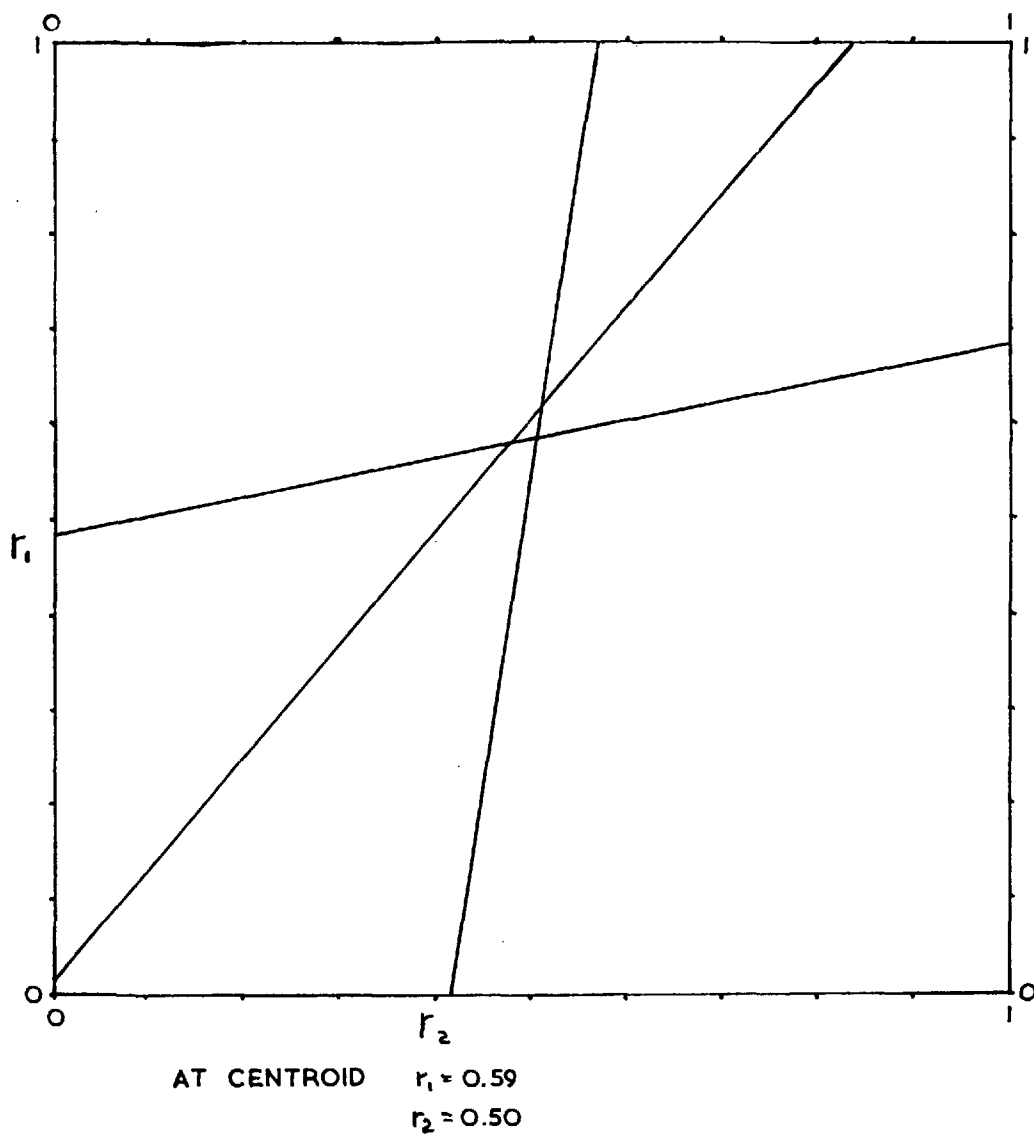


FIG. 7
MONOMER REACTIVITY RATIOS;
STYRENE - METHYL METHACRYLATE.

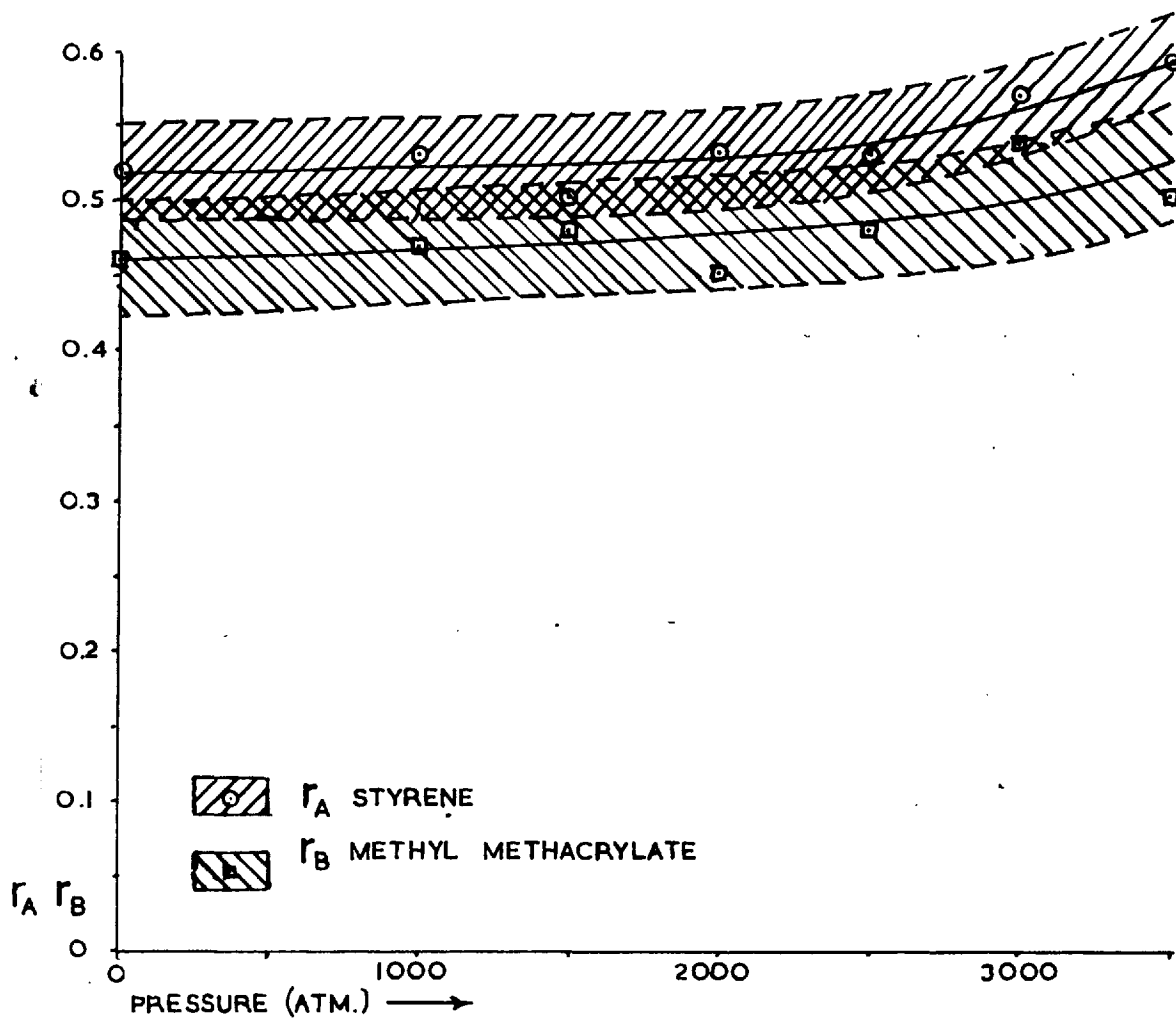


FIG. 8

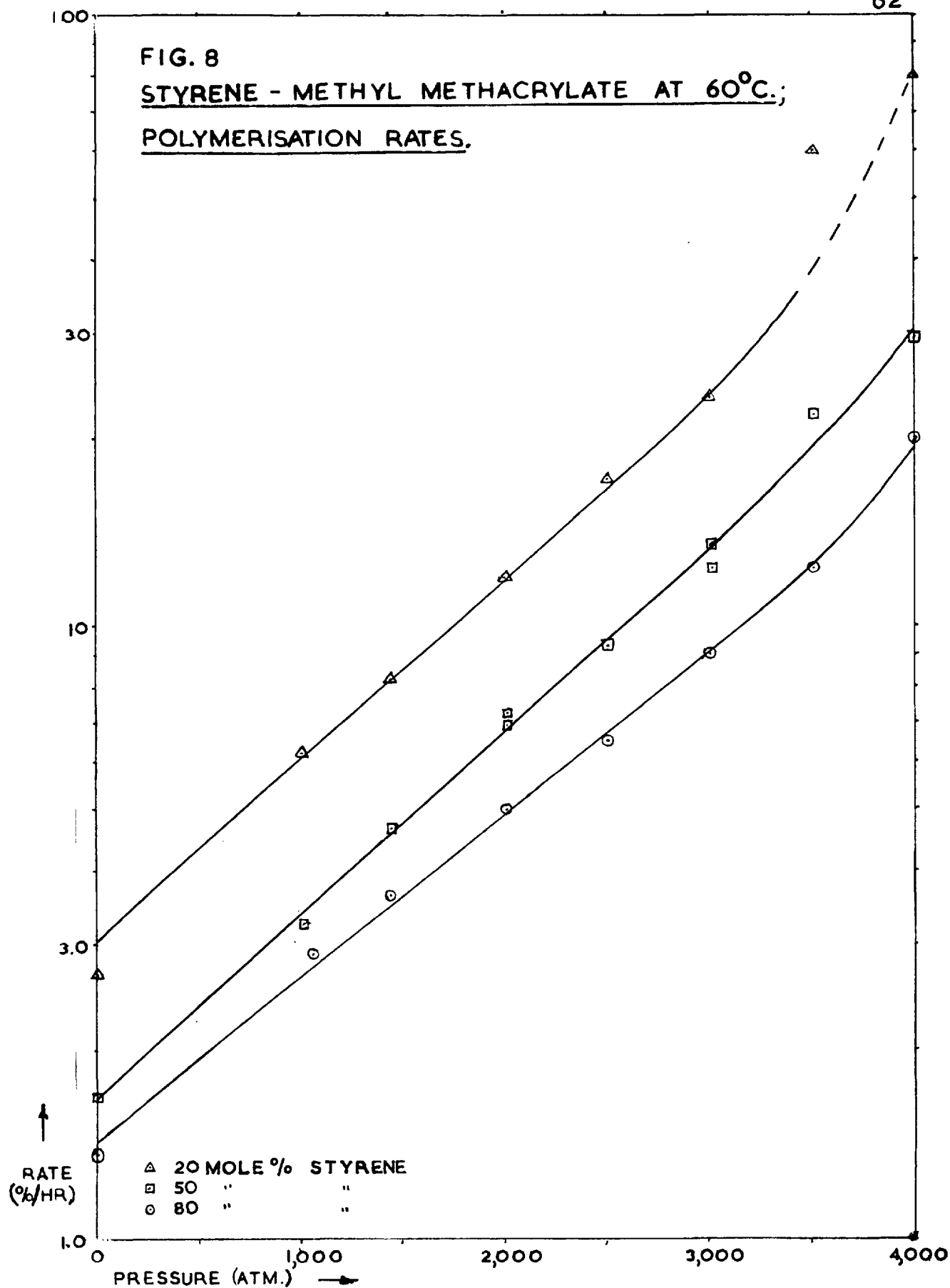
STYRENE - METHYL METHACRYLATE AT 60°C.;POLYMERISATION RATES.

FIG.9

STYRENE - DIETHYL FUMARATE AT 60°C.;
POLYMERISATION RATES.

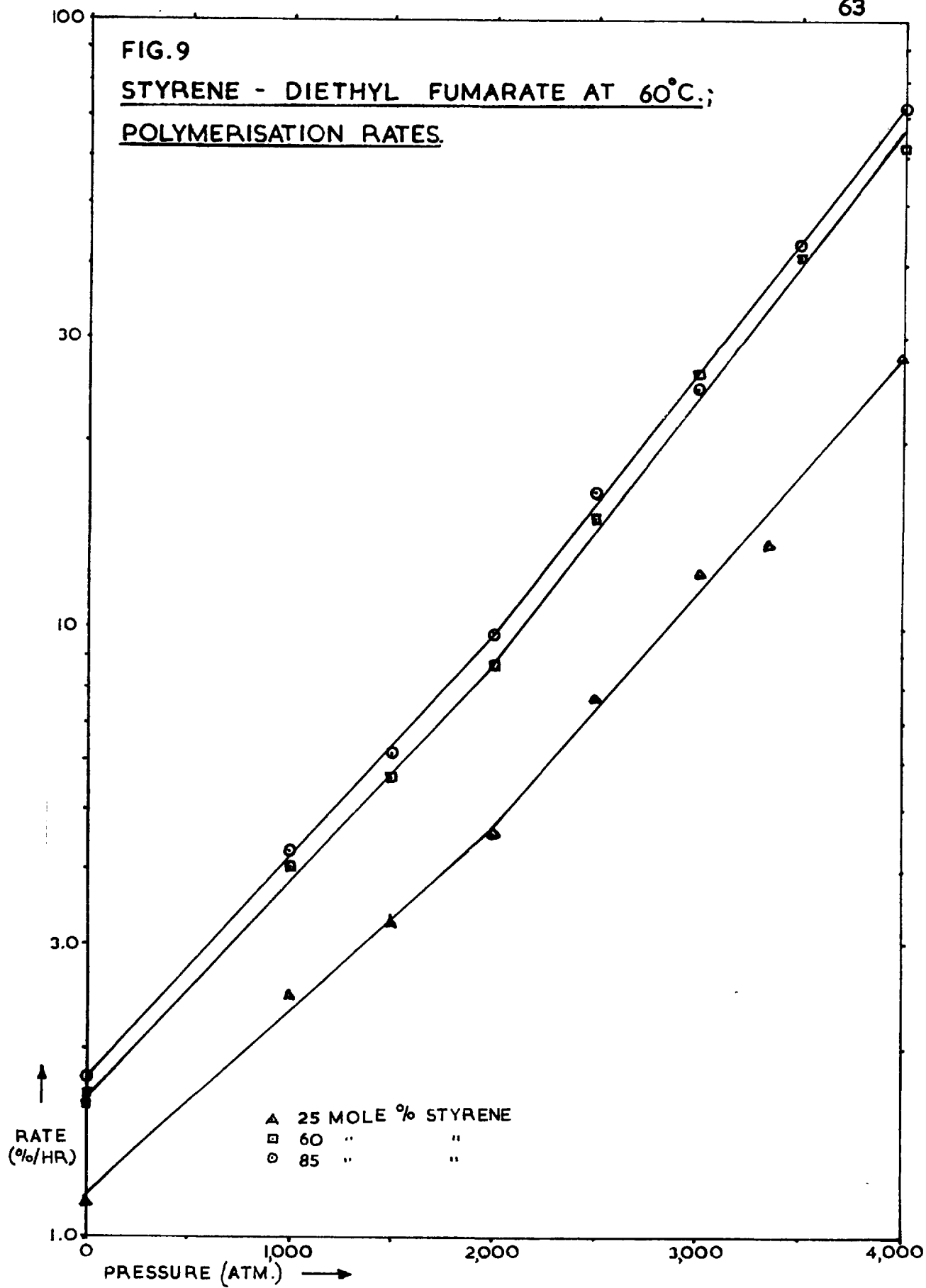
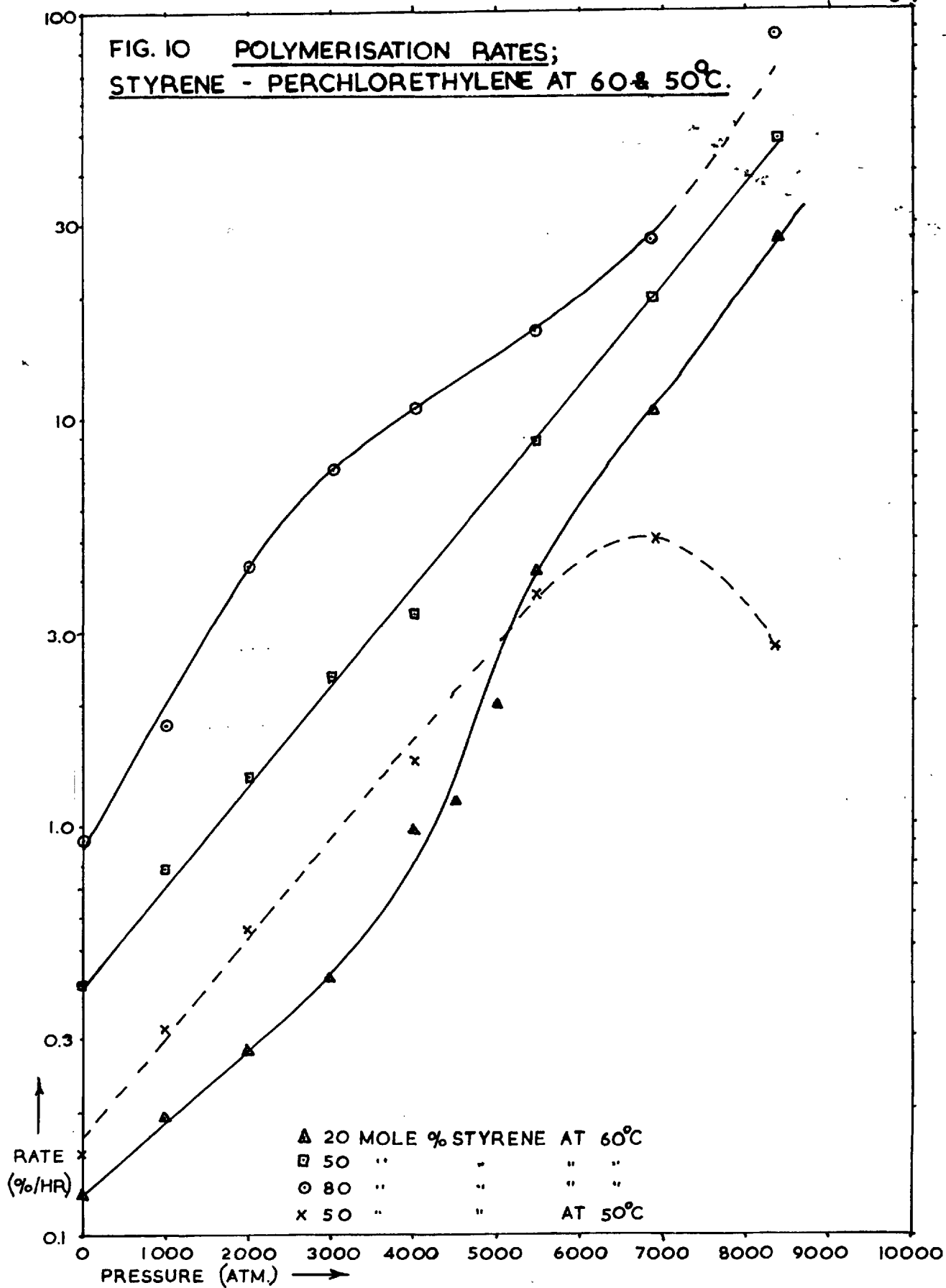


FIG. 10 POLYMERISATION RATES;
STYRENE - PERCHLORETHYLENE AT 60 & 50°C.



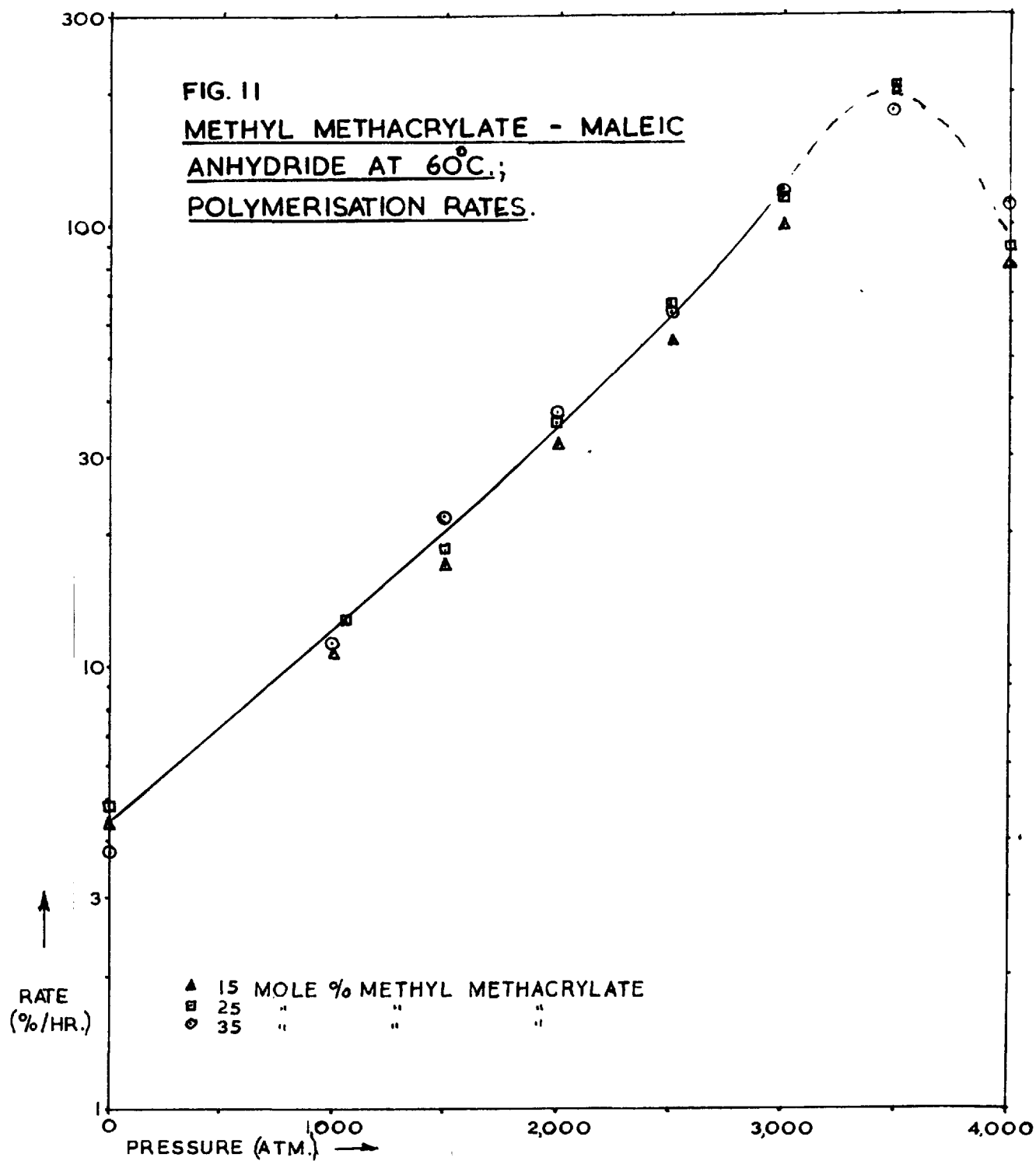


FIG. 12 STYRENE - METHYL METHACRYLATE;
VARIATION OF ϕ WITH PRESSURE
AND MONOMER COMPOSITION AT 60°C.

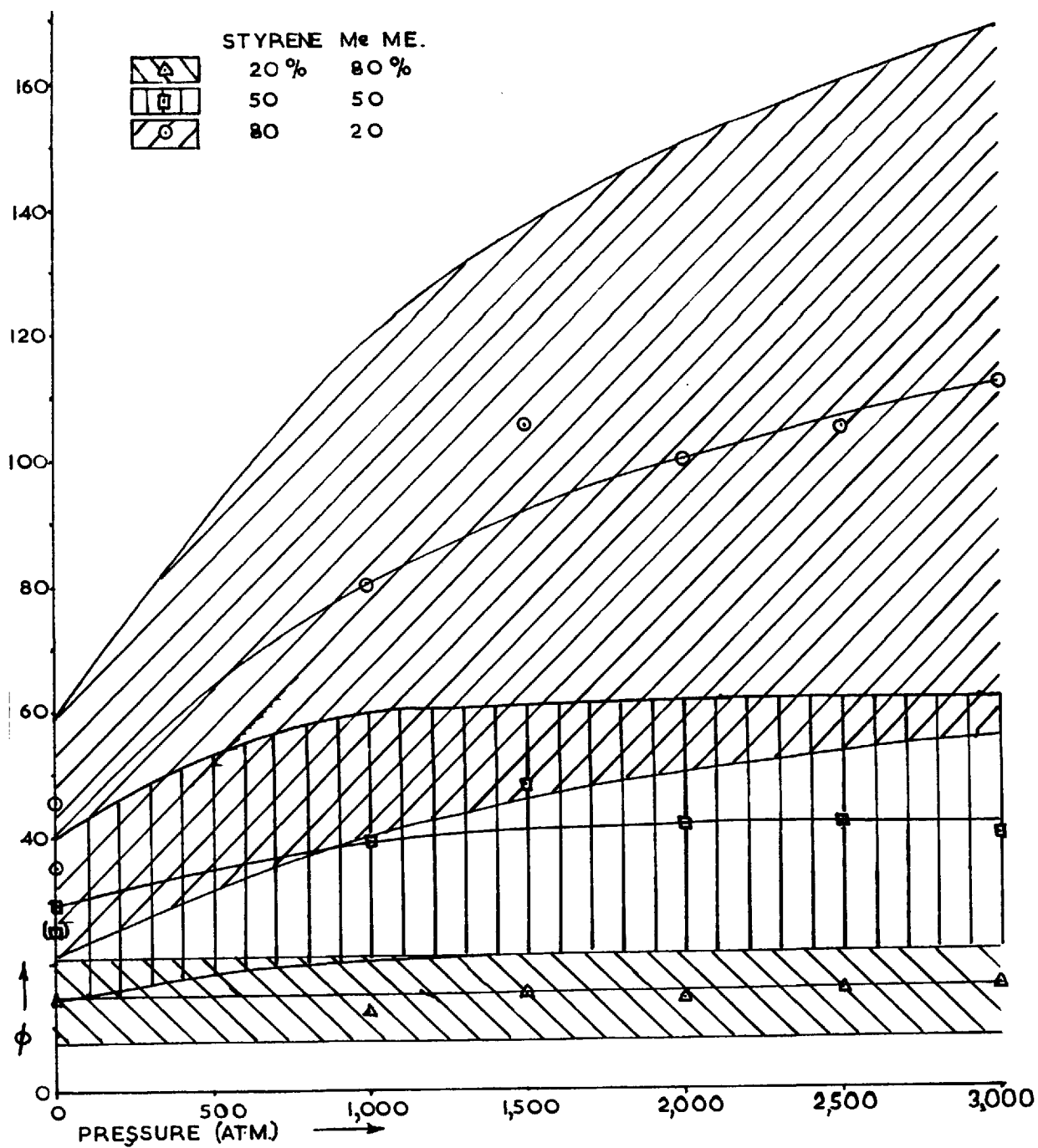


FIG.13

STYRENE - METHYL METHACRYLATE COPOLYMERS;

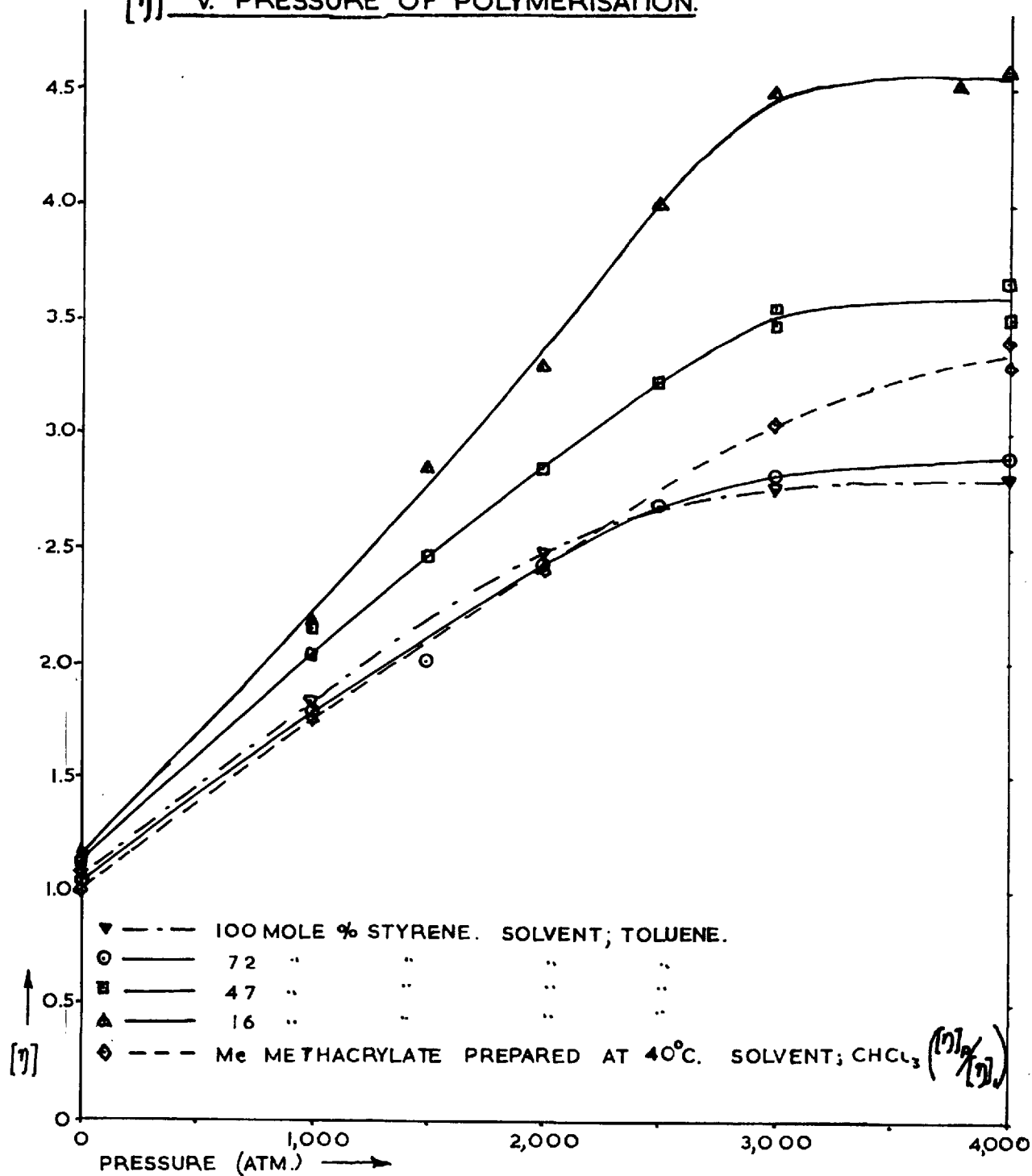
[η] V. PRESSURE OF POLYMERISATION.

FIG.14 STYRENE - DIETHYL FUMARATE
COPOLYMERS; $[\eta]$ v. PRESSURE
OF POLYMERISATION

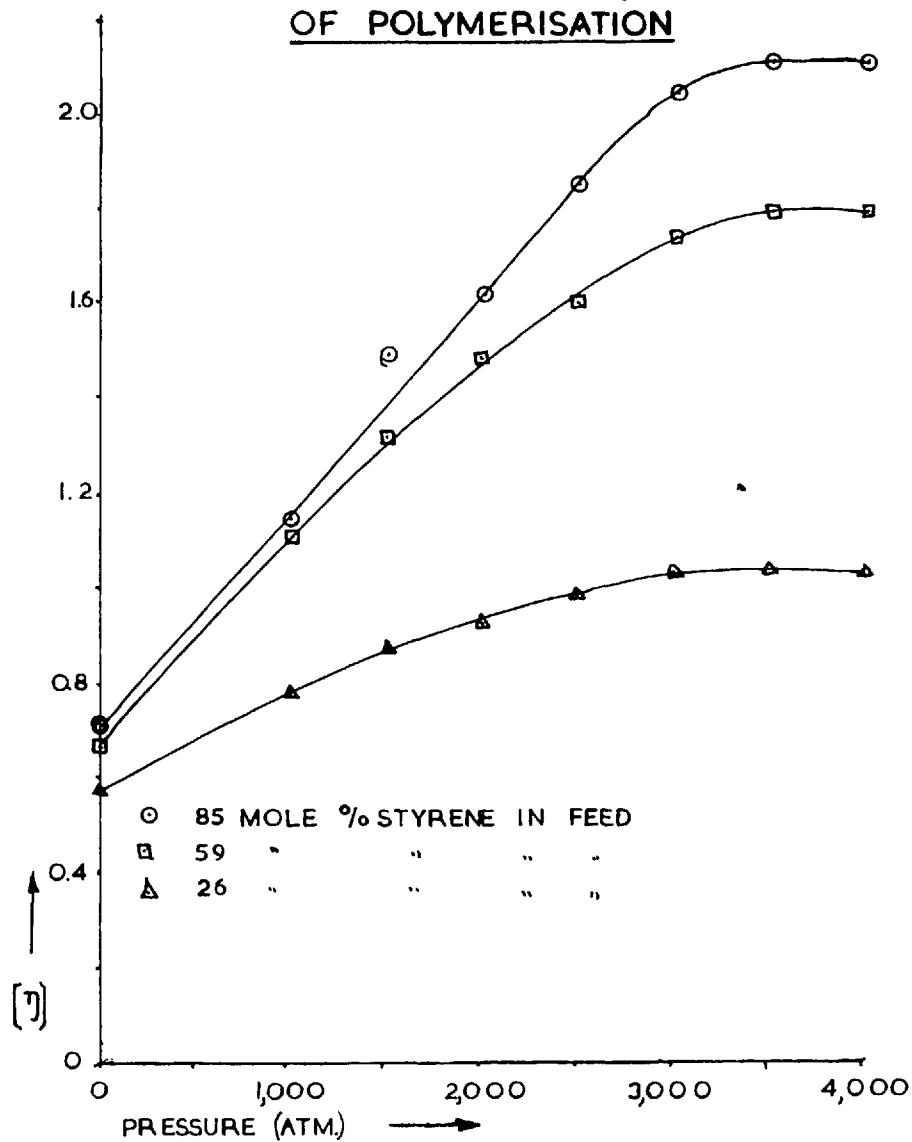


FIG. 15

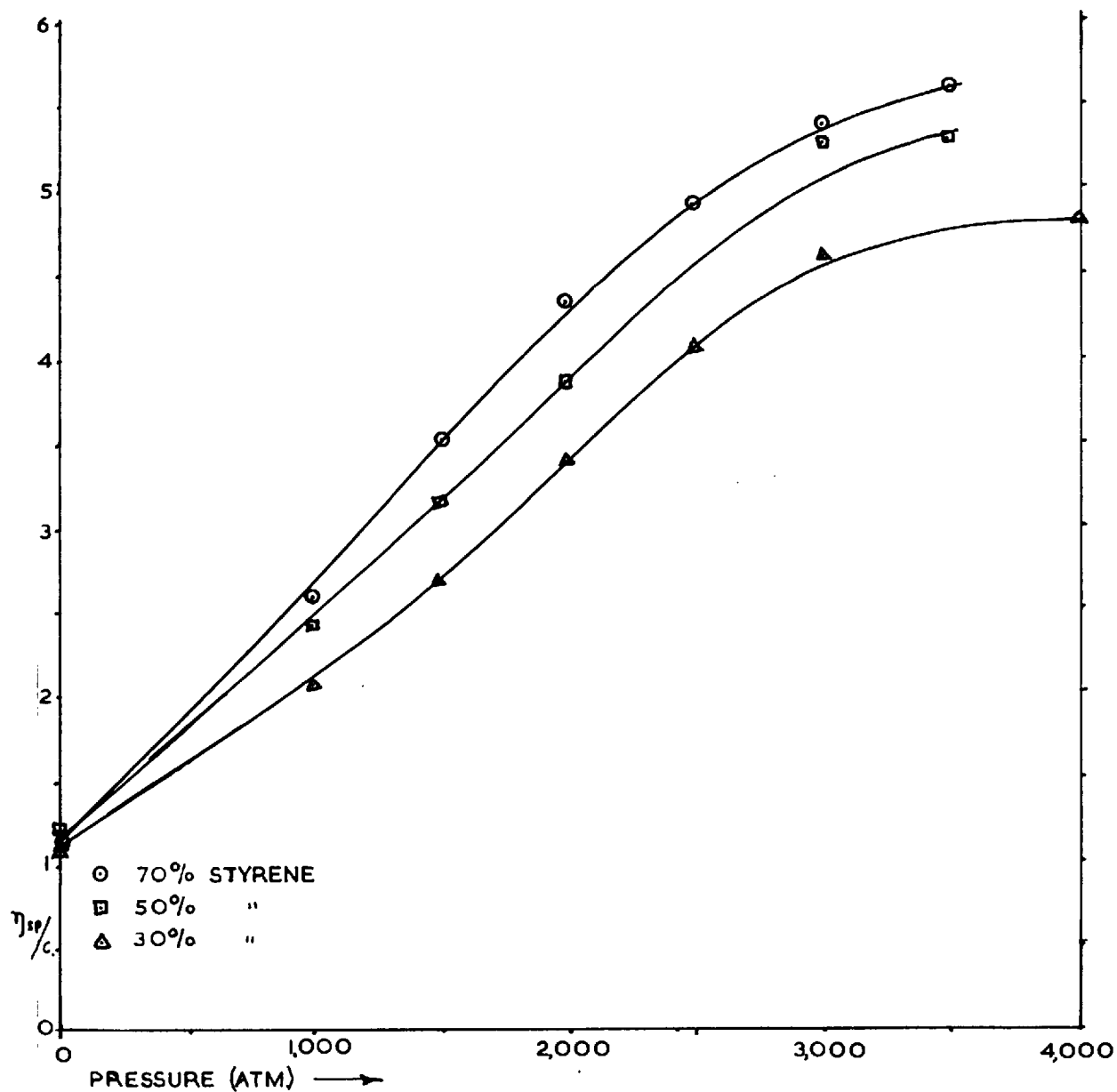
METHYL METHACRYLATE - MALEIC ANHYDRIDECOPOLYMERS; $[\eta]$ V. PRESSURE OFPOLYMERISATION.

FIG. 16

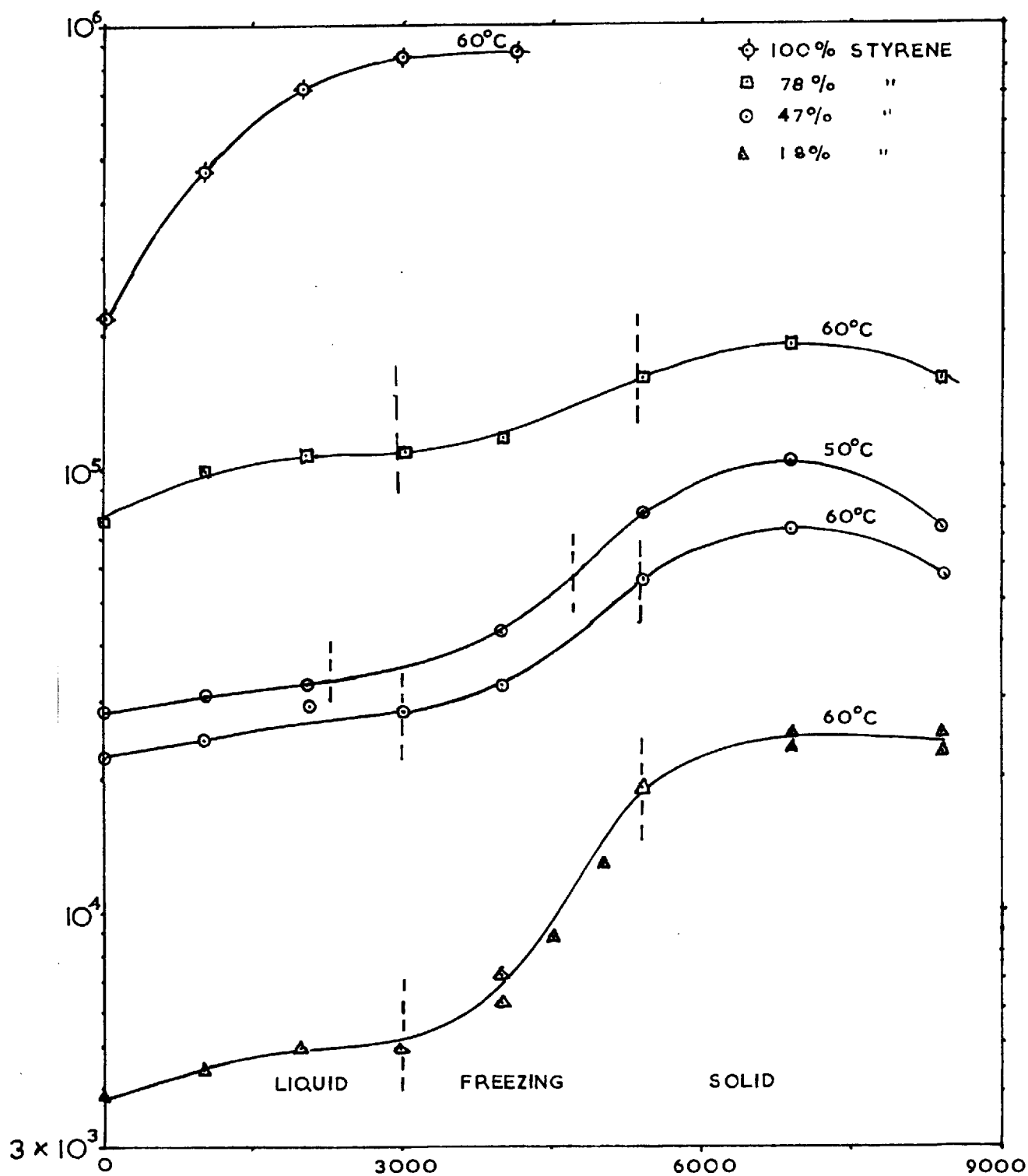
STYRENE - PERCHLORETHYLENE MOLECULAR WEIGHTS.

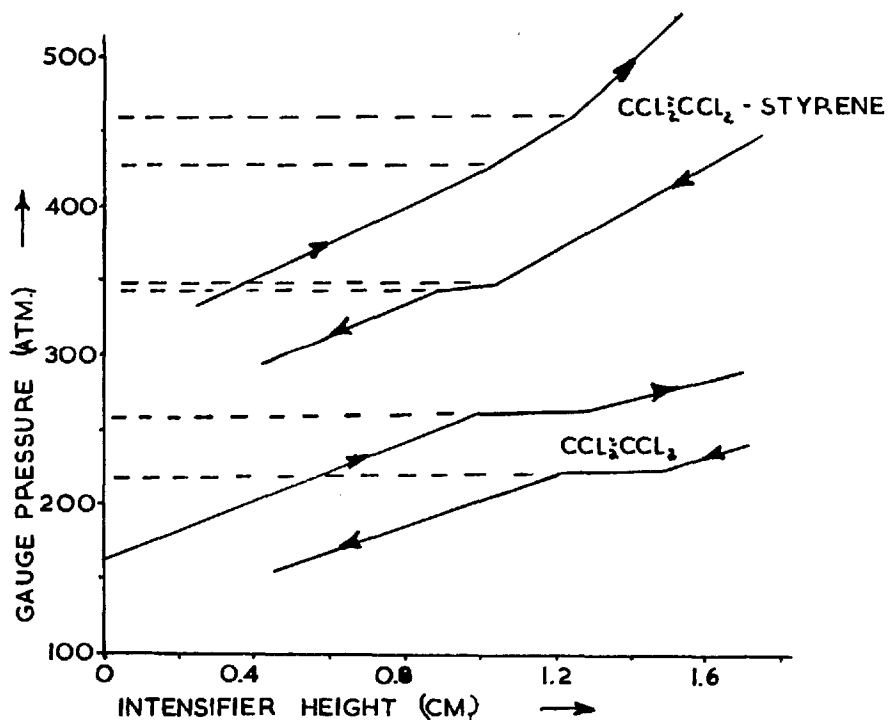
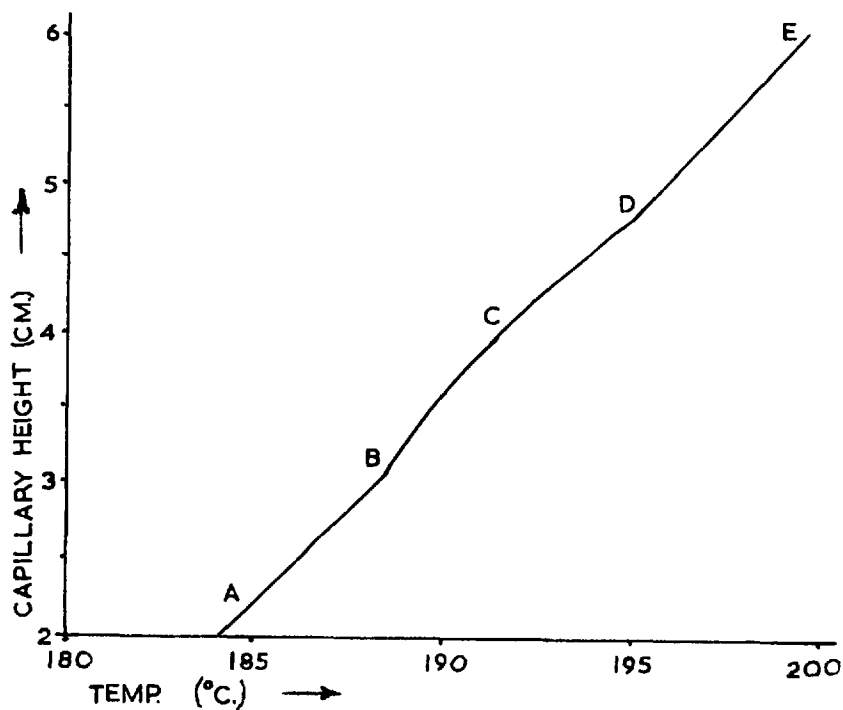
FIG. 17 FREEZING PRESSURE DETERMINATION.FIG. 18 MELTING POINT DETERMINATION.

FIG. 19 STYRENE - METHYL METHACRYLATE
COPOLYMER MELTING POINTS.

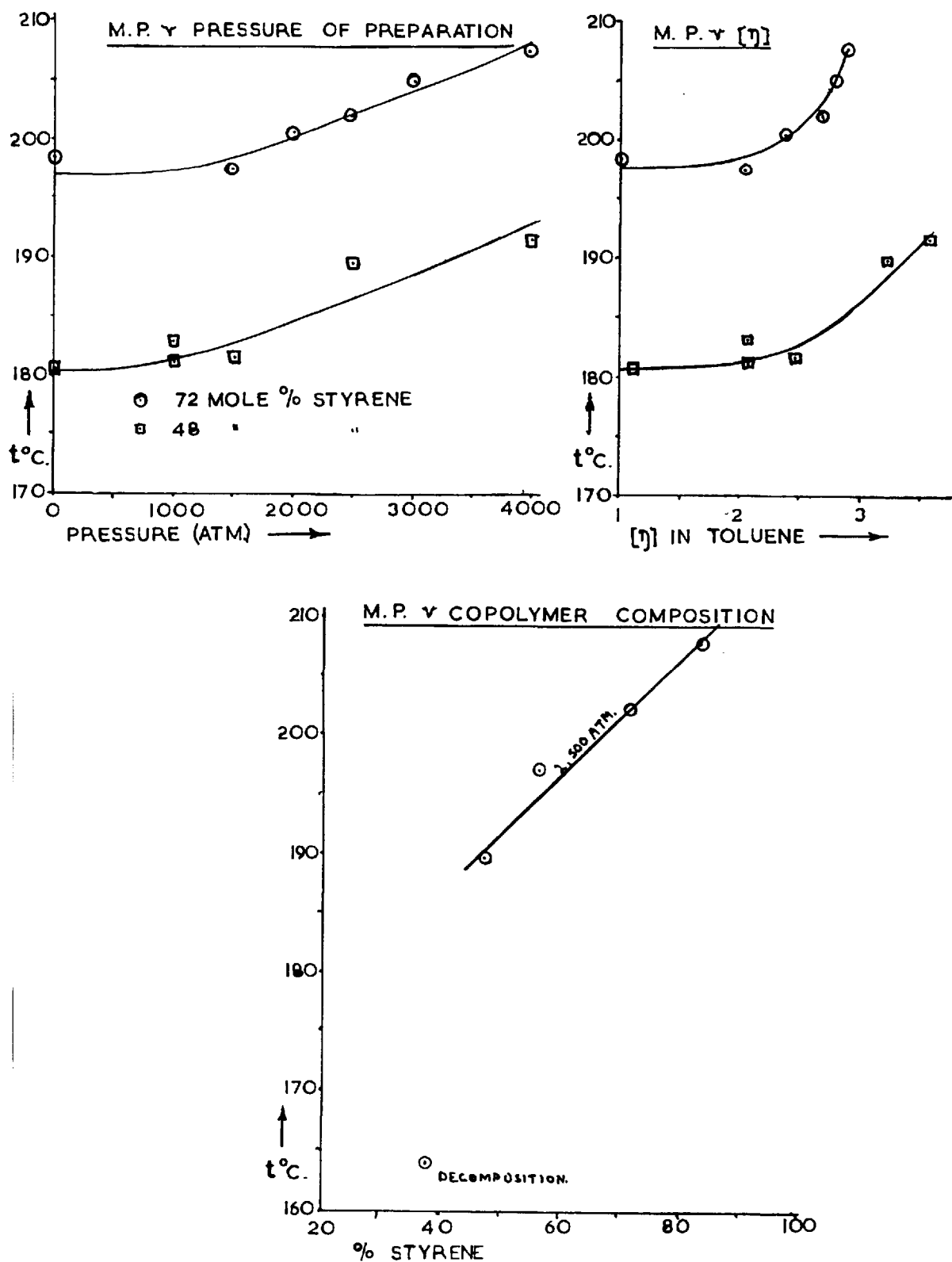
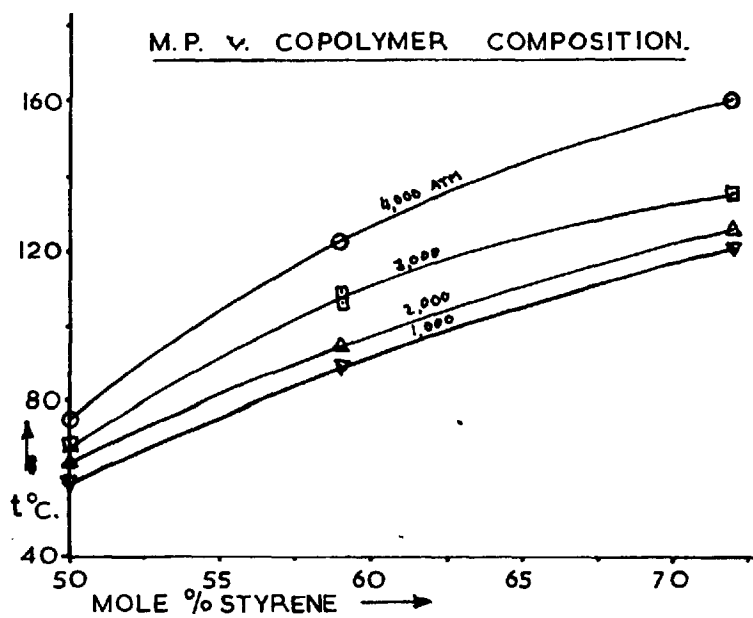
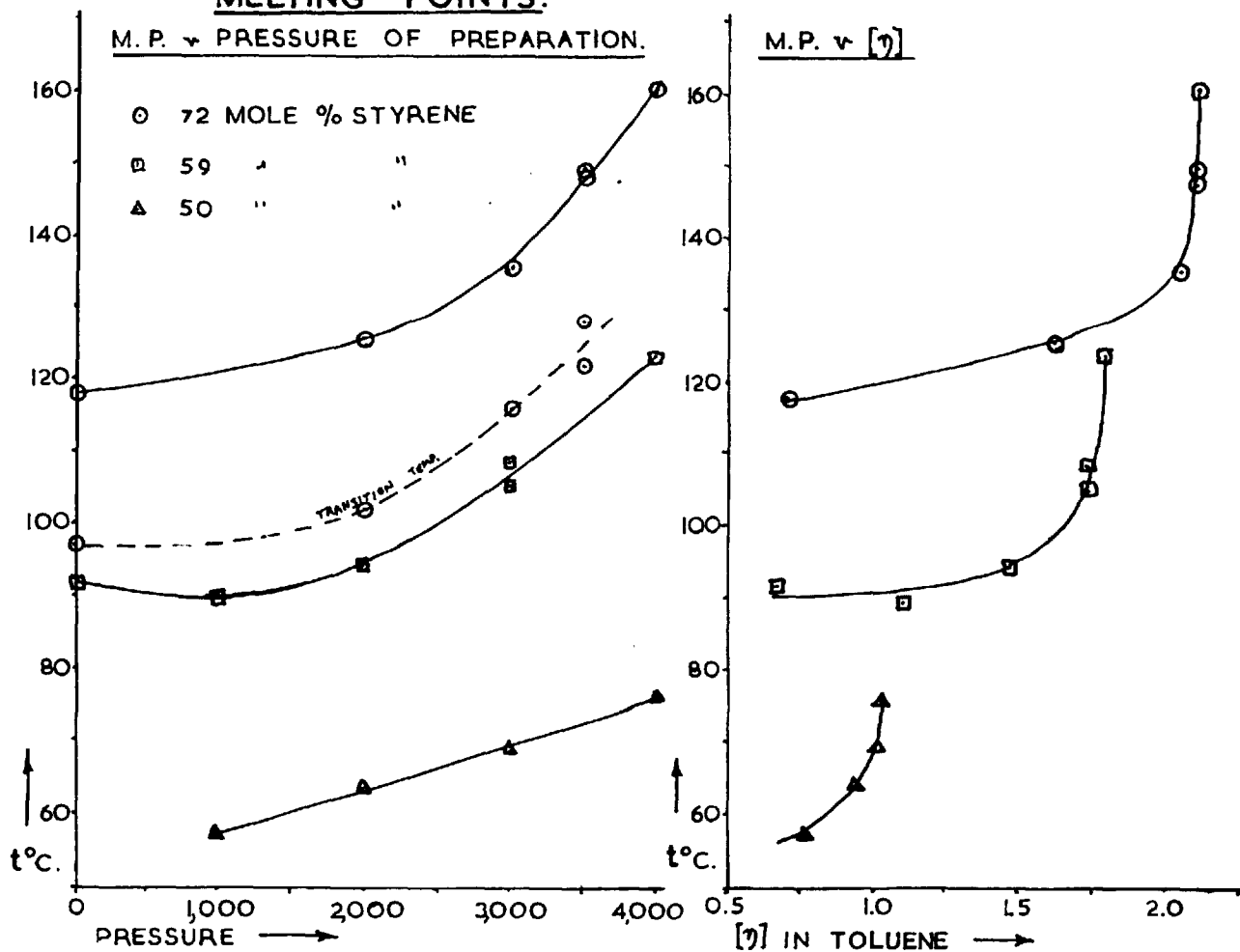


FIG.20 STYRENE - DIETHYL FUMARATE COPOLYMER
MELTING POINTS.



PART 4.Discussion.

The purpose of the work described in this thesis was to study the effect of pressure upon the reactions involved in copolymerisation and the nature of the copolymers produced. It is seen from the experimental results that in general the systems studied behave in a manner similar to single monomer systems. The overall rates of reaction increase roughly exponentially with pressure and molecular weights are increased by increase in reaction pressure up to about 3,000atm. above which pressure the increase in molecular weight is far less pronounced. These findings are similar to those arising from homopolymerisation studies. High pressures do not appear to overcome high degrees of steric hindrance or the effects of resonance stabilisation so that maleic anhydride, diethyl fumarate and perchlorethylene do not enter copolymer molecules to an extent exceeding 50% of the polymer chain units. Further conclusions arising from the study are that monomer ratios are constant within the experimental error over the pressure range employed and that increase of pressure favours the crossed termination of radicals in the styrene - methyl methacrylate system.

A) Monomer Reactivity Ratios.

As has been mentioned earlier, pressure appears to have little or no effect on monomer reactivity ratios, any changes which have been observed lying within the limits of experimental error. It is unlikely that changes in the values of r_a and r_b are masked by viscosity effects at the higher pressures because it seems that the mobilities of the monomer molecules A and B, are still not a controlling factor in the propagation step even at the highest pressures as, otherwise, this would show itself as an irregularity in the $\log(\text{rate})$ v. pressure plots.

This leads us to the conclusion that the rates of $A\cdot + A$ and $A\cdot + B$ and of $B\cdot + B$ and $B\cdot + A$ reactions are affected to similar extents by increase in pressure, that is, that $\Delta V_{paa}^\ddagger \approx \Delta V_{pab}^\ddagger$ and $\Delta V_{pbb}^\ddagger \approx \Delta V_{pba}^\ddagger$. Absolute values of k_{paa} and k_{pbb} at high pressures from which the cross propagation reaction rate constants may be deduced, may be most conveniently determined by homopolymerisation studies from which $\Delta V_{paa}^\ddagger$ and $\Delta V_{pbb}^\ddagger$ may also be deduced. Unfortunately, the only data on the pressure effect on k_p values is that of Nicholson and Norrish⁽²⁰⁾ who have calculated the absolute velocity constants for the photo-initiated polymerisation of styrene at 30°C. under pressure. From these results

$\Delta V_{paa}^\ddagger \approx -14 \text{ cc./mole}$ for styrene at 30°C . $\Delta V^\ddagger$ is not quite temperature independent, decreasing slightly with increasing temperature. It is, however, reasonable to infer from this that $\Delta V_{pab}^\ddagger$ is of the order of -14 cc./mole , where A is a polystyryl radicle and B is either a methyl methacrylate or a diethyl fumarate molecule.

B) Polymerisation Rates.

The increase in polymerisation rates with increasing pressure is as would be expected where initiation takes place by a unimolecular decomposition, slightly retarded by pressure, followed by propagation reactions with large entropy factors, considerably accelerated by pressure, and termination reactions which, although having large entropy factors, are slightly retarded by pressure. Increase in reaction rates due to concentration changes brought about by pressure are also possible but these will be very slight due to the low compressibilities of the reagents.

The effects of pressure on the component reactions of polymerisation and on concentrations are given individual consideration below.

a) Initiation rates.

Variation of initiation rate with composition is

one of the factors which will affect the overall polymerisation rate. Studies of the rate of decomposition of benzoyl peroxide by Bartlett and Nozaki⁽³⁵⁾ in various solvents shows that the rate is sensitive to the nature of the solvent. In many cases, as well as a spontaneous first order decomposition, a higher order induced chain decomposition occurs but this chain decomposition is effectively stopped by the presence of free radicle acceptors such as polymerisable monomers or iodine, as has been shown by Swain, Stockmayer and Clarke.⁽³⁶⁾

The effect of pressure on the spontaneous first order reaction has received some attention from various workers and $\Delta V^\ddagger$ for this reaction generally does not vary much from one solvent to another as may be seen from the figures below;

Solvent	Temp.	$\Delta V^\ddagger$	Ref.
	°C.	cc./mole.	
Acetophenone	60	4.8	21
Allyl Acetate	60	4.7	21
Toluene	50	4.8	37
CCl ₄	60	10.5	38

The behaviour in carbon tetrachloride seems to be somewhat anomalous if the results from which the $\Delta V^\ddagger$

values are calculated are correct.

b) Propagation rates.

In propagation reactions it is necessary for a monomer molecule, favourably orientated, to approach the free radicle end of a growing chain. The probability factor for entry into the transition state is therefore rather low and is associated with a negative entropy of activation. Negative entropies of activation are in turn associated with rigid, compressed transition states and thus with negative volumes of activation. It will be seen in the next section that termination rates are not very greatly affected by pressure and so much of the pressure effect on the overall rates of copolymerisation must be attributed to acceleration of the propagation reaction. In the section on monomer reactivity ratios it was pointed out that $\Delta V^\ddagger$ for propagation reactions is of the order of 10-20cc./mole.

c) Termination Rates.

There are several factors which affect the magnitude of the termination reaction rate constants. The variation of these rate constants has an effect

upon the overall reaction rate which is dependent, among other things, upon the proportions of co-monomers present in the reaction medium.

Diffusion control.

The reaction rate constant, k_t , for termination may be expressed as

$$k_t = \frac{k_c k_d}{k_c + k_d} \quad (31) \text{ where } k_c \text{ is the chemically}$$

controlled reaction rate and k_d is the diffusion controlled rate constant. $k_d \propto D$, the diffusivity of the polymer radicles in the reaction medium and if the Stokes - Einstein relation is obeyed $D \propto \eta^{-1}$ where η is the viscosity of the medium.

$$\text{Hence, } k_t = \frac{k_c k'_d}{k_c/\eta + k'_d} \quad (32)$$

Under conditions where $k_d \gg k_c$, $k_t = k_c$ and where $k_d \ll k_c$, $k_t = k_d = k'_d \eta^{-1}$.

In the latter regime, then, $k_t \propto \eta^{-1}$ and Vaughan⁽³²⁾ has attempted to show, on the basis of the Rabinowitch equation that the termination reaction in the polymerisation of styrene may be diffusion controlled although certain simplifying assumptions had to be made in the course of the calculations.

Benson and North⁽¹²⁾ have carried out polymerisations of methyl methacrylate and of butyl acrylate in viscous

solvents and found that $k_t \propto \eta^{-1}$ for methyl methacrylate and that the other system also tended towards a viscosity limitation of k_t at high solvent viscosities. It is further suggested by Bengough and Melville⁽³³⁾ that in the polymerisation of vinyl acetate the propagation reaction may also be diffusion controlled at high degrees of conversion where the presence of large amounts of polymer considerably increases the bulk viscosity of the medium.

In polymerisation reactions at high pressures the bulk viscosity is increased by the effect of pressure itself as well as by the presence of polymer. Nicholson and Norrish,⁽²⁰⁾ have attempted to estimate the effect of pressure on the viscosity of styrene and correlate this with the values they found for the termination rate constants (derived on the assumption that transfer reactions were negligible under their experimental conditions). They assumed that the viscosity of styrene would be affected by pressure in the same manner as that of toluene and they found that $k_t \propto (\eta_{\text{tol}})^{-\frac{1}{2}}$ approximately.

The ϕ factor.

The variation of polymerisation rate with monomer composition is dependent to a large extent on the ϕ

factor where its value is much greater than unity. Difficulties arise in the calculation of ϕ through insufficient knowledge of the initiation rates and the absolute values of the homopolymerisation rate constants. Melville and Valentine suggest that the rate of initiation with benzoyl peroxide in the styrene - methyl methacrylate system does not vary linearly with monomer composition, but in deducing this from molecular weights they have assumed that termination takes place solely by disproportionation. Since this work was published it has been established that poly-styryl radicals combine rather than disproportionate and that a significant amount of combination also occurs with methyl methacrylate radicals. It is also likely that the cross-termination reaction occurs to a large extent by combination. The reactions carried out by these workers were photo-initiated and the slightly differing u.v. absorption coefficients of the two monomers also contribute to the apparently non-linear variation. Taking these factors into consideration, the initiation rate shows a very nearly linear variation with monomer composition.

For equimolar quantities of each monomer and assuming combination, $\phi = 30$ from their results which

agrees well with $\phi = 29$ found in this work and $\phi = 25$ from the results of Mayo and Lewis.⁽³⁰⁾

A further obstacle lies in the way of estimating ϕ at high pressures and this is the insufficiency of data concerning the pressure effect on the homopolymerisation rate constants. Consequently, it has only been possible to calculate ϕ for one system. The estimates of ϕ for the highest pressures in the styrene - methyl methacrylate system may be in error by as much as $\pm 60\%$ through error in the δ values used and experimental errors.

The variation of ϕ with monomer composition found here and by Melville and Valentine⁽³⁹⁾ is not a unique property of this system and has also been found with styrene - butyl acrylate (by Bradbury and Melville,⁽⁴²⁾ and Arlman and Melville⁽⁴⁰⁾), with styrene - diethyl fumarate (by Walling and McElhill⁽⁴¹⁾) and with several other monomer pairs.

Three conclusions emerge from this study of ϕ ;

- i) ϕ is greater than unity,
 - ii) ϕ varies with monomer composition,
 - iii) ϕ is probably increased by pressure,
- and these are considered in more detail below.

i) The magnitude of ϕ .

That ϕ is greater than unity, i.e. k_{tab} is greater than the geometric mean of k_{taa} and k_{tbb} , indicates that crossed termination is a preferred reaction, in the same way as crossed propagation reactions are preferred in all the systems so far studied ($r_a, r_b > 1$). The Alfrey - Price^(47,48,49) treatment of radicle reactivities expresses the propagation constants in the form

$$\begin{aligned} k_{paa} &= P_a Q_a \exp(-e_a^2) \\ k_{pab} &= P_a Q_b \exp(-e_a e_b) \\ \text{etc.} \end{aligned}$$

where P_a is related to the reactivity of radicle A.
and Q_a is related to the reactivity of molecule A
 e_a and e_b are functions of the charges on the respective groups and are assumed to be the same on the radicle as on the monomer. On this basis

$$r_a = (Q_a/Q_b) \exp(-e_a^2 + e_a e_b) \quad (33)$$

$$\text{and } r_b = (Q_b/Q_a) \exp(-e_b^2 + e_a e_b) \quad (34)$$

Treating the termination constants in the same way

$$\begin{aligned} k_{taa} &= P_a^2 \exp(-e_a^2) \quad \text{etc.} \\ \text{so } \phi^2 &= \exp(e_a - e_b)^2 = (r_a r_b)^{-1} \end{aligned} \quad (35)$$

This scheme shows several theoretical weaknesses, but there does seem to be a general tendency for ϕ to vary with $(r_a r_b)^{-\frac{1}{2}}$ from system to system. The

equating of charges on monomer molecules and radicle groups seems rather unjustified as does the assumption that the head to tail propagation reactions are sterically comparable with the head to head termination reaction. Unfortunately there have been no studies carried out on systems where there is no alternating tendency and r_a or $r_b > 1$ so further comparison of ϕ with $(r_a r_b)^{-\frac{1}{2}}$ is not possible.

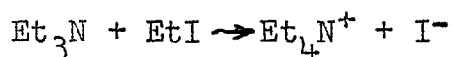
Styryl radicles have a slight negative polarity at the radicle end due to the influence of the phenyl group and methyl methacrylate radicles show an opposite polarity. As these dissimilar radicles approach each other in the termination reaction an induced charge will also be produced which further favours the crossed reaction. The small permanent charges would in like manner discourage the combination of like radicles.

ii) The variation of ϕ with monomer composition.

It is fairly safe to assume that an alternating tendency in copolymerisation is due either to polar effects (permanent and induced charges) between the reacting species, or to steric effects or to both. Although it has been found that r values are peculiarly insensitive to environmental changes, it might be

expected that a change in the electrical properties of the medium should affect reactions where polar effects play a part.

Menschutkin⁽⁵⁰⁾ showed that the reaction



proceeds more rapidly in polar solvents and places solvents in the order $\text{MeOH} > \text{EtOH} > \text{Me}_2\text{CO} > \text{C}_6\text{H}_6 > \text{C}_6\text{H}_{14}$ which is the order of decreasing dielectric constant. Laidler and Hinshelwood⁽⁵¹⁾ have shown that this is not due to an interaction between the solvent and the amine, but rather an effect on the activated complex.

In general it seems that where the transition state is more ionic than the reactants solvation favours the existence of the transition state and thus accelerates the reaction, lowering the activation energy by an amount equal to the solvation energy. Conversely, where the transition state is less ionic than the reactants one would expect solvation to retard a reaction.

Pepper⁽⁵²⁾ in studies of the cationic polymerisation of α -methyl styrene has found that both the rate of reaction and the degree of polymerisation increase with the dielectric constant of the reaction medium. From this it is inferred that as the propagation reaction

between an ion and a molecule should be reduced by increase in the dielectric constant, ϵ , the termination reaction, which involves the neutralisation of two ions, must be even more markedly reduced.

The variation of ϕ with monomer composition is consistent with the idea that crossed termination proceeds via an activated complex which is less polar than the reactants. Solvation occurs in methyl methacrylate (estimated $4.5 < \epsilon < 20$) to a greater extent than in styrene ($\epsilon_{20} = 2.4$),⁽⁴⁾ and therefore the rate of disappearance of the polar radicles by cross termination is reduced by the polar effects of the methyl methacrylate monomer which is present.

The insensitivity of monomer reactivity ratios to variation in the dielectric constant of the reaction medium may, it has been suggested, be because the energy and entropy changes on solvation mutually compensate.

Barb⁽⁵³⁾ has offered an alternative explanation for the variation of ϕ with monomer composition. It is pointed out that for a monomer mixture rich in A the probability that the penultimate unit of a polymer radicle should be an A unit is high, whereas for low concentrations of A in the feed the penultimate unit is probably of type B. If the penultimate units

do affect reaction rates, this should be more apparent in head to head terminations where the side groups of the penultimate units approach more closely than in the head to tail crossed propagation reaction, which explains the insensitivity of monomer reactivity ratios to change in reactant composition.

iii) The variation of ϕ with pressure.

The way ϕ is affected by pressure depends on the way pressure affects the individual termination reactions. It is usually supposed that the bimolecular termination reaction becomes diffusion controlled at high pressures. This idea is supported by the fact that polymer molecular weights increase, with pressure of reaction only over a certain pressure range. These considerations are outlined in C below.

The effect of pressure on the viscosity of liquids is to produce a roughly exponential increase.

$\eta_{4000\text{atm.}}/\eta_{1\text{atm.}}$ has values of about 8 for benzene and toluene and 300 for eugenol, so there is evidently a wide range of pressure effect. The presence of 8% polystyrene of molecular weight 10^6 should increase the bulk viscosity of the monomer about 100-fold. A similar, or even greater increase is likely with methyl methacrylate. Kammeyer⁽⁵⁴⁾ has found that

pressure has a negligible effect on the relative viscosities of polystyrene fractions at concentrations up to 2.5 g./l. in benzene for pressures up to 1,000atm. If this holds true for higher pressures and concentrations it seems that degree of conversion has a far greater effect on viscosity than does pressure, as the pressure effect is more likely to resemble that for toluene than for eugenol. This being the case, diffusion control of the termination reaction is almost as likely at atmospheric pressure, and if it occurs it should be obvious as a lack of linearity in the time v. conversion curve, as has been noted in the bulk polymerisation of methyl methacrylate at conversions above about 20%. This situation has not been apparent in any of the reactions described in this thesis where the time of reaction has been varied under identical reaction conditions.

As $k_t \propto \eta^{-1}$ approximately for diffusion control, one would expect a roughly exponential decrease in k_t with pressure, when diffusion conditions obtain. The mobilities of A• and B• radicals should be essentially the same for a given feed composition as they have the same size distribution and overall composition, and differ only in the nature of their

end groups. So viscosity should have the same effect on both A• and B• mobilities. As T_{ab} is apparently greater than $(T_{aa} T_{bb})^{\frac{1}{2}}$ and the values of T_{aa} and T_{bb} do not differ greatly, diffusion control of the cross termination reaction should occur at lower values of η than control of the A• + A• and B• + B• reactions. This would produce pressure effects in the opposite sense to those observed experimentally, i.e. ϕ would decrease with pressure. Further, where complete viscosity control of all the termination reactions obtains, the rates of the three reactions would be the same and ϕ would be unity.

That ϕ is considerably greater than unity and that ϕ increases with pressure, which increases viscosity, indicates that the termination reactions are not fully diffusion controlled and that A• + A• and B• + B• reactions are retarded more than the cross termination. There must therefore be some other explanation for the behaviour of ϕ with pressure.

From the transition state theory

$$\frac{\partial \ln \phi}{\partial P} = \left[\frac{1}{2}(\Delta V_{Taa}^\ddagger + \Delta V_{Tbb}^\ddagger) - \Delta V_{Tab}^\ddagger \right] / RT. \quad (36)$$

In the styrene (A) - methyl methacrylate (B) system $\ln \phi$ does not vary linearly with pressure which

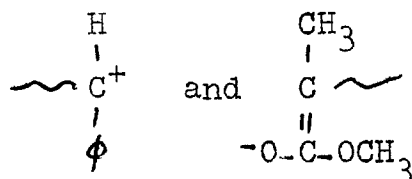
indicates that the activation volumes are pressure dependent. Except for low styrene concentrations ϕ increases with pressure so that, under most conditions

$$\Delta V_{Tab}^{\ddagger} < \frac{1}{2}(\Delta V_{Taa}^{\ddagger} + \Delta V_{Tbb}^{\ddagger})$$

The activation volume for a reaction can be considered to consist of two parts. The intramolecular volume change, $\Delta V_1^{\ddagger}$, in a bimolecular or biradicle reaction is the result of the reactants entering into a more compact transition state and the intermolecular volume change, $\Delta V_2^{\ddagger}$, is caused by a change in the electrostriction of the solvent brought about by change in the polarity of the reactants. For a fully developed ionic charge $\Delta V_2^{\ddagger}$ may be as high as 30cc./mole in a polar solvent.

$\Delta V_1^{\ddagger}$ will therefore be negative for A - A, B - B and A - B termination reactions. The positive $\Delta V_2^{\ddagger}$ caused by the release of solvent from the solvated radicles should be greatest where similar radicles react and polarisation is suppressed. In cross termination the polarities of the radicle ends are increased by induction. Walling^(6,9) has suggested that in systems showing a strong alternating tendency the radicle polarities may become so highly developed in the cross propagation reactions that electron

transfer takes place. Electron transfer is even more likely in the head to head termination than in the head to tail propagation as the electron attracting and repelling groups then enter into even closer proximity. Electron transfer seems possible in the styrene - methyl methacrylate system if the forms



and their resonance hybrids are produced. Molecular models show that the carboxymethyl and phenyl groups can approach each other closely enough for such a transfer to take place. The two radicals would then remain together in this form in the transition state until their orientation permits the formation of a covalent bond. Formation of the ion-pair precedes the reaction and ensures that more A - B diffusion controlled collisions are effective than A - A and B - B collisions. Relative to the A - A and B - B reactions, then, the transition state for A - B reactions may be expected to be more highly solvated and thus have a lower $\Delta V_2^\ddagger$ which would explain the increase of ϕ with pressure.

An increase of ϕ with pressure is not found at high methyl methacrylate feed compositions where the penultimate chain units are predominantly methyl methacrylate. This may be because the higher polarity of the methyl methacrylate penultimate units is not suppressed to the same extent as that of less polar styrene units in the termination reaction. Molecular models also show that penultimate methyl methacrylate groups may hinder charge transfer through interference of the oxygen atom with that of a methyl methacrylate terminal units. If this is so, the effect of desolvation on the termination reactions will be more similar for A - A, B - B and A - B reactions at high methyl methacrylate concentrations, and desolvation will be less than under conditions where penultimate styrene units are predominant. It follows, then, that the pressure effect through the intermolecular volume changes will be more similar for the three termination reactions and the value of ϕ will be less sensitive to pressure change at high methyl methacrylate concentrations.

Concentration and Composition effects.

The variation of reaction rate with the composition

of the feed is remarkably small in the case of methyl methacrylate with maleic anhydride. It may be, however, that in the system at high pressures, some maleic anhydride crystallises out of the liquid phase so that the reaction medium is not varied as much as would appear from the feed compositions. Due to the presence of benzene as diluent in this reaction a phase separation of this type would not greatly affect the initiator concentration, so the reaction rate would not be greatly affected on this count.

In the styrene - diethyl fumarate system the overall rate at 1 atm. differs only slightly from that of pure styrene, even when the diethyl fumarate content of the feed is as high as 50 mole %. The rate is, however reduced when the feed consists predominantly of the ester. At higher pressures the rate of polymerisation is accelerated more than that of pure styrene. The coincidence of reaction rates in the styrene - diethyl fumarate system, then, does not depend necessarily on some physical cause, but rather on the values of the individual velocity constants and the variation of initiation rate with monomer composition.

C) Molecular Weights.

From the variation of copolymer limiting viscosity numbers it appears that increase in pressure of reaction produces an increase in molecular weight for pressures up to 3,000 atm. above which pressure the molecular weight tends to a constant value. This has been attributed in homopolymer systems to a reduction in the termination rate constant and roughly parallel increases in the rates of propagation and transfer reactions with pressure. Merrett and Norrish⁽¹⁹⁾ pointed out that transfer and propagation both involve reaction between a small molecule and a growing radicle whereas the mutual termination of chains takes place between two macroradicals. Walling and Pellon⁽²¹⁾ have shown that transfer constants are little affected by pressure and it seems from the work described here that the same is true of monomer reactivity ratios. This implies that in eqn. 19-22 the term (i) is reduced by increase in pressure while the transfer terms are hardly affected.

The situation is complicated in copolymer systems by the complexity of the termination and transfer terms. Without accurate knowledge of copolymer molecular weights,

and reliable data on the crossed terminations and the ratios k_t/k_t it is impossible to deduce the values of the crossed transfer rate constants k_{fab} and k_{fba} .

The behaviour of the styrene - perchlorethylene system is quite different from the others and it has been shown earlier that copolymerisation does not occur. It seems clear from the marked reduction in the molecular weight of polystyrene brought about by the addition of perchlorethylene to the monomer that the transfer constant, C_s , is very high.

The ratio s/m of solvent units to monomer units in polymer molecules is given by

$$\frac{s}{m} = \frac{k_f [M\cdot] [S]}{k_p [M\cdot] [M]} = C_s \frac{[S]}{[M]} \quad (37)$$

and from carbon analyses on the lower molecular weight polystyrenes produced in the presence of perchlorethylene

$$C_s = \frac{d \ln [S]}{d \ln [M]} \approx 6 \times 10^{-3}$$

for pressures up to 2,000 atm. C_s cannot be deduced for higher pressures due to the uncertainty of the composition of the monomer feed caused by freezing out of the solvent. The value $C_s = 6 \times 10^{-3}$ is close to that for the transfer reaction of carbon tetrachloride with styrene where $C_s = 9.2 \times 10^{-3}$ at 60°C.

The increase in molecular weight for pressures

between 3,000 and 5,500 atm. is presumably due to reduction in the solvent concentration in the liquid phase through pressure freezing. At pressures above 5,500 atm. it is difficult to interpret the results as the reaction may be taking place in the solid phase or in a super-pressed liquid. Even when answers to these questions are found there are still the questions of how the benzoyl peroxide initiator decomposes at such high pressures and in what physical state the growing polymer molecules are.

D) Melting Points.

The melting point of a solid is given by the ratio

$$T_m = \Delta H_m / \Delta S_m \quad (38)$$

and for members of a homologous series

$$\Delta H_m = A + Bn \quad \text{and} \quad \Delta S_m = C + Dn$$

where A, B, C and D are constants and n is the number of chain units. As n increases $T_m \rightarrow B/D$ and the melting point should become constant where $Bn \gg A$ and $Dn \gg C$. An empirical relation, $1/T_m = a + b/n$ (39) where a and b are constants, exists according to Mark⁽⁵⁶⁾ and gives rise to the same condition at high values of n, i.e. when $n \gg b$, $T_m \rightarrow a^{-1}$. Fox and Flory⁽⁵⁷⁾ have determined the second order transition

temperature for polystyrene fractions and from their results it seems that the transition temperature becomes independent of molecular weight for $n > 10^3$ indicating that the factors A and C for melting should be relatively unimportant also at molecular weights above about 10^5 .

It is evident, however, that these considerations do not cover the variation of copolymer melting points found in the work where copolymers prepared at the highest pressures have similar viscosity molecular weights but show considerable differences in melting points. There are two factors which affect the applicability of eqns. 38 and 39 to the copolymers whose melting points have been determined and these are firstly, that they are strictly applicable only to fractionated homologues where for a given sample there is not a wide range of n , and secondly, that they will apply only to homologues which have the same structures. The copolymers may fail to fulfill both these conditions as they are unfractionated and therefore each contains molecules of widely differing molecular weights and it is possible that samples prepared at the higher pressures, where transfer reactions are increasingly significant, have molecular

structures which are modified slightly by the presence of branches and cross-links. It would be useful to have some data on the melting point of poly(vinyl acetate) prepared at different pressures, as this monomer shows a gel effect at quite low conversions and is particularly susceptible to transfer reactions. It is more likely, therefore, to have a branched structure at lower pressures and it would be interesting to compare results with those found for the copolymers to see if the up-turn shown in figs. 18 and 19 occurs at appreciably lower pressures.

Part 5Table 1.

i) Styrene Polymerisation at 3,000atm. and 60°C.

Tube dia. (mm.)	Mole % Bz ₂ O ₂	Polymer (%)	Time (min)	Rate (%/hr)	Solvent for Precipitation
12	0.043	7.50	75	6.00	E
12	0.043	7.30	75	5.84	E
12	0.043	7.76	75	6.21	E
12	0.043	8.35	75	6.67	E
5	0.043	7.30	75	5.84	E
5	0.043	7.80	75	6.24	E
5	0.043	7.61	75	6.09	E
5	0.043	7.55	75	6.04	B
5	0.043	7.72	75	6.18	B
5	0.043	7.62	75	6.10	B
5	0.043	7.86	75	6.29	M
5	0.043	7.49	75	5.99	M
12	0.427	16.6	50	19.9	E
12	0.427	15.5	50	18.6	M
5	0.427	16.1	50	19.3	E
5	0.427	16.5	50	19.8	M

E 1:2 epoxypropane B benzene M methyl ethyl ketone.

ii) Styrene Polymerisation at 60°C. using 0.1mole% Benzoyl Peroxide.

Press. (atm.)	% Poly.	Time (hrs)	Rate (%/hr)	in Molecular Toluene Weight	
1	8.30	3.34	1.55	1.06	0.22x10 ⁶
1,000	8.64	3.00	2.88	1.83	0.47
2,000	7.80	1.50	5.20	2.48	0.72
3,000	9.98	1.00	9.98	2.77	0.85
4,000	6.33	0.33	19.0	2.80	0.87x10 ⁶

iii) Methyl Methacrylate Polymerisation at 40°C
using 0.1 mole % Benzoyl Peroxide.

Press. % Poly. Time Rate $[\eta]$ in
Chloroform

(atm.)		(min.)	(%/hr)	
1	1.66	180	0.55	6.85
1,000	1.97	120	0.99	12.2
2,000	2.70	60	2.70	16.6
3,000	4.17	30	8.34	
3,000	4.98	40	7.47	21.1
4,000	4.41	10	26.5	23.3
4,000	6.53	15	26.2	22.4
4,000	17.22	34	30.4	

iv) Methyl Methacrylate Polymerisation at 45°C
using 0.0413 mole % Benzoyl Peroxide.

Press. % Poly. Time Rate
(atm.) (hrs.) (%/hr)

1	2.03	3	0.68
1	2.08	3	0.69
2,000	3.18	1	3.18
2,000	3.15	1	3.15

1 0.49 Results of Melekhina
2,000 9.25 and Kuvshinsky. (22)

v) Styrene-Methyl Methacrylate Copolymerisation at 60°C
using 0.1 mole % Benzoyl Peroxide.

Press. (atm)	Mole frn. Styrene in feed.	% Poly.	Time (min)	Rate %/hr	%C in Poly.	Mole frn. Styrene in Poly.	$[\eta]$ in Toluene
1	0.1883	6.65	150	2.66			1.11
1	0.4798	7.54	270	1.68			1.12
1	0.7868	8.25	360	1.37			1.01
1,000	0.1911	8.89	85	6.27			2.19
1,000	0.1913	6.84	65	6.31	68.71	0.263	
1,000	0.4803	8.17	150	3.27	76.03	0.487	2.03
1,070	0.7863	8.67	180	2.89			1.78
1,500	0.1904	8.66	63	8.24	68.75	0.264	2.86
1,500	0.4807	7.07	91	4.66	76.16	0.490	2.47
1,500	0.7837	9.90	163	3.64			2.01
2,000	0.2211	8.07	40	12.1	70.32	0.311	3.30
2,000	0.4785	6.92	60	6.92	76.23	0.493	
2,000	0.4786	7.23	60	7.23	76.37	0.497	2.85
2,000	0.7864	7.50	90	5.00	83.82	0.732	2.43
2,500	0.0988	13.00	12	65.0	65.18	0.156	
2,500	0.1903	12.90	45	17.2	69.29	0.280	4.01
2,500	0.3338	6.75	30	13.5	72.86	0.389	
2,500	0.4855	9.28	60	9.28	76.46	0.500	3.23
2,500	0.6284	8.65	55	9.43	79.15	0.584	
2,500	0.7865	6.48	60	6.48	83.99	0.727	2.72
2,500	0.8860	8.03	60	8.03	88.20	0.871	
3,000	0.1904	9.68	25	23.2	68.17	0.246	4.05
3,000	0.4796	13.72	60	13.7	75.54	0.471	
3,000	0.4798	9.36	45	12.5	76.29	0.495	
3,000	0.4805	8.23	37	13.3			3.55
3,000	0.7861	11.28	75	9.01	83.89	0.734	2.82
3,500	0.1894	10.02	10	60.1	68.63	0.260	
3,500	0.4798	7.31	20	21.9	76.48	0.501	
3,500	0.7859	8.36	40	12.6	84.02	0.737	2.87
3,800	0.1883	13.50	10	c.80			4.10
4,000	0.4814	11.03	22	29.4			3.60
4,000	0.7868	8.32	25	20.0			2.90

vi) Styrene-Diethyl Fumarate Copolymerisation at 60°C.
using 0.1 mole% Benzoyl Peroxide.

Press. atm.	Mole frn. Styrene in feed.	% Poly.	Time min.	Rate %/hr	%C in Poly.	Mole frn. Styrene in Poly.	$[\eta]$ in Toluene
1	0.2629	4.54	240	1.14	69.49	0.498	0.57
1	0.5858	6.03	225	1.61	73.18	0.600	0.67
1	0.5862	7.02	250	1.69	72.86	0.591	
1	0.8475	5.37	180	1.79	78.12	0.724	0.71
1,000	0.2608	8.50	210	2.43			0.78
1,000	0.5862	8.12	120	4.06			1.10
1,000	0.8472	4.75	70	4.24			1.14
1,500	0.2609	6.52	121	3.24	70.55	0.529	0.88
1,500	0.5858	7.51	80	5.63	72.34	0.579	1.32
1,500	0.8478	8.18	80	6.13	78.04	0.721	1.49
2,000	0.2626	7.61	100	4.56			0.93
2,000	0.5851	8.71	60	8.71			1.48
2,000	0.8462	8.10	50	9.71			1.62
2,500	0.1669	3.02	45	4.03	69.29	0.492	
2,500	0.2629	3.82	30	7.64	70.43	0.524	0.98
2,500	0.5862	7.53	30	15.1	72.76	0.589	1.59
2,500	0.8472	8.14	30	16.3	77.18	0.701	1.81
3,000	0.2635	7.14	35	12.2			1.03
3,000	0.5854	8.54	20	25.6			1.74
3,000	0.8463	12.04	30	24.1			2.06
3,340	0.2625	4.53	20	13.6	70.09	0.516	1.03
3,500	0.5858	10.26	15	41.0	73.02	0.597	1.79
3,500	0.8469	10.58	15	42.3	77.17	0.700	2.14
4,000	0.2615	5.55	12	27.7			1.03
4,000	0.5852	10.22	10	61.3			1.78
4,000	0.8465	14.22	12	71.1			2.13

vii) Styrene-Perchloroethylene Polymerisation at 60°C.
using 0.1 mole % Benzoyl Peroxide.

Press. atm.	Mole frn. Styrene in feed.	% Poly.	Time hr.	Rate %/hr	%C in Poly.	Mole frn. Styrene in Poly.	$[\eta]$ in Toluene
1	0.1828	9.37	75	.125	89.45	0.977	0.064
1	0.4710	9.66	23.8	.406			0.186
1	0.7789	5.52	6	.920			0.446
1,000	0.1834	5.00	26	.192			0.071
1,000	0.4724	9.61	12.3	.778			0.198
1,000	0.7805	5.92	3.3	1.78			0.540
2,000	0.1834	5.85	21	.278	89.10	0.974	0.077
2,000	0.4711	4.63	3.5	1.32	91.36	0.993	0.227
2,000	0.7800	4.34	1	4.34	91.48	0.994	0.576
3,000	0.1835	6.28	15	.419			0.076
3,000	0.4716	8.43	3.7	2.30			0.220
3,000	0.7790	6.91	0.9	7.54			0.604
4,000	0.1858	9.66	10	.966			0.094
4,000	0.4710	8.73	2.7	3.27			0.242
4,000	0.7786	6.98	0.67	10.5			0.604
4,500	0.1833	9.32	8.25	1.13			0.115
5,000	0.1835	7.87	4.0	1.98			0.148
5,400	0.1820	8.59	2.0	4.30			0.200
5,400	0.4713	8.64	1.0	8.64			0.371
5,400	0.7805	8.16	0.5	16.3			0.764
6,890	0.1839	7.65	0.75	10.2			
6,890	0.4712	9.92	0.5	19.8	91.36	0.993	0.455
6,890	0.7791	11.28	0.42	27.1			0.853
8,360	0.1834	9.10	0.33	27.3	90.20	0.983	0.235
8,360	0.4716	9.60	0.20	48.0			0.370
8,360	0.7794	28.9	0.33	87.0			0.739

viii) Styrene-Perchloroethylene Polymerisation at 50°C.
using 0.1 mole % Benzoyl Peroxide.

Press. atm	Mole frn. Styrene in feed	% Poly.	Time hrs.	Rate %/hr	(η) in Toluene
1	0.4738	4.70	30	.157	0.218
1,000	0.4732	6.98	22	.317	0.235
2,000	0.4720	6.60	12	.556	0.242
4,000	0.4738	4.99	3.5	1.43	0.294
5,400	0.4738	4.90	1.33	3.67	0.467
6,890	0.4720	5.17	1.0	5.17	0.561
8,360	0.4738	2.71	1.0	2.71	0.434

ix) Perchloroethylene Polymerisation at 60°C.
using 0.1 mole % Benzoyl Peroxide.

Press. atm	% Solids	Time hr	Rate %/hr	Cryoscopic M.W.
1	0	360	0	-
3,180	0.30	19.1	0.016	
5,400	0.24	21.3	0.011	
11,320	0.28	43.0	0.006	360
11,320	0.32	14.7	0.022	300
11,320	1.40	27.0	0.052	980
11,320	0.82	28.0	0.029	420

x) Methyl Methacrylate-Maleic Anhydride Copolymerisation
at 60°C. using 0.1 mole % Benzoyl Peroxide.

Press. atm	Mole frn. Me. Me. in feed	% Poly.	Time min	Rate %/hr	%C in Poly.	Mole frn. Me. Me. in Poly.
1	0.6987	11.33	60	11.3		
1,000	0.6984	8.15	25	19.6	58.63	0.875
1,000	0.6979	5.41	15	21.6		
1,500	0.6991	11.56	25	27.7		
1,500	0.6976	7.89	18	26.3		

xi) Methyl Methacrylate - Maleic Anhydride at 60°C
in 50 mole % Benzene using 0.05 mole % Benzoyl
Peroxide.

Press.	Mole Frn. Me. Me. in Feed.	Mole Frn. Mal Anh. in Feed.	%Poly.	Time	Rate	%C in Poly.	Mole Frn. Me. Me. in Poly.	^x SP/C
(atm)				(min)	(%/hr)			
1	0.1488	0.3493	8.68	120	4.34	56.87	0.712	1.10
1	0.2511	0.2527	12.81	160	4.80	56.92	0.718	1.18
1	0.3462	0.1498	3.75	60	3.75	57.86	0.803	1.15
1,000	0.1500	0.3480	8.25	50	9.90			2.04
1,040	0.2510	0.2523	12.63	60	12.6			2.42
1,000	0.3462	0.1498	5.89	35	10.1			2.69
1,500	0.1498	0.3504	8.47	30	16.9			2.67
1,500	0.2506	0.2528	9.00	30	18.0			3.16
1,500	0.3469	0.1495	10.45	30	20.9			3.54
2,000	0.1499	0.3501	10.12	20	30.4	56.06	0.637	3.38
2,000	0.2514	0.2523	11.03	20	33.1	57.92	0.810	3.87
2,000	0.3471	0.1499	11.50	20	33.7	58.96	0.904	4.35
2,500	0.1488	0.3493	11.85	15	47.4			4.06
2,500	0.2525	0.2518	19.40	20	58.2			4.64
2,500	0.3453	0.1503	13.94	15	55.8			4.89
3,000	0.1503	0.3500	16.19	10	97.1			4.59
3,000	0.3510	0.2522	17.99	10	108			5.08
3,000	0.3465	0.1499	17.80	10	107			5.37
3,500	0.1491	0.3472	33.02	10	194			4.33
3,500	0.2513	0.2528	33.5	10	201			5.27
3,500	0.3485	0.1506	27.7	10	166			5.60
4,000	0.1501	0.3475	9.27	7	79.5			5.27
4,000	0.2528	0.2522	10.27	7	88.0			
4,000	0.3460	0.1498	12.37	7	106			

^x η SP/C Determined in dry acetone at C = 0.23g/100ml.

Table 2.

Polymer Melting Points.

i) Styrene - Methyl Methacrylate Copolymers.

Pressure of Preparation. (atm.)	1	1,000	1,500	2,000	2,500	3,000	4,000
% Styrene in Poly.	Melting Points (°C.)						
100				215.0			
84					207.5		
72	198.5		197.5	200.5	202.0	205.0	207.5
57					197.0		
48	180.5	182.0	181.5		189.5		191.5
38					164.0		
26		166.0				162.0	

Decomposition with the evolution of gas.

ii) Styrene - Diethyl Fumarate Copolymers.

Pressure of Preparation. (atm.)	1	1,000	2,000	3,000	3,500	4,000
% Styrene in Poly.	Melting Points (°C.)					
100			215.0			
72	117.5 (96.5)		125.5 (102.0)	135.5 (116.5)	148.5 (125.0)	160.5
59	91.5	89.5	94.5	107.0		123.5
50		57.5	64.0	69.0		76.0

(Figures in brackets indicate the temperature of a second order transition.)

Table 3.

Test for copolymerisation in Styrene - Methyl Methacrylate system: Precipitation of copolymer from a 2g./100ml. solution in Chloroform by Methanol.

Volume of Soln. (ml.) MeOH added to produce first ppt. (ml.) Total MeOH added. (ml.) % Polymer Ppted. MeOH added per ml. soln. (ml.)

(ml.)	(ml.)	(ml.)		(ml.)
10 ^a	10.5	11.7	13	1.17
5	5.35	6.0	18	1.20
5	5.25	7.5	35	1.50
5		8.75	58	1.75
5		10.0	76	2.00
10 ^b	10.4	25.0	92	2.50
5		15.0	98	3.00

- a) The precipitate from this test contained 77.78% C and thus contained 54% Styrene units.
- b) The filtrate from this test, on drying was found to contain 74.18% C indicating the presence of 43% Styrene units.

Table 4.Freezing Pressures.

- i) Freezing pressure of Perchloroethylene at 60°C determined in vessel B.

Pressure increasing		Pressure decreasing	
Gauge Reading	Intensifier Height	Gauge Reading	Intensifier Height
(atm.)	(cm.)	(atm.)	(cm.)
165	8.020	288	9.700
180	8.208	245	9.700
198	8.378	238	9.680
208	8.498	230	9.613
224	8.644	230	9.602
239	8.810	224	9.536
260	8.986	224	9.488
263	9.140	220	9.412
263	9.180	220	9.364
263	9.276	211	9.256
270	9.366	208	9.172
272	9.446	205	9.086
278	9.540	202	9.014
288	9.700	198	8.974

From fig. 17 P_f for increasing pressure is 263atm.
 gauge, i.e. true pressure = 3,360atm.
 P_f for decreasing pressure is 200atm.
 gauge, i.e. true pressure = 2,850atm.

ii) Freezing Pressure of a Styrene - Perchlorethylene Mixture.

(Composition of mixture; Styrene 18.15, Perchlor-ethylene 81.65, Quinol 0.20 mole %.)

Pressure Increasing		Pressure Decreasing	
Gauge Reading	Intensifier Height	Gauge Reading	Intensifier Height
(atm.)	(cm.)	(atm.)	(cm.)
305	6.980	445	8.758
317	7.088	435	8.700
325	7.220	415	8.556
335	7.290	397	8.414
343	7.380	379	8.296
355	7.494	360	8.162
364	7.564	347	8.040
375	7.662	342	7.924
388	7.756	337	7.866
399	7.840	330	7.756
415	7.948	315	7.650
430	8.046	305	7.514
448	8.170	296	7.420
465	8.276		
483	8.372		
506	8.460		
525	8.536		

From fig. 17 P_f range for increasing pressure is

430-460 atm. gauge, i.e. true
pressure range 5,800-6,300 atm.

P_f range for decreasing pressure is

342 - 348 atm. gauge, i.e. true
pressure range 5,300-5,400 atm.

Table 5.Monomer Reactivity Ratios.

i) Styrene (A) - Methyl Methacrylate (B).

Press. (atm.)	r_a	r_b
1	0.52	0.46
1,000	0.53	0.47
1,500	0.50	0.48
2,000	0.53	0.45
2,500	0.53	0.48
3,000	0.57	0.54
3,500	0.59	0.50

(The results for 1 atm. are those of
Mayo and Walling.⁽²⁴⁾)

ii) Styrene (A) - Diethyl Fumarate (B).

Press. (atm.)	r_a	r_b
1 ^x	0.30	0.07
1	0.35	0.03
1,500	0.26	0.01
2,500	0.27	0.02
3,500	0.30	0.02

^xThese results for 1 atm. are those of Lewis and Mayo⁽²³⁾.

iii) Methyl Methacrylate (A) - Maleic Anhydride (B).

Press. (atm.)	r_a	r_b
1	6.7	0.02
1	2.1	0
2,000	2.4	0
1 ^x	3.5	0.03

These results for 1 atm. are those of de Wilde and Smets⁽²⁵⁾.

^xResults of Blackley and Melville⁽²⁶⁾.

iv) Styrene (A) - Perchloroethylene (B).

(r_b is assumed to be zero.)

Press. (atm.)	r_a Mole % styrene in feed		
	80	50	20
1	288		
2,000	46	167	236
6,890		190	
8.360			240

C.f. value of r_a 185 at 1 atm. given by Doak. (27)

Table 6.

Viscosity Molecular Weights and Compositions of
Some Styrene - Perchloroethylene Polymers.

Mole frn. Styrene in feed.	Press. of Polymern.	M.W.	Styrene units	P.C.E. units	%P.C.E. From M.W.	%P.C.E. from C analysis
0.1831	1	3,900	36	1	2.8	2.3
0.1834	2,000	5,000	47	1	2.4	2.6
0.4711	2,000	29,700	283	1	0.4	0.7
0.7800	2,000	109,000	1030	1	0.1	0.6
0.4712	6,890	111,500	1070	1	0.1	0.7
0.1834	8.360	22,900	219	1	0.5	1.7

Table 6.

Styrene - methyl methacrylate system;
 Variation of ϕ with Pressure and Monomer
 Composition.

Pressure (atm.)	ϕ Mole frn. Styrene.		
	0.79	0.48	0.19
1 ^x	35	25	14
1	46	29	14
1000	80	39	12
1500	106	48	15
2000	100	41	13
2500	105	42	15
3000	112	40	16

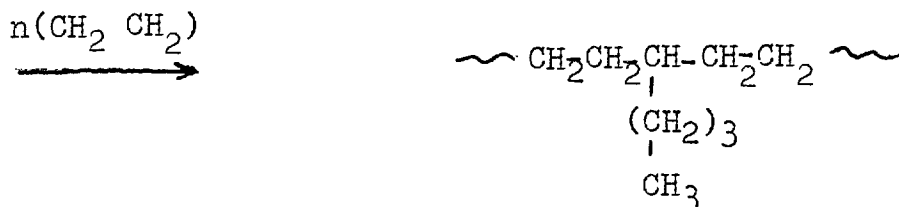
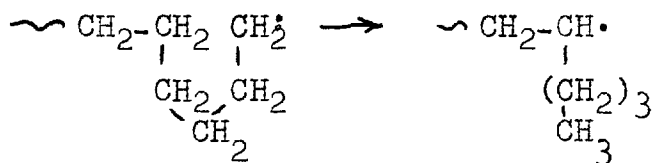
^xFrom results of Mayo and Lewis. (30)

Section 2. GRAFT COPOLYMERISATION.

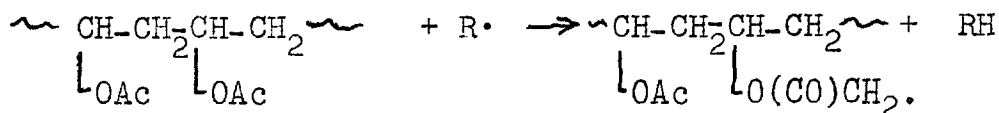
Part I. Introduction.

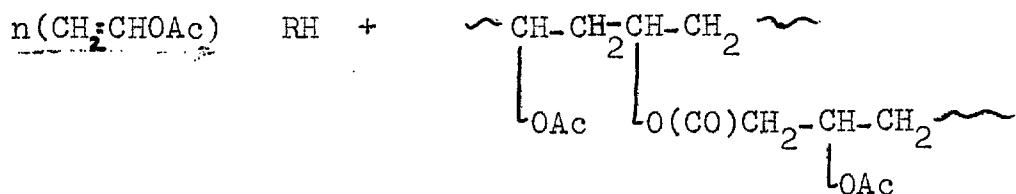
A. General Review of Free Radicle Graft Copolymerisation.

The term 'graft polymer' is used to describe macromolecules built up of repeating units and consisting of a linear 'backbone' or 'trunk' chain onto which are attached 'side' chains or 'branches' of a different chemical type. Analogous structures can arise in the homopolymerisation of some monomers where transfer to polymer takes place, such as in the polymerisation of ethylene;



and vinyl acetate;





A graft copolymer is a branched polymer in which the trunk chain and branches are built up of different monomer units. There are several ways of preparing graft copolymers, many of which involve preparing a copolymer trunk chains in which one of the co-monomers contains a functional side group which can initiate grafting. Another method is to prepare a trunk polymer containing radicals or groups which can be extracted by a free radicle to leave a centre on the trunk chain which is capable of propagation with a second monomer.

Many ingenious and elegant methods for the production of graft copolymers are described in the report of the 1957 symposium on block and graft copolymers.⁽⁵⁸⁾ Other surveys of graft copolymer systems are mentioned in the bibliography.^(59,60,61)

B. The Effects of Ionising Radiation.

One method of preparing graft copolymers involves the production, directly or indirectly, of free radicles

by ionising radiation. Polymers, when subjected to ionising radiation, undergo changes in properties which depend on the nature of the polymer but are practically independent of the type of radiation, whether it is α , β , γ , fast neutrons or X-rays^(62,63,64) The G_r value (number of chemical changes per 100eV) for a given polymer is independent of the radiation intensity and other conditions such as temperature, but the type of reaction occurring may vary.

The initial effect of radiation on a polymer is to produce free radicals.⁽⁶⁵⁾ Whether these are produced mainly by scission of the main chain or by the dislocation of side groups depends upon the structure of the polymer. As a general rule, mono-substituted polyethylenes tend to lose side groups whereas 1:1 di-substituted ethylenes undergo more chain scission.⁽⁶⁶⁾ Polyethylene behaves as a mono-substituted polymer, partly because of the branched structure it possesses as a result of the transfer reaction described above. Examples of the behaviour of some polymers are;

Poly-	Predominant Reaction	$G_{\text{cross-link}}$	G_{scission}
Ethylene	Cross-linking	1	2-3
Styrene	Cross-linking	0.15	0.03
Methyl Methacrylate	Chain-Scission	0	1.7

The low G_r values for styrene are attributed to the shielding effect of the benzene rings.⁽⁶⁷⁾

Highly crystalline polymers of the type which usually tends to cross-link under the influence of radiation, such as high density polyethylene or some polymers at low temperature, do not have the same mobility of polymer chains. Cross-linking therefore occurs to a lesser extent, and broken bonds remain in the polymer as 'frozen' free radicals whose presence may be detected by electron spin resonance measurements.^(68,69)

When oxygen is readily available to a cross-linking type polymer while it is being irradiated, for example when thin films or filaments are irradiated in air or oxygen, peroxidic linkages are produced.^(70,71) Below are given the G_r values for some polymer model compounds subjected to 75kV X-rays in the presence of oxygen;⁽⁶⁶⁾

Peroxide	n Heptane	Isocotane	Toluene	Benzene
ROOR'	2.2	1.3	1.2	0.2-0.3
ROOH	1.2	0.7	0.4	0
HOOH	0.3	0.3	0.2	0.2-0.3
Total	3.7	2.3	1.8	0.5

Irradiated Polymers as Polymerisation Initiators.

Both frozen free radicles and peroxidised polymers are capable of initiating vinyl polymerisation. In the former case the technique has often been used of swelling the polymer in the monomer to be grafted and then irradiating. This causes initiation through the production of radicle sites on the polymer and through breakdown of the monomer into radicles so that an intimate mixture of graft and linear polymers results.^(72, 73, 74, 82) The life time of frozen free radicles is low in polymers where the chain segments have much mobility and they combine in a short time thus losing their ability to initiate polymerisation.⁽⁷⁵⁾ Irradiation of polymer in nitrogen followed by rapid immersion in monomer has been used to produce graft copolymer⁽⁷⁶⁾ as has irradiation in vacuo.^(77, 78) In this second case a comparison has been made between the grafting rates of high and low density polyethylene which indicated that the trapped radicles are situated principally in the crystalline regions of the polymer.

Polymer Peroxides.

The peroxidic linkages produced in the presence of oxygen have received far more study than frozen free radicles and are much more conveniently used in the

production of graft copolymers.^(75,77,79,80) These polymer-peroxides are fairly stable at room temperatures and can be stored for a considerable time without losing their activity. They initiate polymerisation at appreciable rates when immersed in monomers at higher temperatures. The rate of grafting varies linearly with pre-dose for doses up to about 8Mrad., providing the dose rate is not too high and sufficient oxygen is available to the polymer during radiation.

The thermal decomposition of polymer peroxides has been successfully employed in the grafting of a variety of monomers.

C. Kinetics of Polymer Peroxide Initiated Grafting.

It is believed that the vinyl polymerisation theory outlined in the first part of this thesis for catalysed homopolymerisation is applicable to graft copolymerisation initiated by polymer peroxides. Shinohara and Tomioka⁽⁶⁹⁾ polymerised N vinyl 2 pyrrolidone onto filaments of irradiated polyethylene and treated the resulting grafted filaments with a water soluble dye. They showed by photomicrographs that the grafted region advances inwards from the surface of the filament as the polymerisation proceeds. This they

explained by the suggestion that the monomer, which is a poor solvent for polyethylene, is nevertheless able to swell the graft copolymer produced initially on the surface of the filament and therefore advances into the polymer on a 'diffusion front'.

Using the symbol $\begin{array}{c} | \\ \cdot \end{array}$ for an oxidised polymer unit whose structure is $\begin{array}{c} \text{CHO} \cdot \\ | \end{array}$, the kinetic scheme may be written;

1) Initiation,



followed by



2) Propagation.



3) Transfer

i) to monomer



ii) to initiator

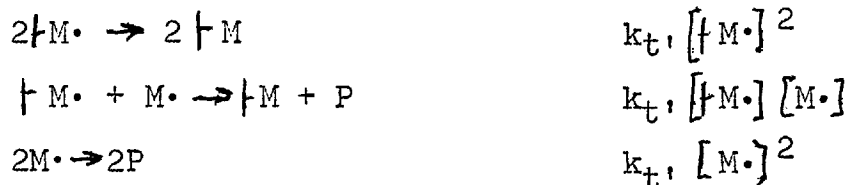


4) Termination.

i) combination



ii) disproportionation



Parallel with the peroxide initiated reaction thermal reaction may also take place. This would give rise to linear polymers and to branched polymers when the radicals terminate with growing radicals arising from the peroxide initiated reaction.

In the absence of thermal polymerisation the only linear polymer to be produced should arise through the transfer reaction 3(i) above.

For steady state conditions, then,

$$[R\cdot] = [M\cdot] + [\dot{M}] = (k_i [I]/T)^{\frac{1}{2}} \quad (40)$$

where $T = k_t + k_t$,

so that the rate of disappearance of monomer is

$$-\frac{d[M]}{dt} = k_p [R\cdot] [M] = k_p (k_i [I]/T)^{\frac{1}{2}} [M] \quad (41)$$

D. Effect of Heterogeneity.

Under reaction conditions where the polymer peroxide is insoluble in the monomer and the graft copolymer is swollen by the monomer but not soluble, the concentrations of the reactants will be dependent on the site of the reaction. In terms of the Laplace equation the

concentration of monomer at distance x from the surface of a thin sheet of solid polymer of thickness L at time t is given by

$$-D \frac{\partial^2 [M]}{\partial x^2} = \frac{\partial [M]}{\partial t} + k_p [R\cdot] [M] \quad (42)$$

where $t \geq 0$, $x = 0$ $[M] = [M]_{\text{saturation}}$

$t = 0$, $x = 0$ $[M] = 0$

$t \geq 0$, $x = L/2$ $\frac{\partial [M]}{\partial x} = 0$

It is evident, then, that only when the diffusivity, D , of the monomer in the substrate is very large compared with $k_p [R\cdot]$ will $[M]$ reach a uniform value in the mass of the insoluble polymer independent of x . Even under these conditions, a steady free radicle concentration will not be achieved as the concentration of monomer M will be dependent upon the degree of advancement of the reaction which will affect the equilibrium swelling and hence the effective volume of the reaction medium.

E. Scope of Work.

The object of the work described in this section was to survey briefly the effects of pressure on graft copolymerisation and in particular to see whether halogenated ethylenes can be grafted onto

irradiated polyethylene (which might confer some degree of flame proofing) and whether a graft copolymer of vinyl acetate on polystyrene could be produced by the use of an irradiated substrate and high pressures. Attempts to produce polystyrene - vinyl acetate graft copolymers by a free radicle mechanism at 1atm. have been unsuccessful.(92)

Part II. Experimental Procedure.

Materials.

The purification of many of the materials used has been described in Section 1 of this thesis. Other materials are listed below;

a) Polyethylene: This was obtained as film 0.001" thick from British Visqueen Ltd. It was twice soaked in 1:2 epoxypropane for several hours to remove antioxidant.

b) Polystyrene; Film 0.002" thick was obtained from S.I.C. Plastics Ltd. and was washed in methanol before use.

c) Trichlorethylene was obtained from B.D.H. and was distilled. The fraction boiling 86.5 to 87.0°C. was collected.

d) cis Dichlorethylene (B.D.H.) was fractionated and the cut 58.5 to 59.5°C. was retained.

e) Vinyl acetate supplied by L. Light and Co. contained the inhibitor diphenylamine. It was purified by vacuum distillation to separate from the inhibitor after which it was kept for 24 hrs. at room temperature with about 0.01g/100ml. benzoyl peroxide. The remaining monomer was then distilled off at reduced

pressure under nitrogen and stored in vacuo at 0°C. The purified monomer was never stored for more than 48 hrs. before use.

f) Trans dichlorethylene was obtained from L. Light and Co. and was further fractionated. The cut boiling 47.5 to 48.0°C. was retained.

g) Vinylidene chloride containing *hydroquinone* inhibitor was obtained from the Distillers Company. The inhibitor was removed by alkali washing as with styrene and the monomer was distilled under an atmosphere of nitrogen (Boiling range 31.2 to 32.0°C at 760 mm.)

Irradiation of Polymers.

The polymer films were subjected to γ radiation from an 1,100 Curie Co^{60} source. The active length of the source is $4\frac{1}{2}$ " and its diameter is $9/16$ ". Radiation intensities at various radial distances from the centre of the source determined by ferrous sulphate dosimetry are given in the table below;⁽⁹¹⁾

Radius (cm)	5	6	7	8	9	10	11	12
Intensity (Mrad/hr)	.325	.237	.181	.143	.117	.096	.081	.069

The films were mounted on a squirrel cage arranged about the source so that all the film was at the same radial distance from the source and air was

readily available to the surfaces of the polymers during irradiation.

Polyethylene film was irradiated at a distance of 10.3cm. from the centre of the source where the radiation intensity is 0.09Mrad/hr. for 89hrs., giving a total dose of 8Mrad.

Polystyrene film was given a larger dose, as polystyrene has a larger G_r value, receiving 58Mrad in 37 $\frac{1}{4}$ hrs. at 7.6cms. where the intensity is 0.155Mrad/hr.

Irradiated films were stored for several weeks at room temperature before use to allow the free radicle products to neutralise themselves.

Grafting Reaction.

The high pressure apparatus used was that described in the first half of this thesis. The monomers styrene, methyl methacrylate, perchlorethylene, trichlorethylene, vinylidene chloride, trans dichlorethylene and cis dichlorethylene were each subjected, while in contact with irradiated polyethylene, to high pressures. The weights of monomer and film were measured beforehand. On removal from the reaction vessel the polyethylene film, which was not soluble in any of the monomers used was washed repeatedly in 1:2 epoxypropane until no further weight change was noted on holding the washed

film under high vacuum for several hours. With the monomers styrene and methyl methacrylate, samples of the liquid phase were taken and precipitated in methanol as in section 1 to determine the weight of homopolymer formed. Liquid samples from the halogenated ethylene systems were evaporated in vacuo to determine the % solids and for these monomers no homopolymer was detected except vinylidene chloride.

In the styrene and methyl methacrylate systems a considerable weight increase of the irradiated film was found and quantities of homopolymer were also produced. Blank runs with non-irradiated film were therefore also carried out for these two systems at 60°C. and various pressures to determine how much of the polymerisation is caused by thermal reaction and by polymer peroxides which may have been present as a result of aerial oxidation of the film.

Attempts were also made at grafting vinyl acetate monomer onto irradiated polystyrene at several pressures and temperatures. In this system the substrate is soluble in the monomer and so the technique used in estimating the products of polyethylene grafting could not be employed. Samples of the reaction products were therefore taken and freeze-dried in dioxan to

estimate the unreacted monomer.

Tests carried out on mixtures of irradiated polystyrene and poly(vinyl acetate) showed that while both monomers are soluble in ethyl methyl ketone, the polystyrene was insoluble in a 3:1 mixture by volume of methanol and ethyl methyl ketone. The poly(vinyl acetate) remaining in solution could be precipitated by the addition of a large excess of water. The precipitates did not coagulate, even on standing for several weeks, unless a few drops of electrolyte were added. Results for a mixture of monomers corresponding in composition to the products of the grafting reaction carried out at 2,000atm. and 60°C. are given below to show the effectiveness of the separation;

Composition of mixture;

Irradiated polystyrene	-0.2824g.
Poly(vinyl acetate) prepared at 2,000atm. 60°C.	-0.0706g.
Total	<u>-0.3530g.</u>

Precipitated from 3:1 MeOH:E.M.K.	-0.2706g.
Precipitated from filtrate by water	-0.0807g.
Total	<u>-0.3513g.</u>

A similar precipitation method was used with the reaction products.

Two further tests were carried out on the 2,000atm. 60°C. reaction products and the results were compared with those of similar tests on homopolymer mixtures of

the same composition: Solution viscosities in benzene at 30°C. were determined for the supposed graft copolymer, for a mixture of the homopolymers of the same composition, and of the homopolymers separately at various concentrations. From these results $[\eta]$ and Huggin's k' were found. Comparison was also made between the copolymer and the mixture by measuring the turbidity of 0,2g./100ml. solutions on addition of various volumes of methanol.

Tests were also carried out at 4,000 atm. and 60°C. on the bulk copolymerisation of three mixtures of styrene and vinyl acetate with 0.1 mole% benzoyl peroxide to see whether increase in hydrostatic pressure would alter the monomer reactivity ratios from their atmospheric pressure values. The techniques employed were in every respect similar to those described in section 1 for the copolymerisation of styrene and methyl methacrylate.

Part III. Experimental Results.

A) The results of reactions using irradiated polyethylene are given in tables 7(i) to (iii) and in fig. 21.

In the system using styrene monomer little difference in the rate of production of homopolymer was found when using irradiated or non-irradiated polyethylene. At 1 atmosphere pressure the homopolymerisation rate is not much greater than the ~~ter~~ thermal rate at 60°C. estimated as 0.09%/hr.⁽⁹³⁾ On the other hand the rate of production of polymer insoluble in epoxypropane is about 15 times as great when irradiated polymer is used. That polymer insoluble in epoxypropane is produced is considered sufficient justification for assuming that a graft copolymerisation has occurred.

The effect of pressure is to increase both the homopolymerisation rate and the grafting rate. The homopolymerisation rate increases almost exponentially with pressure, the rate at 3,000atm. being about ten times the atmospheric value. Graft polymerisation rates are increased about 18-fold by an increase in pressure from 1 to 3,000atm., application of higher

pressure producing no further increase in the rate.

Considerable increases in the size of the film were found when large amounts of monomer were grafted onto them. For example, a polyethylene film which showed an 80% weight increase on grafting increased its linear dimensions by about 30%.

Despite great care in the purification of the monomer, the measured rates of reaction of methyl methacrylate with irradiated polyethylene were completely irreproducible. Tests on non-irradiated polyethylene produced no measurable polymer. Irradiated films showed considerable weight increases in some cases. The irreproducibility may have been caused by the formation of some polymerisation inhibitor or retarder during the course of the reaction.

No weight increase in irradiated films was observed on heating under pressure with chlorinated ethylenes, except in the case of vinylidene chloride. It was only with this monomer that large quantities of homopolymer were produced. Hydrolysis of the homopolymer and the film with alcoholic potassium hydroxide produced a dark brown coloration which was bleached to a golden yellow by oxidation with chlorine water. (Polyethylene film which had not been in contact with

vinylidene chloride did not show these effects.) Hydrolysis of the film from the reaction at 3,000atm. in vinylidene chloride followed by oxidation with chlorine water and extraction with boiling methanol reduced the weight of the film almost to its original un-reacted value and removed the yellow coloration. This indicates that the weight increase may have been caused by occluded homopolymer and not by a graft reaction with vinylidene chloride. The results of this test are given below;

Weight of reacted film

Theoretical weight of polyethylene 0.0946g.

Weight of poly(vinylidene chloride) 0.0857g.

(c.f. weight from chlorine analysis) 0.0089g.

Weight of film after treatment as described above. (0.0076g) 0.0862g.

B) The results of the reactions of vinyl acetate with irradiated polystyrene are given in table 7(iv).

Although it was found that mixtures of irradiated polystyrene and poly(vinyl acetate) could be effectively separated by precipitation of the polystyrene from a solution in ethyl methyl ketone by methanol, the reaction products described in table 7(iv) could not be separated by this technique. It appears that

increase in reaction pressure increases the rate of consumption of vinyl acetate and that at a given pressure increase in reaction time causes increase of the solubility of the reaction products in the ketone-alcohol mixture.

Comparison of the solution viscosities of the 2,000 atm. reaction products with those of physical mixtures of irradiated polystyrene and poly(vinyl acetate) prepared at 2,000 atm. of the same composition showed some differences in the Huggin's k' values. (See table 8 i) The k' value for the reaction product was found to be greater than that for the mixture or either of its components. This in itself does not provide conclusive proof that the reaction product is a graft copolymer, but polymers with branched structures do tend to have higher k' values than linear polymers.

The addition of methanol to a solution of the 2,000atm reaction product in ethyl methyl ketone does not produce as much turbidity as does addition to a similar solution of a polymer mixture. (see table 8 ii and fig. 22) Further, the maximum turbidity for the reaction product in the solvent-precipitant mixture is reached at a higher concentration of precipitant than for the mixture. This indicates that

the polystyrene, which is normally insoluble in methanol has been 'solubilised' to some extent by the reaction, which can only be explained by the production of a graft copolymer with the vinyl acetate.

C) The copolymerisation of styrene and vinyl acetate showed similar characteristics at 4,000atm to those at 1 atm (see table 7 v) Increase in the vinyl acetate content of the feed produced a reduction in the overall rate of reaction. The determination of monomer reactivity ratios is very sensitive to errors in carbon analyses. On the basis of an assumed value $r_B = 0.01$ (B = vinyl acetate) r_A was found to be 32. The error in this value is probably very large. The values found by May et al. at 60°C are $r_A = 55 \pm 10$, $r_B = 0.01 \pm 0.01$.

FIG. 21 STYRENE - POLYETHYLENE GRAFTING RATES.

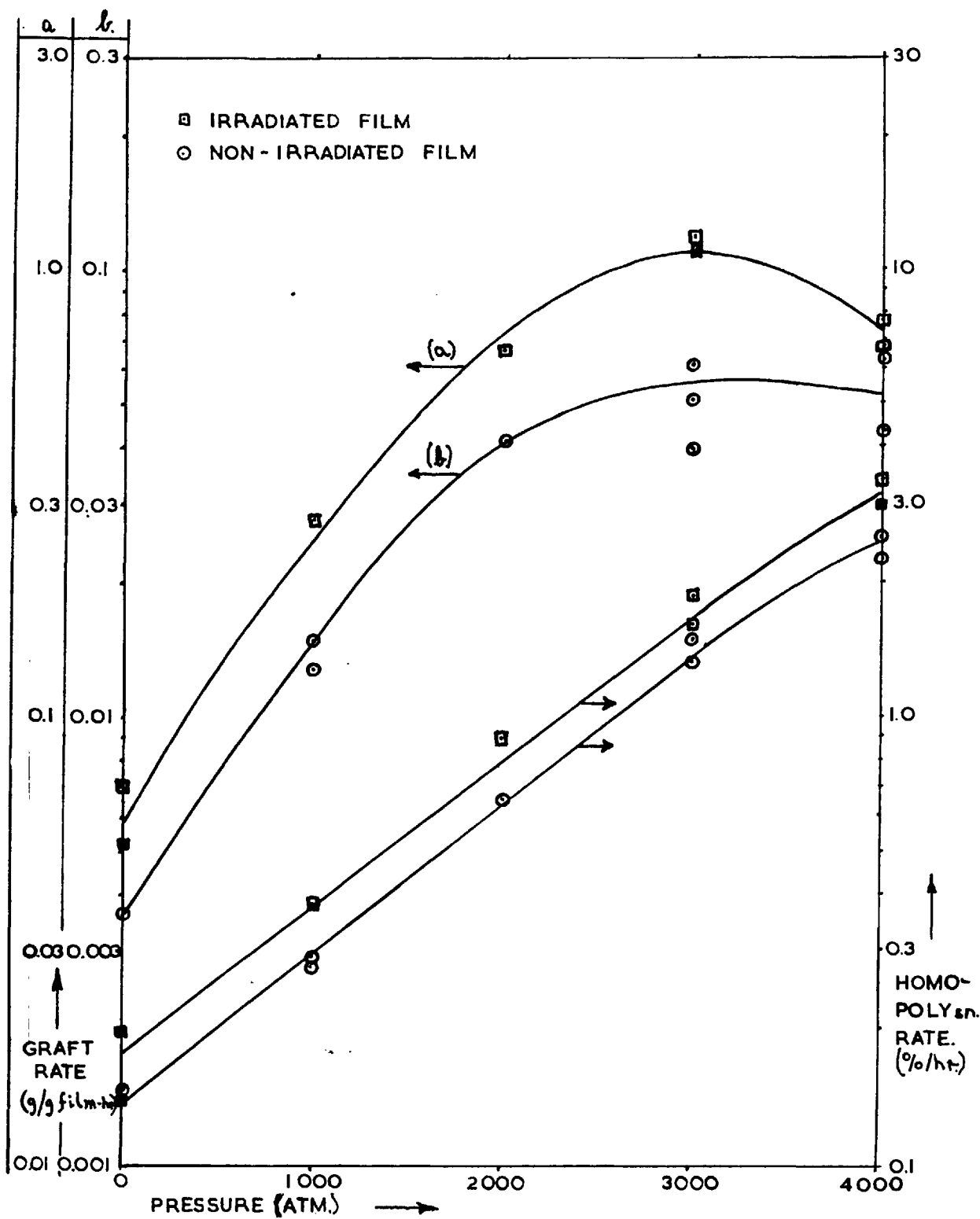
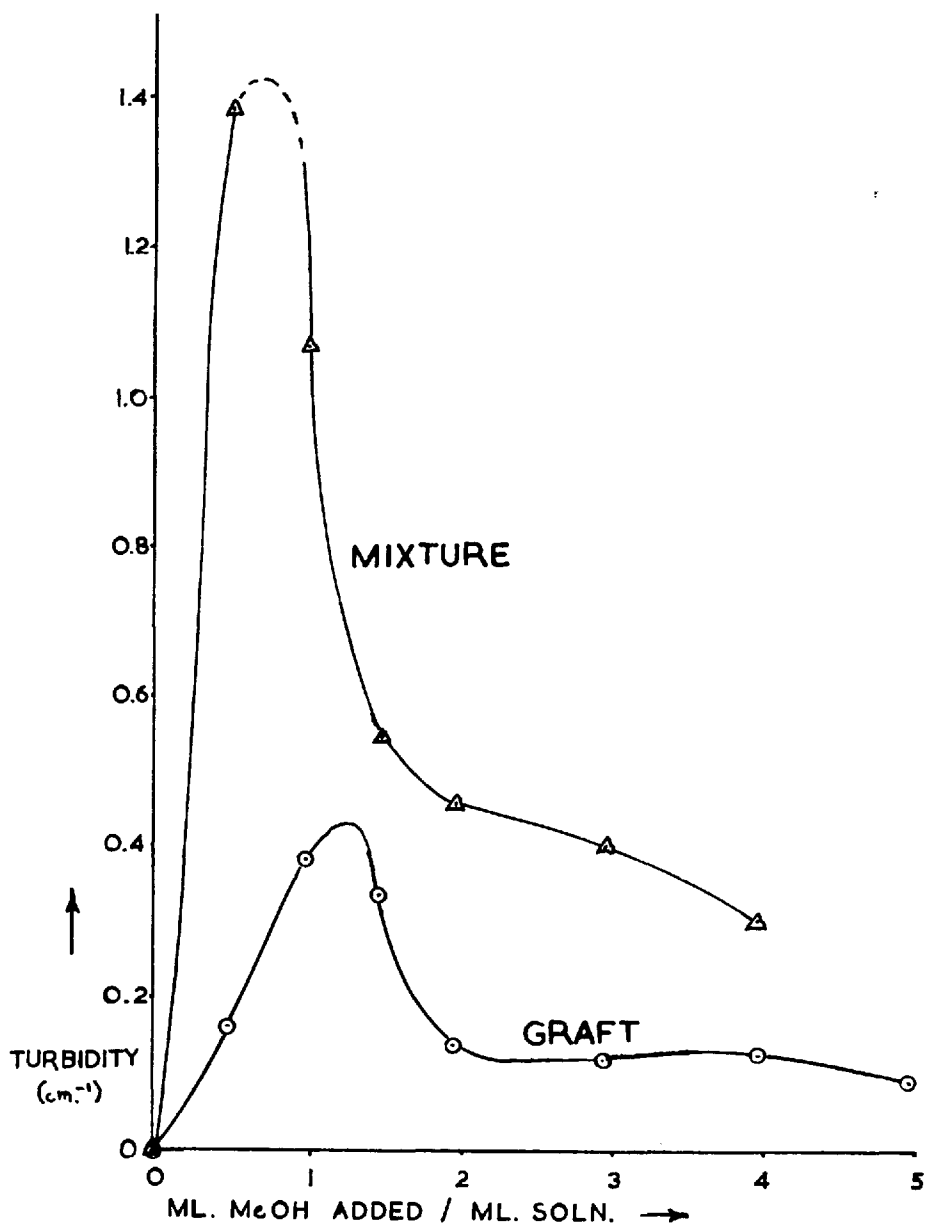


FIG. 22. TURBIDITY OF VINYL ACETATE -
STYRENE POLYMER SOLUTIONS



PART IV.Discussion.

Two main factors emerge from this study of graft copolymerisation. Firstly, some vinyl monomers polymerise readily in systems containing high polymer peroxides to give graft copolymer products, and secondly, pressure increases the rate of graft copolymerisation. It was also found that high pressures did not overcome the steric hindrance caused by the presence of chlorine in substituted ethylenes.

A) The structure of polymers.

Irradiated polyethylene film after immersion for some time in the monomers styrene or methyl methacrylate showed weight increases of several percent. This weight increase could have been produced by the homopolymerisation of the monomers within the film but this is considered an unlikely explanation as, even after prolonged soaking in 1:2 epoxypropane which is a good solvent both for polystyrene and for poly(methyl methacrylate), no reduction in the weight of the film was effected. From this it is inferred that the polymer produced during the immersion was chemically bonded to the substrate and not merely physically

mixed with it. This chemical bonding could only occur through the production of a graft copolymer.

Tests with non-irradiated polyethylene also produced some graft copolymer with the above mentioned monomers, possibly due to a reaction initiated by the decomposition of peroxides in the polyethylene film which had been produced by aerial oxidation.

Parallel with the production of graft copolymer some homopolymer was also produced in these systems. Some of this is accountable for by thermal polymerisation in the styrene system but more is produced in both systems when grafting occurs to a greater extent. Some homopolymer must therefore arise as a result of the grafting reaction and is probably produced as a result of monomer transfer.

In the presence of the chloroethylenes perchloroethylene, trichlorethylene and cis and trans 1:2 dichlorethylene irradiated polyethylene showed no increase in weight indicating that no grafting took place. The steric hindrance caused by the chlorine atoms would account for this as these compounds also defy all attempts to produce high molecular weight homopolymers from them. An alternative explanation is that the monomer transfer constants for these

monomers are so high that no high molecular weight products are obtained. This explanation is less acceptable as there is no large quantity of oily residue of low molecular weight polymers found in the liquid phase after maintaining these monomers for considerable lengths of time under conditions where polymerisation has been shown to take place.

The reason why practically no graft copolymerisation of vinylidene chloride onto polyethylene took place is not very clear. The monomer has a reactivity comparable with that of styrene and molecular models show that there should be no steric hindrance to the grafting reaction. There is a possibility that the strongly electronegative oxygen substituent on the polyethylene chain causes an unfavourable orientation of the vinylidene chloride so that the possibility of an addition reaction is reduced.

Evidence has been put forward to show that vinyl acetate can be grafted onto irradiated polystyrene. Attempts to graft this monomer onto polystyrene by other free radical mechanisms have been unsuccessful. This is probably due to the low reactivity of the polystyryl radicals caused by resonance stabilisation and the low reactivity of vinyl acetate monomer.

This phenomenon gives rise to the very high (≈ 55) reactivity ratio for styrene and the low value (≈ 0.01) for vinyl acetate when these two monomers are copolymerised. When irradiated polystyrene is used as the substrate resonance stabilisation of the polystyryl radicle is no longer possible as the radicle is of the etheric form $\text{C}_6\text{H}_5.\overset{\text{O}\cdot}{\underset{\text{O}}{\text{C}}}$ instead of being a substituted methyl radicle $\text{C}_6\text{H}_5.\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\cdot$, enabling the graft reaction to take place more easily.

The tests on the copolymerisation of styrene and vinyl acetate at 4,000atm. indicate that the reactivity of polystyryl radicles is not very greatly affected by pressure. This further indicates that the graft reaction takes place through the agency of polystyrene-oxy radicles and not polystylyl radicles.

B) Reaction Rates.

The only system from which reproducible rate data were obtained was styrene - polyethylene. The absence of reaction of methyl methacrylate with non-irradiated polyethylene and the apparent randomness of the rates with irradiated film indicate that some reaction may take place in this system to produce a polymerisation inhibitor or retarder.

High pressure should show the same effects as outlined in the first part of this thesis and should affect i) reaction rate constants according to the magnitudes of the respective activation volumes, ii) diffusion rates, iii) concentrations and iv) possibly overcome some degree of steric hindrance;

i) The effect of pressure on the reaction rate constants k_p , k_{fm} , k_t and k_{tr} , should be the same as in the corresponding homopolymerisation of the monomer M. as the reactions will proceed via the same transition states and therefore have the same volumes of activation. The decomposition of initiator should have a $\Delta V^\ddagger$ corresponding approximately to a 10% stretching of the dissociating bond without change in the molecular cross-section.⁽⁸¹⁾

ii) The process of diffusion of a fluid through a rubber or other thermoplastic material is considered to take place by dissolution of the fluid in the surface of the solid followed by a liquid-type diffusion of the solute molecules through 'holes' in the solid. These holes occur through the thermal vibrations of the polymer chain segments.⁽⁸⁶⁾ The diffusion within the polymer is assumed to obey Fick's law and D , the diffusivity, has an energy of activation, E_d , in

common with other rate processes and is given by the relation $D = D_0 \exp(-E_d/RT)$ (43)

where D_0 is a temperature independent factor.

Barrer⁽⁸⁷⁾ has pointed out that viscous flow of polymers is also considered to take place by a 'hole' mechanism and the activation energies for the viscous flow of rubbers are of the same order as E_d (about 10kcal.) for these materials.

No work has been published on the effect of pressure on diffusion rates of liquids or gases in solids although liquid-liquid systems have received some attention as have the self diffusion rates of some solids at high pressures.^(83,84,85) For self diffusion it has been found that pressure has an effect corresponding to an activation volume

$$\Delta V^\ddagger = -RT \partial \ln(D/\nu d_i^2) / \partial P \quad (44)$$

where ν is a characteristic frequency related to the thermal motion of the molecules and d_i the equilibrium lattice distance. $\Delta V^\ddagger$ is found to be almost half the molar volume of the elements in question, that this diffusion process takes place by a hole mechanism in which there is some relaxation of crystal structure around the hole.

From the above considerations it seems, then,

that increase in hydrostatic pressure should cause a decrease in the rate of diffusion of a monomer through an insoluble polymer.

iii) The solubility of monomer in the polymer will be affected by pressure in a manner depending on whether the dissolution causes a net increase or decrease in the volume of the system. Ideally the volume change is zero and in most real cases the volume change is small where the solute and solvent are chemically similar, so that the pressure effect on solubility should not be great.

The direct effect of pressure on concentration, as distinct from the effect on diffusion rates, is probably small, consisting of a slight enhancement of solubility if there is a slight decrease in volume on dissolution or a reduction if there is a volume increase, coupled with a slight increase in concentrations due to the compression of the system.

iv) It has been mentioned earlier that pressure does not overcome large degrees of steric hindrance so that perchlorethylene, and maleic anhydride do not polymerise to any appreciable extent even at pressures as high as 4,000atm. and above. It is to be expected, then, that pressure should not have any

remarkable effect on the polymerisability of vinyl compounds which show large degrees of steric hindrance when attempts are made at graft copolymerisation.

The increase in the rate of production of homopolymer with pressure in the styrene system is comparable with increases found for this monomer under other conditions, which indicates that the effect may be accounted for by a negative overall activation volume for this process. The slope of the $\ln(\text{homopolymerisation rate})$ v. pressure plot is slightly steeper than that found for the benzoyl peroxide initiated reactions. This may well be because the activation volume is less positive for thermal initiation than for peroxide catalysed initiation.

The initial slope of the $\ln(\text{graft rate})$ v. pressure plot is steeper than that of the homopolymerisation rate curve, although this polymerisation is initiated by a decomposition reaction which should be retarded by pressure. This may be accounted for by the fact that the mobility of the growing polystyrene chains in the polyethylene film is severely restricted so that the termination reaction is retarded by pressure which reduces the chain mobility. The termination rate is therefore lower than in the liquid phase.

Increase in pressure would therefore increase the lifetime of the growing radicals and thus tend to increase the overall rate.

At pressures above 2,000atm. the tendency of grafting rate to increase with pressure is less marked. It may be that above 2,000atm. the viscosity of the medium is increased to such an extent by pressure that the mobility of the monomer in the polymer film is reduced sufficiently for monomer diffusion to become the controlling factor in the propagation step. In the regime of full diffusion control of the propagation reaction, increase of pressure reduces the availability of monomer to the growing chains by increasing the viscosity of the medium so that the propagation rate is reduced. These conditions are realised at pressures above about 3,000atm. in this system.

PART VTables of ResultsTable 7.

i(a) Irradiated polyethylene-styrene reactions
at 60°C. Pre-dose; 8Mrad.

Press	Time	Wt. of	Wt. of	Film	Homopolymer	Graft	Homo-
		Monomer	before	after	sample	ppt.	rate
atm.	hr.	g.	g.	g.	g.	g.	g/ghr. %/hr.
1	7	5.356	.1279	.2404	1.9878	.0469	.052 .139
1	17	5.226	.1281	.1908	1.6413	.0299	.070 .199
1,000	5.5	5.249	.1274	.3224	1.9976	.0424	.276 .386
2,000	3	5.320	.1359	.3922	1.8907	.0507	.626 .890
3,000	1	5.372	.1228	.2678	2.3141	.0440	1.18 1.90
3,000	1.5	5.253	.1358	.3632	1.2980	.0256	1.12 1.32
4,000	0.675	5.324	.1385	.2000	2.4540	.0544	.771 3.33
4,000	1	5.276	.1203	.2139	1.6502	.0476	.667 2.88

i(b) Blank polyethylene - styrene reactions
at 60°C.

Press	Time	Wt. of	Wt. of	Film	Homopolymer	Graft	Homo-
		Monomer	before	after	Sample	Ppt.	Rate
atm.	hr.	g.	g.	g.	g.	g.	g/ghr. %/hr.
1	20.2	5.259	.1372	.1475	2.2050	.0663	.0036 .149
1,000	18.3	5.463	.1332	.1639	2.0126	.1030	.0127 .280
1,000	20.8	5.488	.1426	.1860	1.2974	.0765	.0146 .284
2,000	21	5.128	.1332	.2490	0.6354	.0887	.0413 .666
3,000	1.5	5.2710	.1315	.1393	3.1220	.0786	.0396 1.68
3,000	3.1	5.267	.1382	.1642	2.0032	.0912	.0613 1.49
3,000	4.7	5.258	.1380	.1711	0.7427	.0518	.0514 1.49
4,000	1	5.323	.1344	.1432	2.5510	.0568	.0654 2.23
4,000	2.8	5.378	.1316	.1474	1.5882	.1110	.0437 2.54

ii(a) Irradiated polyethylene - methyl methacrylate reactions at 60°C. Pre-dose; 8 Mrad.

Press	Time	Wt. of Monomer	Wt. of Film Before	Wt. of Film After	Homopolymer Sample	Graft Ppt.	Homo- Rate	Homo- Rate
atm.	hr.	g.	g.	g.	g.	g. g/ghr.	%/hr.	
1	3.0	5.750	.1315	.1956	3.9090	.0260	.163	2.22
1	1.0	5.423	.1226	.1225	5.3850	trace	-	-
1	4.4	5.623	.1322	.9212	0.3066	.0111	1.36	.823
1,000	1.0	5.627	.1435	.1698	4.4651	.0443	.183	.993
1,000	1.7	5.792	.1379	.2054	2.9548	.0357	.228	.711
1,000	3.0	5.528	.1295	.4748	0.3230	.0099	.888	1.02
2,000	1.0	5.687	.1373	.1870	1.5472	.0618	.362	3.99
2,000	2.0	5.701	.1249	.2028	0.3847	.0131	.312	1.70
3,000	0.5	5.722	.1366	.1419	4.4385	.0134	.077	.604
3,000	1.1	5.590	.1307	.1578	1.9920	.0372	.189	1.70
3,000	1.5	5.636	.1352	.1707	1.6811	.0488	.175	1.93
4,000	0.5	5.709	.1280	.1414	1.4109	.0281	.209	3.98
4,000	1.0	5.625	.1385	.1650	1.0940	.0320	.191	2.92

ii(b) Blank polyethylene - methyl methacrylate reactions at 60°C.

Press	Time	Wt. of Monomer	Wt. of Film before	Wt. of Film After	Homopolymer Sample	Graft Ppt.	Homo- Rate	Homo- Rate
atm.	hr.	g.	g.	g.	g.	g. g/ghr.	%/hr.	
3,000	0.5	5.737	.1388	.1386	4.860	0	0	0
3,000	1.5	5.750	.1315	.1316	4.692	0	0	0
4,000	3.0	5.692	.1391	.1391	4.588	0	0	0
4,000	6.0	5.718	.1362	.1361	4.983	0	0	0

iii. Irradiated polyethylene - chloroethylene reactions. Pre-dose; 8 Mrad.

Monomer	Temp. °C.	Press. atm.	Time. hr.	Grafting g/g film -hr.	Homopolymer %/hr.
$\text{CCl}_2=\text{CCl}_2$	60	1,000	16	nil	nil
	60	3,000	7	"	0.005
	60	3,000	24	"	0.004
	80	4,000	48	"	0.006
$\text{CCl}_2=\text{CHCl}$	60	4,000	24	nil	0.005
	70	5,000	48	"	0.004
$\text{CHCl}=\text{CHCl}$ (cis)	55	3,000	22	"	0.005
	75	5,000	48	"	0.002
$\text{CHCl}=\text{CHCl}$ (trans)	50	5,400	21	nil	0.038
	55	3,000	24	"	0.039
$\text{CH}_2=\text{CCl}_2$	45	1	4.75	Nil	0.063
	45	3,000	2.25	"	1.11

iv. Irradiated polystyrene - vinyl acetate reactions at 60°C. Pre-dose 58 Mrad.

Press	Time	Wt. of Monomer	Wt. of Film	Wt. of Sample	Solids	Ppt in MeOH: E.M.K	Ppt in Water	Theor PolyS	Wt. PVAc. /g. film -hr.
atm.	hr.	g.	g.	g.	g.	g.	g.	g.	-
1	47	5.828	.4210	4.7424	.3334	.2286	.0844	.3425	trace
2,000	50	5.410	.3909	5.0884	.4600	-	-	.3675	.005
4,000	6	5.684	.1852	-	.0679	.0693	trace	-	-
4,000	22	5.390	.3637	5.1310	.5766	trace	.5760	.3460	.030
8,360*	2	3.685	.4092	2.3832	.3618	.1025	.2588	.2645	.184

*The temperature here was 68°C.

Table 7.v.

Copolymerisation of Styrene (A) and Vinyl Acetate
(B) at 60°C. using 0.1 mole % Benzoyl Peroxide.

Mole frn. A in feed	Reaction Time (min.)	Wt.% Poly.	Rate (%/hr)	%C in Poly.	Mole frn. A in Poly.
0.1668	60	3.04	3.04	88.92	0.8743
0.4443	30	4.94	9.88	91.88	0.9693
0.7602	38	10.27	16.2	92.43	0.9881

From these results, assuming $r_b = 0.01$, $r_a \approx 35$
c.f. Mayo et al.⁽⁹⁵⁾ $r_b = 0.01 \pm 0.01$, $r_a = 55 \pm 10$

Table 8.

i). Viscosity tests in benzene at 30°C.

Solute	$[\eta]$	k'
A. Graft copolymer prepared at 60°C, 2,000atm.	0.82	0.38
B. Irradiated polystyrene	0.67	0.32
C. Poly(vinyl acetate) prepared at 60°C, 2,000atm.	0.92	0.20
D. Mixture of B and C above with composition as A.	0.84	0.22

ii). Turbidity tests.

Wavelength 700m μ . Light path 1cm.

a) Graft copolymer solution as in A above;
0.2000g/100ml. ethyl methyl ketone.

Ml. MeOH added per ml. soln.	Transmissivity, T (arbitrary units)	T_0/T	Turbidity, (cm ⁻¹)
0	104.8	1	0
0.5	88.7	1.180	.165
1	71.6	1.465	.382
1.5	74.9	1.400	.336
2	91.8	1.142	.133
3	93.3	1.123	.116
4	92.6	1.132	.124
5	96.5	1.087	.083

b) Polymer mixture as in D above; 0.2000g/100ml.
ethyl methyl ketone.

Ml. MeOH added per ml. soln.	Transmissivity, T (Arbitrary units)	T_0/T	Turbidity, (cm ⁻¹)
0	99.2	1	0
0.5	25.0	3.97	1.38
1	34.0	2.92	1.07
1.5	57.6	1.72	0.543
2	62.7	1.58	0.458
3	66.5	1.49	0.400
4	73.7	1.35	0.298

Conclusion.

It is required that the candidate for a Ph.D. degree should indicate clearly how his work has contributed to knowledge of the subject. Listed below, therefore, are the main facts which have been noted in the course of this work.

1. The rate of free radicle vinyl copolymerisation is accelerated by increase of pressure.

2. Increase of reaction pressure increases the molecular weight of the polymer products in a manner similar to that found in homopolymerisation studies.

3. Increase of reaction pressure increases the melting points of polymer products in a manner not solely attributable to increase in polymer chain lengths.

4. Pressure has little or no effect on the values of monomer reactivity ratios in the systems studied.

5. The ϕ factor for termination in the styrene - methyl methacrylate system is dependent on pressure and monomer composition.

6. Styrene does not copolymerise with perchlorethylene but perchlorethylene acts as a chain transfer agent where $C_s \approx 6 \times 10^{-3}$ in styrene at 60°C .

7. Pressure does not overcome large degrees of steric hindrance.

8. Pressure accelerates the rate of grafting of styrene onto irradiated polyethylene film in a manner consistent with the idea that diffusion control of the termination and propagation reactions is brought about by high pressure.

9. Methyl methacrylate may be grafted onto irradiated poly-ethylene and vinyl acetate may be grafted onto irradiated polystyrene at high pressures.

10. Chloroethylenes cannot be grafted onto irradiated polyethylene at high pressures under the experimental conditions employed in this work.

The results have been interpreted in terms of the accepted kinetic theories of polymerisation and further evidence has been put forward which is in agreement with the concept that polarisation is of importance in the system styrene-methyl methacrylate which shows a strong alternating tendency.

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