

A THERMODYNAMIC STUDY OF POLYMER COMPATIBILITY

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by

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## ABSTRACT

Calculations show that the Flory equation of state theory can give the same qualitative descriptions of the compatibility behaviour of polymer mixtures as McMaster's modified treatment.

The conventional equations which relate  $\chi$  to the residual chemical potentials cannot be used in the cases where  $\chi$  is concentration dependent.

When the Flory theory is used to calculate the phase boundaries of practical systems, the interaction entropy parameter  $Q_{12}$  is found to play an important role.  $Q_{12}$  may be negative or positive depending on whether the mixture has specific interactions.

The similarity of the equation of state properties of the pure polymers determines the compatibility of polymer mixture in which dispersion forces predominate. The sign of the heat of mixing of oligomeric analogues cannot be guaranteed as an indication of compatibility of polymer mixtures.

A theory for inverse gas chromatography of two-phase blends has been developed. The difference between the specific retention volumes of one-phase and two-phase blends has been considered.

One component used in this study is chlorinated polyethylene which has been prepared by a modified method.  $^{13}\text{C}$ -NMR and differential thermal analysis show that the polymer has a homogeneous chlorine distribution.

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## 1. INTRODUCTION

### 1.1. The significance of the thermodynamic study of polymer mixtures

In recent years the study of compatibility of polymer mixtures has drawn more and more attention. This is because blending polymers is recognised as a good and important method for obtaining new materials in industry. The polymer industry has produced a whole catalogue of products classified as plastics (thermoplastics, elastomers), thermosets, elastomers (rubbers), fibers and coatings. This is a result of fruitful studies on the methods of synthesis and in many cases, on the discovery of new powerful catalysts. The cost of developing new products is large.

Just as copolymerization gives an opportunity to fully use the variety of monomers, polymer blending lets us fully use a variety of polymers. Because of synergism, homogeneous compatible polyblends often have excellent properties. They are also stable. But this does not mean that a partially miscible or incompatible polyblend could not find use. The merit of the tailoring technique of polymer blending is not only in the variety of starting polymers which could be used for blending, but also in the morphological structure which could be created for polyblends. For high impact polymers, a certain range of distribution of rubber particles is needed to form the so-called "island-sea" structure which is particularly useful for absorbing impact energy. Blending methods in industry are relatively simple: in-situ polymerization could be done during production, while mechanical mixing could even be done during processing. The cost of development is low.

The study of compatibility includes many aspects such as the

preparation of polyblends, the relation between structure and property and the thermodynamics and kinetics of phase separation. Among these the thermodynamic study plays a basic role for understanding polymer compatibility. It tells us why the polymers could be mixed and under which conditions the polyblend is stable. It can also explain how the thermodynamic properties of the blend can change upon mixing. These properties are the equation of state parameters such as the density, the thermal expansion coefficient and the thermal pressure coefficient, and the transition temperatures such as the melting point and the glass transition temperature etc.

The thermodynamics of polymer mixtures follows the development of the thermodynamics of polymer solution. In theory, the polymer solution could be considered as a polymer mixture if the degree of polymerization of polymer 1(solvent) is taken as 1. Gee and Treloars' classic work<sup>1</sup> on the measurement of the changes in the thermodynamic functions when mixing rubber and benzene and the Flory-Huggins lattice model theory of polymer solution<sup>2</sup> in the 1940's laid the foundation of this branch of polymer science. In the 1960's Rowlinson's discovery<sup>3</sup> of the lower critical solution temperature(LCST) of certain polymer solutions, studies concerning the concentration dependence of the interaction parameter and a new generation of theories, of which the Flory equation of state theory<sup>4</sup> is a representative, gave a deeper understanding of the subject. Hence, the thermodynamic study of high molecular weight polymer mixture has come after both the mature development of experimental methods for liquid oligomers and the development of theories for the miscibility of high polymers.

The thermodynamic study of polymer mixtures has already led to some inspiring results. Allen, Gee and Nicholson<sup>5</sup> discovered a peculiar

shape (shoulder or two peaks) of the cloud point curve when they studied the oligomeric polystyrene and polysiloxane system. McMaster<sup>6</sup> explained the LCST behaviour of polyblends using the equation of state theory. In order to explain the phase boundaries etc. of practical systems some fundamental problems have been discussed in the literature, such as the energetic and entropic changes between different species in the mixtures<sup>7</sup>, the composition dependence of the interaction parameter<sup>8</sup> and possible changes of the degree of freedom of molecules in the blend<sup>9</sup> etc. Undoubtely these will promote the further study of the subject.

#### 1.2. Methods for studying the thermodynamics of polymer mixtures

For a thermodynamic study we should

a) Determine the phase boundaries of the polyblend, namely, the binodal, the spinodal and the critical point. In practice we often obtain the cloud points at which homogeneous mixtures become turbid. It is believed that the cloud points are inbetween the binodal and the spinodal. The dependence of phase boundaries on pressure can also be measured.

b) Explain the phase boundary and discuss the origins of the compatibility of the system investigated.

There are a number of methods for determining the phase boundary, of which the most common is optical clarity. A compatible homogeneous polyblend is always transparent. Turbidity indicates phase separation because the phase separated particles, which have different refractive indices, scatter light when they reach the dimensions of the wavelength of light. The method has some constraints: Firstly, it needs large enough difference of refractive indices ( $\Delta n$  should be greater than 0.01). Secondly, the phase separated particle should

have a large enough size. Sometimes dynamic mechanical relaxations show two loss peaks but the sample is still transparent<sup>10</sup>. This is because turbidity appears at the latter stage of phase separation. Generally it is believed that dynamic mechanical relaxation can detect the domain structure at molecular level ( $\sim 100\text{\AA}$ ). Whereas the optical wavelength is around  $4000\text{--}8000\text{\AA}$ , so optical turbidity can only detect domain structure at  $0.5\mu$ . Lastly, if two incompatible polymers form a macrolamina, the blend is still transparent. This may happen when casting a film from a solution which is already separated into two layers.

The turbidity experiment is usually carried out by scanning temperature and at the same time observing the optical clarity of blend films or oligomer mixtures directly by eye or by measuring the scattered<sup>11-13</sup> or transmitted light<sup>14</sup>.

Another optical method is thermal optical analysis (TOA)<sup>15</sup>, which observes the relaxation of the stress-strain-induced birefringence in scratches on the surface of the sample. Optical and electromicroscopy as a function of temperature can also be used for observing the phase structure.

Dynamic mechanical relaxation and dielectric relaxation cannot easily be used to determine phase boundaries and are not suitable for giving proof of miscibility in some composition ranges where the  $T_g$  of the homogeneous phase may happen to fall in the two phase region. Usually, however, for practical reasons "one single phase  $T_g$ " is taken as a criterion for miscibility of polymer blends.

Differential thermal analysis (DTA) measures the temperature difference between a sample and a reference during heating at a set rate. Differential scanning calorimetry (DSC) measures the energy

required to keep the sample and the reference at the same temperature during a programmed heating. Both reflect the changes of enthalpy in a sample. Dilatometry measures the volume change of a blend on heating. All these methods are based on changes of properties at the glass transition. In principle, they can only be used to verify the phase structure, but in some cases they can also be used to determine the phase boundary if a series of blends are available which have been carefully annealed at different temperatures beforehand. When determining the phase boundary, the experiment needs to proceed fast enough so that the phase situation of the sample does not change during the test.

In order to search for the origin of compatibility, free energy of mixing and heat of mixing should be measured. Using osmotic pressure (dilute and concentrated solution) and vapour absorption etc. the free energy of mixing over the whole range of composition can be measured accurately for polymer solutions. These methods are impossible for a polymer mixture. In the literature there are two indirect methods suggested for polymer mixtures. These are inverse gas chromatography<sup>16</sup> and vapour absorption<sup>17</sup>. They have to use Hess' s law cycle for the state function. By subtracting the free energy of mixing of the polymer and solvent, that of the two polymers is obtained. The methods are, however, not very accurate.

For determining the heat of mixing of oligomers the heat can be measured directly by calorimetry. But for polymer mixtures the heat can only be calculated through Hess'es law, if the heats of mixing of polymer/solvent and blend/solvent are measured separately.

The excess volume of mixing is also a measure of the strength of interaction between two mixed species. Using the Flory equation of

state theory, the interaction energy parameter  $X_{12}$  can be estimated. The change of volume on mixing<sup>18</sup> or the density of polyblends<sup>19</sup> can be measured. Small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) can also be used to measure the dimensions of the polymer chain or the second virial coefficient and from these one may deduce the interaction parameter using solution theory.<sup>20</sup>

Another method of studying the systems is Fourier transform infrared spectroscopy (FTIR). Here a particular thermodynamic parameter is not measured but the interactions between groups on different chains is observed by the band shifts of these groups. Research<sup>4</sup> shows that in many cases a specific interaction is the driving force to form compatible blends.<sup>21</sup>

In order to explain the phase boundary, there are two methods. The equation of state model requires parameters such as the thermal expansion coefficient, the thermal pressure coefficient, the density and an interaction parameter between two polymers. The theory successfully explains the occurrence of an LCST as well as an upper critical solution temperature (UCST), it gives qualitative conclusions about the dependence of the phase boundary on molecular weight and molecular weight distribution, the equation of state parameters, the interaction parameter and pressure etc. The Flory-Huggins model requires an interaction parameter but only explains the occurrence of a UCST. This theory has been adapted by Koningsveld<sup>8</sup> to explain some peculiar shape of the cloud point curves of oligomer mixtures.

The experimental study of phase equilibrium in polymer mixtures is more difficult than in polymer solution or solutions of low molecular weight compounds. Extremely slow diffusional processes limit the attainment of equilibrium in the phase separation process.

Traditional methods of measuring phase boundaries, free energies of mixing and heats of mixing etc. are not applicable to polymer mixtures. One way to overcome this difficulty is by studying oligomeric pairs<sup>5</sup>. These compounds have similar thermodynamic properties to polymers but their mobility makes it possible to measure phase diagrams, phase volumes, heats of mixing etc. accurately and directly. Owing to the large combinatorial entropy of low molecular weight compounds, an LCST may not be found in these systems. We believe that this will not influence their usefulness as a model to simulate the behaviour of polymer mixtures. Both the UCST and LCST are a result of a combination of three contributions: combinatorial entropy, equation of state terms and the interaction parameter. Information about these contributions obtained from oligomer systems should be useful for the study of chemically similar systems of high molecular weight.

In order to separate the factors influencing compatibility, studies of mixtures with continuing change of chemical structures are preferred. As summarized in Koningsveld's lecture<sup>22</sup>, these mixtures are

a) mixtures of homopolymers consisting of chemically identical monomers, but differing in molecular weight distribution (chain length compatibility).

b) mixtures of homopolymers differing in the chemical constitution of their monomers. One monomer has a continuous change of structure, for instance, the change of concentration of a polar group in the monomer.

c) random copolymer/homopolymer mixtures.

d) mixtures of random copolymers built up of the same two monomers, but differing in composition.

The choice of systems, the experimental approach and the choice of theoretical models must all be combined to produce a successful outcome for the work.

### 1.3. The problems to be studied in this work

This work concentrates on some basic problems of the thermodynamic study of polymer mixtures rather than on any particular system. These are:

#### 1.3.1. The interaction parameter $\chi$ in the Flory equation of state theory

One of the purposes of the Flory equation of state theory is to improve the calculation of the interaction parameter  $\chi$ . In the Flory-Huggins lattice model theory  $\chi$  is defined as

$$\chi = z\Delta w_{12}r_1/kT \quad 1)$$

where  $z$  is the lattice coordination number,  $\Delta w_{12}$  is the change in energy for the formation of an unlike contact pair and  $r_1$  is the number of segments in species 1. It can be seen from the definition that  $\chi$  has no composition dependence and is purely a monotonic descending function of temperature. If a solution is athermal ( $\Delta w_{12}=0$ ), it also predicts that  $\chi$  should be zero. Experiments do not verify these predictions. In fact, the value of  $\chi$  is typically in the range 0.3-0.5 at the limit  $\phi_2=0$  (extremely dilute solution), even for nearly athermal solution. In polymer solution  $\chi$  usually increases with concentration, and in many cases the change is large. The disagreement of the theoretical  $\chi$  with experimental values influences the prediction of solution properties.

$\chi$  is originally related to the heat of mixing in the equation for the free energy of mixing

$$\Delta G_m = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi n_1 \phi_2) \quad 2)$$

where  $n_i$  is the molar number and  $\phi_i$  is the volume fraction

of component  $i$ . With successive modifications  $\chi$  has been used to contain all the contributions except for the combinatorial entropy.  $\chi$  is empirically related to the free energy of mixing. Now the problem is how to explain the new  $\chi$ .

The Flory equation of state theory explained  $\chi$  in terms of the equation of state properties of pure substances as well as their interactions. The equations for  $\chi$  in the theory will be discussed later. It is found that the theory has an inherent difficulty in that it produces two concentration dependences of  $\chi$  if calculated from both the solvent and solute residual chemical potentials. This casts some doubts on the usefulness of the equations used for  $\chi$ .

### 1.3.2. A comparison of the Flory theory in the original form with McMaster's treatment

Flory first applied the equation of state theory to the study of phase equilibrium<sup>23,24</sup>. The equations for the binodal, spinodal and critical point were derived at atmospheric pressure. Phase boundaries were calculated for hydrocarbon/perfluorocarbon mixtures. The thermodynamic mixing functions for the polymethylene/polyisobutylene system were calculated on the basis of the characteristic parameters for the respective pure components derived from their equation of state coefficients. They concluded that the positive free energy of mixing signified mutual incompatibility of these polymers at equilibrium.

McMaster modified the Flory theory by introducing a term  $(2\pi m_i kT/h^2)^{\frac{3}{2}} N_i r_i^c$  in the partition function such that<sup>6</sup>

$$Z_i(T,V) = Z_{int}(T) (2\pi m_i kT/h^2)^{\frac{3}{2}} N_i r_i^c q_i \quad 3)$$

where

$$Q_i = Q_i(\text{comb}) \left\{ 4\pi/3 \left[ \gamma_i (v_i^{\frac{1}{3}} - v_i^{*\frac{1}{3}})^3 N_i r_i c_i \right] \right\} \exp(-E_i(0)/kT) \quad 4)$$

In Eq.3  $Z_{\text{int}}(T)$  is the partition function for intramolecular rotation and vibration. These motions are functions of temperature only essentially unaffected by neighbours in the liquid, and, hence, do not enter into the equation of state.  $Q_i$  has the usual meaning as in the Flory theory, that is, the contribution of the combinatorial entropy, the equation of state parameters and the interaction, respectively, as expressed in Eq.4. The extra term introduced is the partition function of translational motion of independent particles with mass  $m_i$ .  $m_i$  is defined as the molecular weight of a segment.  $r_i$  is the number of segments in a polymeric chain.  $c_i$  is the external degrees of freedom,  $c_i < 1$ .  $r_i c_i$  means that the chain can be regarded as  $r_i c_i$  independent particles undergoing translational motion.

McMaster thought that the external or intermolecular degrees of freedom would comprise the lower frequency modes in the isolated molecule. These modes are subject to weaker intramolecular potentials so that interactions with neighbouring chain segments dominate. The weaker intramolecular potentials can be disregarded or treated as effective translational motions.

McMaster's treatment convincingly shows that the equation of state theory is a powerful theoretical model in the study of polymer compatibility. When we apply his treatment to our systems, however, some problems arise. These are:

a) Owing to the assumption of equal core volume,  $v^* = v_1^* = v_2^*$  in the Flory theory,  $m_i$  should have relation

$$m_1 v_{\text{sp1}}^* = m_2 v_{\text{sp2}}^* \quad 5)$$

It cannot arbitrarily assumed that both  $m_1$  and  $m_2$  are the molecular weights of the monomeric segments, as was done in McMaster's paper.

b) In his treatment the contribution of the translational motion term to the free energy of mixing is given by

$$\frac{(2\pi m_1 kT/h^2)^{\frac{3}{2}N_1} r_1 \bar{c} (2\pi m_2 kT/h^2)^{\frac{3}{2}N_2} r_2 \bar{c}}{(2\pi m_1 kT/h^2)^{\frac{3}{2}N_1} r_1 c_1 (2\pi m_2 kT/h^2)^{\frac{3}{2}N_2} r_2 c_2} \quad 6)$$

The numerator is the partition function of the mixture, the denominator is the partition function before mixing. It is assumed that both components have the same  $\bar{c}$  value in the mixture. This means that after mixing all the molecular chain will have the same flexibility no matter how much difference existed between their original  $c_i$  values. It is admitted that because of interactions the mixed components will change their flexibility, but it can hardly be imagined that these chains should have the same  $\bar{c}$  value. The parameter  $c$  in fact reflects the flexibility of the polymeric chain. Beret and Prausnitz<sup>25</sup> discussed the relation between the steric factor  $\sigma$  and the external degrees of freedom  $c$  and obtained

$$3rc = [(r-3)/\sigma] + 6 \quad 7)$$

$$\sigma = (\langle r_0^2 \rangle / \langle r_f^2 \rangle)^{\frac{1}{2}} \quad 8)$$

where  $\langle r_0^2 \rangle$  and  $\langle r_f^2 \rangle$  are the dimension of the polymeric chain in the unperturbed and freely rotating state, respectively. In a statistical theory of polymer solutions Prigogine<sup>26</sup> assumed that  $c_1$  and  $c_2$  remained unchanged after mixing so that this term had no contribution to the free energy of mixing, whereas in McMaster's theory this contribution is relatively large.

c) Since the temperature and volume are fixed in the ensemble of systems under consideration, the Helmholtz free energy  $\Delta F_m$  results from the partition function. When deriving the chemical potential a derivative  $(\partial \tilde{v} / \partial N_1)_{T, V, N_2}$  is needed.

$$\Delta \mu_1 = (\partial \Delta F_m / \partial N_1)_{T, \tilde{v}, N_2} + (\partial \Delta F_m / \partial \tilde{v})_{T, N_1, N_2} (\partial \tilde{v} / \partial N_1)_{T, V, N_2} \quad 9)$$

Sanchez<sup>27</sup> pointed out that this derivative was incorrectly evaluated in McMaster's paper because he calculated  $(\partial \tilde{v} / \partial N_1)_{T,P,N_2}$  rather than  $(\partial \tilde{v} / \partial N_1)_{T,V,N_2}$ .

Therefore, the phase boundaries have been rederived from a complete chemical potential equation in this work (without omitting the pressure term as was done in Flory's paper<sup>23</sup>). The dependence of the equation of state coefficients on temperature and pressure have also been derived. The equations can be used to discuss the pressure dependence of phase boundaries and should reduce to the equations given by Flory at atmospheric pressure.

A comparison between the newly derived equations and McMaster's equations indicates that the Flory theory in the original form is at least as good as McMaster's modified treatment in predicting the compatibility of polymer mixtures.

### 1.3.3. The origins of polymer compatibility

One problem immediately arose on the estimation of the role of the different contributions included in the equation of state theory. Since the combinatorial entropy is small in polymer mixtures, the remaining two factors are the equation of state contribution and the interaction between different species in the mixture. In McMaster's treatment with the assumption  $X_{12}=0$ , where  $X_{12}$  was the interaction energy parameter, the compatibility was discussed with emphasis on the contribution of the equation of state. The calculation predicted that two polymers having molecular weights of  $2 \times 10^5$  (chain length 2000 segments) required a difference in the thermal expansion coefficients of 4% or less in order to have significant mutual solubility. Even at molecular weights as low as  $5 \times 10^4$ , a relative difference of 10% in the thermal expansion coefficients could lead to

virtually complete immiscibility.

Patterson and Robard<sup>28</sup> thought that the effect of free volume on the LCST was exaggerated in McMaster's paper. They considered that a rapid decrease of the specific interaction with increasing temperature in polyblends brought about the LCST, because the balance between the unfavourable free volume effect and the favourable specific interaction at low temperature was broken at high temperature.

In theory, their discussion left two problems to be considered.

a) It is generally recognized that the specific interaction plays a major role in predicting the compatibility of polymer mixtures, but this does not mean that in some cases the equation of state contribution may not play a determining role for compatibility. The problem is how to find the conditions under which the usually less important equation of state contribution becomes important.

b) The Flory equation of state theory only fits experiments qualitatively. The theory probably does not take a correct account of both the equation of state and the interaction contributions. This is especially true in polymer blends where the dispersion forces dominate. Flory and colleagues, however, gave an example in which the thermodynamic mixing functions calculated from the theory were used as a criterion for predicting compatibility for such a system.<sup>24</sup>

In practice, one needs to discuss "similarity" and "dissimilarity" principles in choosing compatible polymer pairs. According to the "similarity" principle the matched polymer pair should have similar chemical structures, their interaction should be small and their equation of state properties should be similar, i.e. the pair should have nearly the same thermal expansion coefficients.

Conversely, the "dissimilarity" principle prefers rather different chemical structures which allows the formation of specific interactions through the functional groups on the matched molecules. Since even the weakest positive dispersion force is large enough to bring about phase separation, the "dissimilarity" principle should give a great probability of finding compatible blends.

In this work four systems have been studied. These are poly(methyl methacrylate) with chlorinated polyethylene (PMMA/CPE), poly(butyl acrylate) with chlorinated polyethylene (PBA/CPE), chlorinated polyethylenes with different chlorine contents (CPE/CPE) and methoxylated poly(ethylene glycol) with methoxylated poly(propylene glycol) (PEGM/PPGM).

The first two systems are known to have specific interactions between CHCl groups in CPE with the oxygen of the carbonyl group in the second polymer. The compatibility study of these two systems is interesting because the interaction between the two species can be changed by adjusting the degree of chlorination of CPE. There have been many attempts to predict the miscibility of PMMA/CPE and related systems, which were summarized by Krause<sup>29</sup>. It is stated that PMMA is incompatible with CPE, the phase boundary behaviour of PMMA with poly(vinyl chloride) is ambiguous (We now know they are compatible according to work in this laboratory<sup>30</sup>), the PMMA with chlorinated poly(vinyl chloride) blend may be compatible or conditionally compatible and the PMMA with poly(vinylidene chloride) blend is incompatible. Hence, it can be seen that a very complicated situation occurs with the variation of chlorine content.

The third system consists of mixtures between different CPEs which are dominated by dispersion forces because no specific

interactions can be formed between the two mixed species. With increasing degree of chlorination CPE changes from a crystalline material to a rubber and then to a glass. The properties of the equation of state parameters are very different for these different materials. The polarity increases with the chlorine content in the polymer. Thus the system provides a unique opportunity to explore the cause of compatibility in polymer mixtures.

There have been previous studies of PEGM/PPGM mixtures. Cooper and Booth<sup>18,31</sup> determined the enthalpy and volume changes on mixing and the cloud point curves. They found that the Flory-Huggins interaction parameter is concentration dependent and attributed this to the differences in the surface to volume ratios of the two components. They also thought that the slight differences in the equation of state parameters such as the thermal expansion coefficient and the thermal pressure coefficient of the two components are the reason for the volume changes on mixing the oligomers. The phase boundaries are explained in terms of the Flory-Huggins theory with a concentration dependent  $\chi$ . Tripathi<sup>32</sup> studied the pressure dependence of the cloud point curve of the system up to 1000 atm. He found a positive pressure dependence of the UCST.

Mixtures with continuous change of chemical structures are extensively used in the study of the four systems. According to Koningsveld's catalogue described previously the first two systems and the third system belong to type c and type d mixtures, respectively, if CPE can be regarded as a copolymer. The last system is the type a mixture where chain length compatibility is concerned.

An analysis of the four systems shows that there are cases in which either the interaction or the equation of state contribution

dominates compatibility behaviour of polyblends, respectively. A negative heat of mixing of an oligomer pair suggests miscibility of the corresponding high polymers while a positive heat of mixing suggests immiscibility, but this is not always true.

#### 1.3.4. Simulation of phase boundaries

In order to make a critical assessment, the theories have been used to simulate the phase boundaries of practical systems. Based on Flory-Huggins' theory, Koningsveld's calculations<sup>33</sup> showed that the location and shape of the phase boundary were dependent on molecular weight, molecular weight distribution and the interaction parameter  $\chi$  etc. Normally, the combinatorial entropy tended to shift the phase diagram towards the composition region in which the constituent with the smaller molecular weight dominates. This results in a regular asymmetric phase diagram. In practice some phase diagrams do not show this effect, the phenomenon is referred to as irregular asymmetry<sup>33</sup>. It was found that the interaction parameter depending on concentration can outweigh this effect. A concentration dependent  $\chi$  with a minimum at a certain concentration used in the adapted Flory-Huggins' theory can explain the bimodality of phase boundaries. The calculations, however, <sup>have been</sup> limited to the UCST behaviour of oligomer mixtures.

Some attempts have been made to apply the equation of state theory to simulate the phase boundaries of polymer mixtures. The success of McMaster's treatment has already been described. The author also tried to apply his treatment to practical systems, which were polystyrene/poly(vinyl methyl ether) and styrene-acrylonitrile copolymer/polycaprolactone mixtures. The experimental data showed far less sensitivity to temperature than the computed curves. The

author attributed this to the inaccuracy of Flory's equation of state for the pure components, the polydispersity of the sample and specific interactions in the systems.

In addition to McMaster's paper, Olabisi<sup>34</sup> tried to simulate the phase boundary for the poly( $\epsilon$ -caprolactone)/poly(vinyl chloride) system. Using the spinodal equation given by McMaster, he found that variations in the exchange energy parameter  $X_{12}$  or the surface area ratio  $S_1/S_2$  led to irregular asymmetry of the critical concentration as well as bimodality of the phase diagram. The condition for generating an irregular asymmetric phase boundary was  $X_{12} < 0$  and  $S_1/S_2 < 1$ .

ten Brinke et al.<sup>9</sup> also found an irregular asymmetric phase diagram for the poly(vinylidene fluoride)/isotactic poly(ethyl methacrylate) mixture. Using the spinodal equation given by McMaster, they found that under the condition  $c_{12} > 0$  and  $m_1/m_2 < 1$ , an irregular asymmetric phase boundary could be computed, where  $m_i$  is the mass of segment and  $c_{12}$  is a quadratic correction coefficient to a linear variation in the number of external degree of freedom. The number of external degrees of freedom per segment in the mixture,  $3c$ , is determined by

$$c = \phi_1 c_1 + \phi_2 c_2 - \phi_1 \phi_2 c_{12} \quad 10)$$

In this work the Flory equation of state theory in the original form has been applied to simulate the phase boundaries of practical systems. Flory's treatment has been shown to be as effective as McMaster's treatment in predicting the compatibility behaviour of polymer mixtures.

The thermodynamic parameters obtained from the heats of mixing and phase boundaries of oligomer mixtures were used as reference

values to calculate the phase boundaries of polymer mixtures. Our purpose is to find the connection between polymer mixtures and their low molecular weight analogues and to explore the characteristics which appear when the theory is applied to the practical systems.

The calculations show that the role of the interaction entropy parameter  $Q_{12}$  is decisive. Without  $Q_{12}$  the theory cannot predict the phase boundary. Further improvement can be made by considering the molecular weight and temperature dependence of the thermodynamic parameters obtained from oligomeric analogues in the calculation.

#### 1.3.5. Inverse gas chromatography (IGC) for the study of one-phase and two-phase polymer mixtures

Because of its convenience and versatility, IGC has found a wide application in polymer research. The technique has been applied to the determination of the first and second order transitions, degree of crystallinity and related physical quantities,<sup>35</sup> to the thermodynamics of polymer solutions<sup>36</sup>, and to the study of polymer compatibility.<sup>37</sup> Recently it was extended to the study of microphase separation phenomenon and domain size in block copolymers<sup>38</sup>.

For the study of polymer compatibility, one important problem is to measure the interaction parameter  $\chi$  between polymer pairs. This can be done by measuring the heat of mixing of oligomers. But the  $\chi_h$  so obtained is only related to the interaction energy. For understanding phase boundaries one needs to measure a  $\chi$  which is related to the free energy of mixing. As discussed in the previous section, vapour absorption and IGC are the two methods for this. Since vapour absorption is a static method which takes a long time to reach equilibrium, the difficulty of maintaining a constant high temperature limits the temperature range of measurements.

IGC is based on observation of the difference of the retention volumes of solvent probes between polymer blends and their pure components. Compatible polymer blends will have a smaller retention volume than the algebraic average of the homopolymers at the corresponding composition. If the blend is phase separated, the retention volume should be the same as the average value.

In this work IGC was studied from a point of view of methodology. The background of the method was examined. A theoretical treatment for two-phase polymer mixtures was developed, which explained the chromatographic properties of phase separated polyblends and, also, provided a theoretical analysis for the microphase separation phenomenon of copolymers. Three compatible systems: PMMA/CPE, poly(ethyl methacrylate)(PEMA)/CPE and PBA/CPE were studied. We used three different columns: a) with packings having polymer blend coatings, b) packed with two mixed packings, each coated with a single polymer and c) packed in series with two single polymers. The columns were run from below to above the phase separation temperatures. Differences of retention volumes between these columns were compared. The results are discussed in terms of the conventional IGC theory and the analysis for phase separated blends which is given in this work.

#### 1.3.6. The microstructure of solution chlorinated polyethylene

The CPE samples were prepared by solution chlorination. Chlorination is a widely used method for modifying polyethylene. The properties of CPE are determined by the degree of chlorination, molecular weight, microstructure of the chain and the technique used for chlorination. The attached chlorine atom destroys the ordered arrangement of the polyethylene chain so that the crystallinity of the polymer decreases. When chlorine content reaches to about 15% by

weight, CPE changes from a crystalline plastic to a typical rubber. The polymer is sticky and tough, and has high elasticity. After containing more than 50% chlorine by weight, CPE becomes hard, the  $T_g$  is above  $35^{\circ}\text{C}$ , the material is a polar plastic.

Chlorination can be carried out in the homogeneous phase (solution) or heterogeneous phase (suspension). In the latter the product usually has a decreasing chlorine distribution from the surface to the core of the suspended particles. If the chlorination proceeds at a temperature lower than the melting point of polyethylene, the crystalline region will not be chlorinated so that the crystallinity of CPE persists up to 56% chlorine content which corresponds to that of poly(vinyl chloride). Solution chlorination is a different technique by which the reaction takes place homogeneously along the dissolved molecular chain. This reaction is easy to handle in the laboratory but difficult industrially because of the technical problems in recovery of solvent and remove of the residual solvent in the product.

There are several reports of the microstructure of CPE<sup>39-42</sup>. The chlorination was shown to be a hindered-type substitution. At low degrees of chlorination most of the substitution takes place at the secondary hydrogen atom position. When the chlorine content exceeds 50%, sequences with more than 4 adjacent methylene groups disappear and the  $-\text{CCl}_2-$  group appears. The sequence distribution is also different between suspension and solution CPE samples.

In this work a modified method for photochlorination of high density polyethylene has been reported. In order to dissolve high density polyethylene thoroughly, chlorobenzene has been used as solvent in case the reaction can proceed at above the melting point

of high density polyethylene. The ordinary inert solvent for chlorination, carbon tetrachloride can only dissolve low density polyethylene at atmospheric pressure and moderate temperature (b.p. of carbon tetrachloride is  $76^{\circ}\text{C}$ ). If this solvent is chosen for high density polyethylene the reaction must proceed at high pressure in order to raise the temperature. This is not convenient for laboratory purposes. Tetrachloroethylene was suggested as solvent for the chlorination of linear polyethylene<sup>43</sup>, but the reaction temperature was around  $100^{\circ}\text{C}$ . The light of a tungsten lamp is acceptable for photo-initiation without the necessity for ultraviolet or fluorescent lamps. The activation energy of the photochlorination appears to be not large in this case.

In order to have a good knowledge of the CPE prepared for the work, the microstructure of CPE has been studied. Various physical properties have been measured. The structure of the chain has been studied using DTA and  $^{13}\text{C}$  high resolution NMR. The results show that the prepared CPE has a more random chlorine distribution than reported in the literature.

## 2. THEORY

### 2.1. Introduction

Classically, the thermodynamic stability of a mixture was considered in terms of the sign of  $\Delta G_m$ , the free energy of mixing. If  $\Delta G_m$  was negative, the mixture was miscible because the free energy of the system decreased after mixing. Now it is known that this is only a necessary condition for miscibility but not a sufficient condition. Many mixtures show partial miscibility while the free energy of mixing is negative over the complete composition range or at least in the phase separation range. The stability of a mixture is also determined by the curvature of  $\Delta G_m$ . In Figure 1  $\Delta G_m$  is a function of temperature and composition. The system at  $T_4$  is miscible in all proportions, it passes through the critical temperature  $T_c$  to the partially miscible range ( $T_1$ - $T_3$ ) although at these temperatures  $\Delta G_m$  is still negative. In the phase diagram of a binary system we have the binodal defined by

$$\Delta\mu_1 = \Delta\mu_1' \quad \text{or} \quad \mu_1 = \mu_1' \quad \text{and} \quad \Delta\mu_2 = \Delta\mu_2' \quad \text{or} \quad \mu_2 = \mu_2' \quad (11)$$

where  $\mu_i$  and  $\mu_i'$  are the chemical potentials of the component  $i$  in the two separated phases, given by

$$\Delta\mu_i = (\partial \Delta G_m / \partial n_i)_{T,P} \quad (12)$$

$$\mu_i = \mu_i^0 + \Delta\mu_i \quad (13)$$

As usual  $\mu_i^0$  is the chemical potential of the pure substance at the same  $T$  and  $P$ , and  $n_i$  is the molar number of component  $i$  in the mixture.

The spinodal is defined by

$$[\partial(\Delta\mu_1/RT)/\partial\phi_2]_{T,P} = 0 \quad (14)$$

and the critical point by

$$[\partial^2(\Delta\mu_1/RT)/\partial\phi_2^2]_{T,P} = 0 \quad (15)$$

where  $\phi_2$  is the volume fraction of component 2 in the mixture.

The spinodal represents the stability limit of a homogeneous system to small amplitude composition fluctuations. In the spinodal  $[\partial(\Delta\mu_1/RT)/\partial\phi_2]_{T,P} < 0$ , so that the system can lower its free energy by demixing into two neighbouring phases. Between spinodal and the binodal the system is metastable. If a composition fluctuation occurs in this region the system will increase its free energy. However the system can decrease its free energy by demixing into two separated phases very different in composition.

The task for the thermodynamic theory of polymer solutions or polymer mixtures is to calculate the theoretical  $\Delta G_m$  and its derivatives with respect to composition.

In this chapter several theories which have been developed in this field will be introduced and the first two problems described in chapter 1 will be discussed, namely, a) the interaction parameter  $\chi$  in the Flory equation of state theory and b) a comparison between Flory's treatment and McMaster's treatment of the equation of state theory.

## 2.2. The Flory-Huggins lattice model theory

Solutions or mixtures are classified into four types according to the heat of mixing and entropy of mixing.

a) Ideal solution

$$\Delta H_m = 0 \quad 16)$$

$$\Delta S_m = -R(n_1 \ln \phi_1 + n_2 \ln \phi_2) \quad 17)$$

b) Athermal solution

$$\Delta H_m = 0 \quad 18)$$

$$\Delta S_m \neq \Delta S_m(\text{ideal}) \quad 19)$$

c) Regular solution

$$\Delta H_m \neq 0 \quad 20)$$

$$\Delta S_m = \Delta S_m(\text{ideal}) \quad 21)$$

d) Irregular solution

$$\Delta H_m \neq 0 \quad 22)$$

$$\Delta S_m \neq \Delta S_m(\text{ideal}) \quad 23)$$

where  $n_1$  and  $n_2$  are molar numbers,  $x_1$  and  $x_2$  are molar fractions. The calculation of  $\Delta S_m(\text{ideal})$  is simply a combination problem in mathematics: in  $N_1 + N_2$  positions  $N_1$  molecules 1 and  $N_2$  molecules 2 are located. The ways of doing this are

$$\Omega = (N_1 + N_2)! / (N_1! N_2!) \quad 24)$$

Using the Boltzmann relation

$$\Delta S_m(\text{ideal}) = k \ln \Omega \quad 25)$$

and with the help of the Stirling approximation

$$N! = (N/e)^N \quad 26)$$

Eq.17 can be derived from Eq.24.

It was soon discovered that polymer solutions were irregular because  $\Delta H_m \neq 0$  and  $\Delta S_m$  was much larger than predicted by Eq.17. In 1941 Huggins<sup>44</sup> and Flory<sup>45</sup> solved this problem independently and simultaneously. Based on the lattice model, they made some assumptions: a) Lattice sites are equal in size for solvent and polymer segment, b) The distribution of segments of a polymeric chain is uniform in the lattice, c) Molecules are randomly distributed in the lattice, and d) Every lattice site has an equal interaction site number  $Z$  with the others, where  $Z$  is the coordination number of the model lattice. Pure liquids and the mixture have the same  $Z$  number.

With these assumptions  $\Delta S_m$  can be calculated. On a lattice of  $N$  ( $N = N_1 + r_2 N_2$ ) sites  $N_1$  solvent molecules and  $N_2$  polymer ( $r_2$ -mer) molecules are located. We first consider  $\nu_{j+1}$ .  $\nu_{j+1}$  is the number of

ways of arranging the (j+1)th polymer molecule on the lattice, after j polymer molecules have already been placed.

$$v_{j+1} = Z(Z-1)^{r-2} (N-rj)^{r-1} / N^r \quad (27)$$

Eq.27 comes from the following argument: the first segment of the (j+1)th molecule can take any one from the remaining (N-rj) sites. The second only has  $Z(N-rj)/N$  sites available, where Z means that the nearest Z sites of the first segment are possible for placing the second segment if they are vacant, while the possibility for vacancy is (N-rj)/N. For the third segment and up to the last segment, the possible sites are  $(Z-1)(N-rj)/N$ . The total number of configurations is

$$\Omega = (1/N_2!) \prod_{j=1}^{N_2} v_j \quad (28)$$

Using the Boltzmann relation and applying Stirling's approximation as before the following equation is obtained.

$$S/k = -N_1 \ln \phi_1 - N_2 \ln \phi_2 + N_2 \{ \ln(rZ) + (r-2) \ln(Z-1) - r + 1 \} \quad (29)$$

where  $\phi_1$  and  $\phi_2$  are volume fractions,  $\phi_1 = N_1/N$  and  $\phi_2 = rN_2/N$ . The term in the brackets is the configurational entropy of the pure polymer which can be designated as  $S_2/k$ , as may be seen by putting  $N_1=0$ . The configurational entropy of the pure solvent,  $S_1/k=0$ , as may be seen by putting  $N_2=0$ . The entropy of mixing is therefore

$$\Delta S_m = -k(N_1 \ln \phi_1 + N_2 \ln \phi_2) = -R(n_1 \ln \phi_1 + n_2 \ln \phi_2) \quad (30)$$

The above derivation can be extended to a solvent which occupies more than one lattice site and the same equation for  $\Delta S_m$  will be obtained.

For calculation of  $\Delta H_m$  the interaction energies of the pure substances are first considered.

$$E_{11} = N_1 r_1 Z (0.5 \xi_{11}) \quad (31)$$

$$E_{22} = N_2 r_2 Z (0.5 \xi_{22}) \quad (32)$$

where  $\xi_{ij}$  is the interaction energy between two monomeric units of

i and j species. For a mixture of  $N_1$  molecules of component 1 and  $N_2$  molecules of 2, the interaction energy is

$$E_{12} = r_1 N_1 Z (0.5 \epsilon_{11} \phi_1 + 0.5 \epsilon_{12} \phi_2) + r_2 N_2 Z (0.5 \epsilon_{22} \phi_2 + 0.5 \epsilon_{12} \phi_1) \quad (33)$$

In the above equation the like and unlike interactions are counted.

The possibility for species 1 to be in contact with species 1 is  $\phi_1$  and with species 2 is  $\phi_2$ , etc. The heat of mixing  $\Delta E_m$  is given by the difference between  $E_{12}$  and  $E_{11} + E_{22}$ .

$$\begin{aligned} \Delta E_m &= E_{12} - (E_{11} + E_{22}) \\ &= Z(N_1 r_1 + N_2 r_2) \phi_1 \phi_2 (\epsilon_{12} - 0.5 \epsilon_{11} - 0.5 \epsilon_{22}) \\ &= Z N_1 r_1 \phi_2 \Delta \epsilon \\ &= n_1 \phi_2 \chi RT \end{aligned} \quad (34)$$

where  $\Delta \epsilon$  is the energy change for forming one contact between 1 and 2,

$$\Delta \epsilon = \epsilon_{12} - 0.5 \epsilon_{11} - 0.5 \epsilon_{22}, \text{ and}$$

$$\chi = Z r_1 \Delta \epsilon / kT \quad (35)$$

$\chi$  is known as the Flory-Huggins interaction parameter. The enthalpy of mixing  $\Delta H_m$  is

$$\Delta H_m = \Delta E_m + \Delta(PV)_m = \Delta E_m + P \Delta V_m + V \Delta P_m \quad (36)$$

where  $\Delta V_m$  and  $\Delta P_m$  are the changes of the volume and pressure of the system during mixing. Usually isobaric processes are discussed so that  $\Delta P_m = 0$ . At atmospheric pressure  $P \Delta V_m$  is much smaller than  $\Delta E_m$ . Hence  $\Delta H_m$  can be approximated to  $\Delta E_m$ .

$$\Delta H_m \cong \Delta E_m = n_1 \phi_2 \chi RT \quad (37)$$

The familiar form of  $\Delta G_m$  is therefore derived.

$$\Delta G_m = \Delta H_m - T \Delta S_m = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi) \quad (38)$$

From the derivation it can be seen that the theory is based on the theories of the regular solutions for small molecules and, hence, bears the features of these theories<sup>46</sup>. The theory grasps the main characteristic of long chain molecules--their flexibility, and the

derived  $\Delta S_m$  can explain the extraordinarily large entropy of mixing. The theory cannot, however, be applied to dilute solutions because assumption 2 does not hold. Neither can it be applied to a system with strong specific interactions because there is a possibility of an ordered structure in the solution.

Applying the theory to phase equilibria, the binodal, the spinodal and the critical point can be obtained using Eqs.11-15.

For the binodal

$$\Delta\mu_1 = \Delta\mu_1' \quad \text{and} \quad \Delta\mu_2 = \Delta\mu_2' \quad (39)$$

where

$$\Delta\mu_1 = RT [\ln\phi_1 + (1-r_1/r_2)\phi_2 + \chi\phi_2^2] \quad (40)$$

$$\Delta\mu_2 = RT [\ln\phi_2 + (1-r_2/r_1)\phi_1 + (r_2/r_1)\chi\phi_1^2] \quad (41)$$

For the spinodal

$$\chi_{sp}/r_1 = \frac{1}{2} [1/(r_1\phi_1) + 1/(r_2\phi_2)] \quad (42)$$

and for the critical point

$$\chi_c/r_1 = \frac{1}{2} (1/r_1^{\frac{1}{2}} + 1/r_2^{\frac{1}{2}})^2 \quad (43)$$

and

$$\phi_{2c} = r_1^{\frac{1}{2}} / (r_1^{\frac{1}{2}} + r_2^{\frac{1}{2}}) \quad (44)$$

In Eqs.42 and 43  $\chi_{sp}$  and  $\chi_c$  are implicit functions of temperature. According to the definition (Eq.35)  $\chi$  is proportional to  $1/T$ , this will result in a very slow change of  $\chi$  over the temperature of phase separation. Hence  $\chi(T)$  must be measured experimentally. In polymer solutions this is done by measuring the dependence of the critical point on the molecular weight<sup>47</sup>. It is assumed that  $\chi$  is composed of a temperature-independent entropy parameter  $k_1$  and a temperature-dependent enthalpy parameter  $\psi_1$ .

$$\chi = \frac{1}{2} - (\psi_1 - k_1) \quad (45)$$

$$k_1/\psi_1 = \theta/T \quad (46)$$

Substitution of Eqs.45 and 46 into Eq.43 yields

$$1/T_c = 1/\theta [1 + 1/\psi_1 (r_1^{1/2}/r_2^{1/2} + r_1/2r_2)] \quad (47)$$

From the measurements of critical points of different molecular weight samples  $\theta$  and  $\psi_1$  can be obtained. Eq.45 then gives the numerical correlation between  $\chi$  and  $T$  for each system.

### 2.3. The Flory equation of state theory

For pure liquids The Flory equation of state theory starts by calculating an approximate partition function for non-attractive molecules. Flory extended Tonk's partition function<sup>48</sup> for a one-dimensional system of  $N$  hard, non-attractive particles arranged on a line of length  $L$  to the three-dimensional case. Tonk's partition function is

$$\Omega = (L - Nl^*)^N / N! \cong (1 - l^*)^N e^{-N} \quad (48)$$

where  $l^*$  is the hard core length of a particle and  $l = L/N$ . Stirling's approximation was used in order to obtain the second expression in Eq.48. Flory's extended equation is

$$\Omega = [\gamma_g e^{\zeta v^*} (\tilde{v}^{1/3} - 1)^3]^{Nrc} \quad (49)$$

where  $v^*$  is the characteristic or hard core volume of a segment,  $v = V/r$ ,  $V$  is the volume of a molecule and  $r$  is the number of segments of the chain molecule.  $\tilde{v}$  is the reduced volume,  $\tilde{v} = v/v^*$ .  $\gamma_g$  is a geometric factor. The parameter  $c$  is introduced such that  $\zeta c$  represents the number of intermolecular degrees of freedom per segment following Prigogine's treatment of the statistics of complicated molecules.<sup>49</sup>

For a system in which there are interactions between molecules, Flory used a "mean" intermolecular attractive energy  $E_0$ ,

$$E_0 = -Nrs\eta/2v \quad (50)$$

where  $s$  is the number of contact sites per segment, which is

proportional to the surface area per segment volume,  $N$  is the number of molecules, and  $-\eta/v$  is the intermolecular energy per contact. Now the partition function should have the form

$$Z = \Omega \exp(-E_0/kT) \quad (51)$$

Defining a reduced temperature as

$$\tilde{T} = T/T^* = 2v^*ckT/s\eta \quad (52)$$

The partition function can be written as

$$Z = \text{const}(\tilde{v}^{\frac{1}{3}} - 1)^{3Nrc} \exp(Nrc/\tilde{v}\tilde{T}) \quad (53)$$

where the constant is independent of  $T$  and  $v$ .

Using

$$P = (kT/Nr)(\partial \ln Z / \partial v)_T \quad (54)$$

the equation of state of a pure liquid is obtained.

$$\tilde{P}\tilde{v}/\tilde{T} = \tilde{v}^{\frac{1}{3}} / (\tilde{v}^{\frac{1}{3}} - 1) - 1/\tilde{v}\tilde{T} \quad (55)$$

where

$$\tilde{P} = P/P^* = 2Pv^{*2}/s\eta \quad (56)$$

The characteristic parameters  $P^*$ ,  $v^*$  and  $T^*$  satisfy the equation

$$P^*v^* = ckT^* \quad (57)$$

It can be seen that the Flory equation of state theory has two important characteristics: a) The calculation of the entropy term  $\Omega$  is connected with the reduced volume  $\tilde{v}$  which changes with temperature and pressure. It reflects the equation of state properties of the substance. b) The parameter  $s$  is involved in the energy term  $E_0$ . Every component has its own  $s$  value. This is contrary to the Flory-Huggins theory where the same value of the coordination number  $Z$  is assigned to each of the components in solution.

If random mixing is assumed, the partition function for a binary liquid mixture can be written as

$$Z = Z_{\text{comb}} \Omega \exp(-E_0/kT) \quad (58)$$

where  $Z_{\text{comb}}$  is the combinatorial factor for intermixing the two components. Segments of both molecules in the mixture are arbitrarily chosen to be of equal core volume. Flory suggests that this choice is not restrictive inasmuch as  $\Omega \exp(-E_0/kT)$  does not depend on the geometry and the disposition of the molecules. The partition function for the mixture is therefore

$$Z = \text{const} Z_{\text{comb}} (\bar{v}^{\frac{1}{3}} - 1)^{3\bar{r}N\bar{c}} \exp(-E_0/kT) \quad (59)$$

where

$$N = N_1 + N_2 \quad (60)$$

$$\bar{r} = (r_1 N_1 + r_2 N_2) / N \quad (61)$$

$$\bar{c} = (r_1 N_1 c_1 + r_2 N_2 c_2) / \bar{r} N \quad (62)$$

Consider the equal core volume as described above, from Eq.61 the core volume relation is derived.

$$\bar{r} N v^* = r_1 N_1 v_1^* + r_2 N_2 v_2^*, \quad \text{with } v_1^* = v_2^* = v^* \quad (63)$$

Now if we redefine  $\phi_1$  and  $\phi_2$  as the segment fractions instead of the volume fractions in the Flory-Huggins theory,

$$\phi_2 = 1 - \phi_1 = r_2 N_2 / \bar{r} N \quad (64)$$

Eq.62 can be rewritten as

$$\bar{c} = c_1 \phi_1 + c_2 \phi_2 \quad (65)$$

The energy  $E_0$  of the mixture takes the form of that for a pure component, i.e.

$$-E_0 = (A_{11} \zeta_{11} + A_{22} \zeta_{22} + A_{12} \zeta_{12}) / v \quad (66)$$

where  $A_{ij}$  is the number of  $i, j$  contacts, each contact being characterized by the energy  $-\zeta_{ij}/v$ . We then have

$$2A_{11} + A_{12} = s_1 r_1 N_1 \quad (67)$$

$$2A_{22} + A_{12} = s_2 r_2 N_2 \quad (68)$$

For a random mixture

$$A_{12} = s_1 r_1 N_1 \theta_2 = s_2 r_2 N_2 \theta_1 \quad (69)$$

The intermolecular energy can be written as

$$-E_0/\bar{r}N = (\theta_1 \gamma_{11} + \theta_2 \gamma_{22} - \theta_1 \theta_2 \Delta \gamma)(s/2v) \quad (70)$$

where

$$\Delta \gamma = \gamma_{11} + \gamma_{22} - 2\gamma_{12} \quad (71)$$

$$s = (s_1 r_1 N_1 + s_2 r_2 N_2) / \bar{r}N = \phi_1 s_1 + \phi_2 s_2 \quad (72)$$

The site fractions  $\theta_1$  and  $\theta_2$  are defined by

$$\theta_2 = 1 - \theta_1 = s_2 r_2 N_2 / (s_1 r_1 N_1 + s_2 r_2 N_2) = s_2 \phi_2 / (s_1 \phi_1 + s_2 \phi_2) \quad (73)$$

By analogy with the energy for a pure component we define

$$-E_0/\bar{r}N = F^* v^* / \tilde{v} \quad (74)$$

for the mixture. Comparison of this equation with Eqs. 70 and 56 gives

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12} \quad (75)$$

where

$$X_{12} = s_1 \Delta \gamma / 2v^{*2} \quad (76)$$

Since Eq. 57 applies also to the mixture, it follows that

$$1/T^* = (\phi_1 P_1^* / T_1^* + \phi_2 P_2^* / T_2^*) / P^* \quad (77)$$

The same form of the equation of state for the mixture as that for a pure liquid can be derived from the partition function. However, the reduced variables  $\tilde{P} = P/P^*$  and  $\tilde{T} = T/T^*$  for the mixture depend on composition.

For a binary mixture the Helmholtz free energy of mixing is

$$\begin{aligned} \Delta F_m &= -RT \ln(Z/Z_1 Z_2) \\ &= RT(n_1 \ln \phi_1 + n_2 \ln \phi_2) + 3\bar{r}Nv^* \{ \phi_1 P_1^* \tilde{T}_1 \ln[(\tilde{v}_1^{\frac{1}{3}} - 1)/(\tilde{v}^{\frac{1}{3}} - 1)] \\ &\quad + \phi_2 P_2^* \tilde{T}_2 \ln[(\tilde{v}_2^{\frac{1}{3}} - 1)/(\tilde{v}^{\frac{1}{3}} - 1)] \} + \bar{r}Nv^* (\phi_1 P_1^* / \tilde{v}_1 + \phi_2 P_2^* / \tilde{v}_2 - P^* / \tilde{v}) \end{aligned} \quad (78)$$

The last term in Eq. 78 is the energy of mixing  $\Delta E_m$  which can be obtained directly from Eq. 74. At atmospheric pressure  $\Delta H_m \approx \Delta E_m$ , we can write

$$\Delta H_m = \bar{r}Nv^* (\phi_1 P_1^* / \tilde{v}_1 + \phi_2 P_2^* / \tilde{v}_2 - P^* / \tilde{v}) \quad (79)$$

or noting Eq. 75,

$$\Delta H_m = \bar{r}Nv^* [\phi_1 P_1^* (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + \phi_2 P_2^* (\tilde{v}_2^{-1} - \tilde{v}^{-1}) + \phi_1 \theta_2 X_{12} / \tilde{v}] \quad (80)$$

The rest of the terms in Eq.78 are the entropy of mixing in which the combinatorial entropy is included. In order to fit the experimental data one more term is included in the entropy of mixing. The term is  $-\bar{r}Nv^* \phi_1 \theta_2 TQ_{12}$ , where  $Q_{12}$  is the empirical interaction entropy parameter.  $Q_{12}$  reflects the change of entropy due to the interaction of unlike segments during mixing<sup>7</sup>. Now we can write

$$\begin{aligned} -T\Delta S_m = & RT(n_1 \ln \phi_1 + n_2 \ln \phi_2) + 3\bar{r}Nv^* \{ \phi_1 P_1^* \tilde{T}_1 \ln [(\tilde{v}_1^{\frac{1}{3}} - 1)/(\tilde{v}^{\frac{1}{3}} - 1)] \\ & + \phi_2 P_2^* \tilde{T}_2 \ln [(\tilde{v}_2^{\frac{1}{3}} - 1)/(\tilde{v}^{\frac{1}{3}} - 1)] \} - \bar{r}Nv^* \phi_1 \theta_2 TQ_{12} \end{aligned} \quad (81)$$

Thus at atmospheric pressure the Gibbs free energy of mixing can be calculated using the ordinary thermodynamic equation.

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (82)$$

At elevated pressure Eq.82 should include the term  $\Delta(PV)_m$  as discussed in Eq.36.

We can, however, use the Helmholtz free energy of mixing to calculate the chemical potential, only noting that the system should be kept at constant temperature and volume.

$$\begin{aligned} \Delta \mu_1 = & (\partial \Delta F_m / \partial n_1)_{T, \tilde{v}, n_2} + (\partial \Delta F_m / \partial \tilde{v})_{T, n_1, n_2} (\partial \tilde{v} / \partial n_1)_{T, \tilde{v}, n_2} \\ = & RT [\ln \phi_1 + (1 - r_1 / r_2) \phi_2] + P_1^* V_1^* \{ 3\tilde{T}_1 \ln [(\tilde{v}_1^{\frac{1}{3}} - 1)/(\tilde{v}^{\frac{1}{3}} - 1)] \\ & + (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + \tilde{P}_1 (\tilde{v} - \tilde{v}_1) \} + (X_{12} - TQ_{12} \tilde{v}) V_1^* \theta_2^2 / \tilde{v} \end{aligned} \quad (83)$$

The first term in Eq.83 is the combinatorial entropy term as in the Flory-Huggins theory. The next two terms reflect the equation of state contribution and interaction contribution. Roughly, it can be said that the second term is the equation of state contribution and the third term is the interaction contribution. However it must be born in mind that the reduced volume  $\tilde{v}$  of mixture contains both contributions as shown from the equation of state, a distinct

separation is impossible.

$\Delta\mu_1$  is the starting point for calculating the phase boundary of a polymer mixture. Using Eqs.11,14 and 15, we can calculate the binodal, spinodal and critical point. The spinodal is

$$\begin{aligned} & -1/\phi_1 + (1-r_1/r_2) - (P_1^* V_1^*/RT_1^*)(\partial\tilde{v}/\partial\phi_2)/[\tilde{v}^{\frac{2}{3}}(\tilde{v}^{\frac{1}{3}}-1)] \\ & + (P_1^* V_1^*/RT)(1/\tilde{v}^2 + \tilde{P}_1)\partial\tilde{v}/\partial\phi_2 + (V_1^* X_{12}/RT)[2\theta_1\theta_2^2/(\tilde{v}\phi_1\phi_2) \\ & - (\theta_2^2/\tilde{v}^2)\partial\tilde{v}/\partial\phi_2] - (V_1^* Q_{12}/R)[2\theta_1\theta_2^2/(\tilde{v}\phi_1\phi_2)] = 0 \end{aligned} \quad (84)$$

where

$$\partial\tilde{v}/\partial\phi_2 = [\partial\tilde{P}/\partial\phi_2 - (1/\tilde{T})(\tilde{P}+1/\tilde{v}^2)\partial\tilde{T}/\partial\phi_2] / \{2/\tilde{v}^3 - \tilde{T}(\tilde{v}^{\frac{1}{3}}-2/3)/[\tilde{v}^{\frac{5}{3}}(\tilde{v}^{\frac{1}{3}}-1)^2]\} \quad (85)$$

$$\partial\tilde{P}/\partial\phi_2 = [P_1^* - P_2^* + X_{12}\theta_2(\theta_1/\phi_2 - 1)]P/P^{*2} \quad (86)$$

$$\partial\tilde{T}/\partial\phi_2 = (P_2^*/T_2^* - P_1^*/T_1^*)T/P^* + [P_1^* - P_2^* + X_{12}\theta_2(\theta_1/\phi_2 - 1)]\tilde{T}/P^* \quad (87)$$

and the critical point

$$\begin{aligned} & -1/\phi_1^2 + (P_1^* V_1^*/RT_1^*)\{(\partial\tilde{v}/\partial\phi_2)^2(1-2/3\tilde{v}^{\frac{1}{3}})/[\tilde{v}^{\frac{4}{3}}(\tilde{v}^{\frac{1}{3}}-1)^2] - (\partial^2\tilde{v}/\partial\phi_2^2) \\ & /[\tilde{v}^{\frac{2}{3}}(\tilde{v}^{\frac{1}{3}}-1)]\} + (P_1^* V_1^*/RT)[(-2/\tilde{v}^3)(\partial\tilde{v}/\partial\phi_2)^2 + (1/\tilde{v}^2 + \tilde{P}_1)\partial^2\tilde{v}/\partial\phi_2^2] \\ & + (V_1^* X_{12}/RT)\{(1/\tilde{v})[2(\partial\theta_2/\partial\phi_2)^2 + 2\theta_2\partial^2\theta_2/\partial\phi_2^2] - (1/\tilde{v}^2)[4\theta_2(\partial\theta_2/\partial\phi_2) \\ & \partial\tilde{v}/\partial\phi_2 + \theta_2^2\partial^2\tilde{v}/\partial\phi_2^2] + (\theta_2^2/\tilde{v}^3)(\partial\tilde{v}/\partial\phi_2)^2\} = 0 \end{aligned} \quad (88)$$

The equations derived here start from the perfect chemical potential. They should be applicable to a discussion of the dependence of the phase boundary on pressure. At low pressures the equations should give the same results as the equations derived by Flory<sup>23</sup>.

In order to use the equation of state theory, three parameters of the equation of state are needed. These are the density  $d$ , the thermal expansion coefficient  $\alpha$  and the thermal pressure coefficient  $\chi$  or the isothermal compressibility coefficient  $k$ . The definitions of these parameters are

$$\alpha = v^{-1}(\partial v/\partial T)_P = (\tilde{T}/T\tilde{v})(\partial\tilde{v}/\partial\tilde{T})_{\tilde{P}} \quad (89)$$

$$k = -v^{-1}(\partial v / \partial P)_T = -(\tilde{P} / P\tilde{v})(\partial \tilde{v} / \partial \tilde{P})_{\tilde{T}} \quad (90)$$

$$\gamma = (\partial P / \partial T)_v = \alpha / k = (\tilde{T}P / T\tilde{P})(\partial \tilde{P} / \partial \tilde{T})_{\tilde{v}} \quad (91)$$

Solving the equation of state (Eq.55) first for  $\tilde{T}$  and then for  $\tilde{P}$ , differentiating the resulting expressions, and finally eliminating  $\tilde{T}$  in each case, the following relations are obtained.

$$(\alpha T)^{-1} = 1/3(\tilde{v}^{\frac{1}{3}} - 1) - 1 + 2\tilde{P}\tilde{v}^2 / (\tilde{P}\tilde{v}^2 + 1) \quad (92)$$

$$(kP)^{-1} = [1/3(\tilde{v}^{\frac{1}{3}} - 1) - 1](1 + 1/\tilde{P}\tilde{v}^2) + 2 \quad (93)$$

$$\gamma T / P = 1 + 1/\tilde{P}\tilde{v}^2 \quad (94)$$

At zero pressure the equation of state reduces to

$$(\tilde{v}^{\frac{1}{3}} - 1) / \tilde{v}^{\frac{4}{3}} = \tilde{T} \quad (95)$$

and the relations for  $\alpha$ ,  $k$  and  $\gamma$  become

$$\alpha T = 3(\tilde{v}^{\frac{1}{3}} - 1) / [1 - 3(\tilde{v}^{\frac{1}{3}} - 1)] \quad \text{or} \quad \tilde{v}^{\frac{1}{3}} - 1 = \alpha T / 3(1 + \alpha T) \quad (96)$$

$$k = 3(\tilde{v}^{\frac{1}{3}} - 1)\tilde{v}^2 / [1 - 3(\tilde{v}^{\frac{1}{3}} - 1)] P^* = \alpha T \tilde{v}^2 / P^* \quad (97)$$

$$\gamma = P^* / T\tilde{v}^2 \quad (98)$$

$\tilde{v}$  and  $P^*$  can be calculated from Eqs.92-94 or Eqs.96-98 if  $\alpha$  and  $k$  or  $\gamma$  are known.  $T^*$  can be calculated from the equations of state (Eqs.55 or 95). The last step is to calculate  $v^*$  using  $d$  and  $\tilde{v}$ . Once the three characteristic parameters  $P^*$ ,  $T^*$  and  $v^*$  are known, any thermodynamic function can be calculated.

In calculating the phase boundary, the dependence of the equation of state coefficients on temperature and pressure should be considered.

$$v = 1/d \quad (99)$$

$$dv(T, P) = (\partial v / \partial T)_P dT + (\partial v / \partial P)_T dP \quad (100)$$

$$d\alpha(T, P) = (\partial \alpha / \partial T)_P dT + (\partial \alpha / \partial P)_T dP \quad (101)$$

$$d\gamma(T, P) = (\partial \gamma / \partial T)_P dT + (\partial \gamma / \partial P)_T dP \quad (102)$$

where

$$(\partial v / \partial T)_P = \alpha v \quad (103)$$

$$(\partial v / \partial P)_T = -kv \quad (104)$$

$$(\partial \alpha / \partial T)_P = \tilde{v}^{\frac{1}{3}} \alpha^3 T / 9 (\tilde{v}^{\frac{1}{3}} - 1)^2 - \alpha / T - 4 \tilde{P} \alpha^3 T \tilde{v}^2 / (\tilde{P} \tilde{v}^2 + 1)^2 \quad 105)$$

$$= \alpha^2 (7 + 4 \alpha T) / 3 \quad P=0 \quad 106)$$

$$(\partial \alpha / \partial P)_T = -\tilde{v}^{\frac{1}{3}} k \alpha^2 T / 9 (\tilde{v}^{\frac{1}{3}} - 1)^2 - (1/P^* - 2 \tilde{P} k) 2 \tilde{v}^2 \alpha^2 T / (\tilde{P} \tilde{v}^2 + 1)^2 \quad 107)$$

$$= k(1 + \alpha T)(3 + 4 \alpha T) / 3T \quad P=0 \quad 108)$$

$$(\partial \gamma / \partial T)_P = -\gamma(1 + 2 \alpha T) / T + 2 \alpha P / T \quad 109)$$

$$= -\gamma(1 + 2 \alpha T) / T \quad P=0 \quad 110)$$

$$(\partial \gamma / \partial P)_T = 1/T + 2 \gamma k - 2 k P / T \quad 111)$$

$$= 1/T + 2 \gamma k \quad P=0 \quad 112)$$

The second problem of using the theory is how to evaluate the interaction energy parameter  $X_{12}$ . In principle this can be done by investigating any thermodynamic properties of the mixture. For polymer solutions or oligomer mixtures  $\Delta H_m$  can be measured. By simulating  $\Delta H_m$  over the whole concentration range  $X_{12}$  can be evaluated. An alternative method is by first evaluating  $B^7$ . The  $B$  is defined as

$$\Delta H_m = B N_1 \phi_2 \quad 113)$$

$$B = \lim(\phi_2 \rightarrow 0) (\Delta H_m / N_1 \phi_2) = \lim(N_2 \rightarrow 0) (\Delta H_m / N_2) (V_1^* / V_2^*) \\ = (V_1^* / \tilde{v}_1) \{ P_2^* [\tilde{v}_1 / \tilde{v}_2 - 1 - \alpha_1 T (1 - \tilde{T}_2 / \tilde{T}_1)] + (1 + \alpha_1 T) (s_2 / s_1) X_{12} \} \quad 114)$$

Extrapolating  $\Delta H_m / N_1 \phi_2$  to  $\phi_2 = 0$ ,  $B$  can be found.  $X_{12}$  can then be calculated directly from the properties of the pure constituents.

$X_{12}$  can also be evaluated from the excess volume of mixing.

If the mixture has an additive volume:

$$\tilde{v}^0 = \phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2 \quad 115)$$

In fact the reduced volume of mixture is  $\tilde{v}$ . The excess volume is

$$\tilde{v}^E = \tilde{v} - \tilde{v}^0 \quad 116)$$

$$\tilde{v}^E / \tilde{v}^0 = \Delta V_m / V^0 \quad 117)$$

where  $V^0$  is the total volume of the mixture if the volume change

$\Delta V_m$  is zero during mixing. In Eq. 117 to calculate  $\Delta V_m (= f(d_i, \alpha_i, \gamma_i, X_{12}))$  the only unknown parameter is  $X_{12}$  as long as all the equation of state

parameters of two mixed components are known.  $\Delta V_m$  can be measured directly during mixing<sup>18,23</sup>, or deduced from the density of the mixture.

$$\Delta V_m/V^0 = 1/(w_1/d_1 + w_2/d_2)d_m - 1 \quad (118)$$

where  $w_1$  and  $w_2$  are the weight fractions,  $d_1$ ,  $d_2$  and  $d_m$  are densities.

IGC can be used to determine the interaction parameter  $\chi$  in polymer mixtures. The theoretical equations will be discussed later.  $\chi$  can be expressed in terms of the residual chemical potential of the equation of state theory (see section 2.5). Thus  $X_{12}$  is evaluated from the  $\chi$  measurement. Olabisi<sup>34</sup> used the  $X_{12}$  so obtained to simulate the phase boundary of polymer mixtures.

$X_{12}$  obtained from  $\Delta H_m$  and  $\Delta V_m$  is only an interaction energy parameter, but the  $\bar{X}_{12}$  obtained from IGC is related to the free energy of mixing,  $\bar{X}_{12} = X_{12} - T\bar{V}Q_{12}$ , which includes the contribution of the interaction entropy between different species.

The last problem of using the theory is the evaluation of  $s_1/s_2$ , where  $s$  is the surface area per unit volume of segment. There are three methods: a) When the crystallographic data are available  $s$  for the polymer can be calculated through an approximation in which the monomeric unit is represented as a cylinder<sup>7,50</sup>. The length of the cylinder  $h$  is the distance per monomeric unit in the  $c$  direction of the unit cell. The radius  $R$  is determined by the characteristic volume  $v^*$ .

$$R = (v_2^*/h\pi)^{\frac{1}{2}} \quad (119)$$

The solvent molecules are represented as spheres, the radius is also obtained from the characteristic volume.

$$R = (3v_1^*/4\pi)^{\frac{1}{3}} \quad (120)$$

b) If the crystallographic data is not available, the length  $h$  is

evaluated by projecting a molecular model onto a piece of paper to measure the contour length. Alternatively, shadows projected for various orientations of the model are traced onto paper.  $s$  is then estimated from the average area of the shadows<sup>7</sup>. c)  $s$  can also be calculated from the group contribution technique of Bondi<sup>51</sup> for computing van der Waals molecular volume and surface area.

#### 2.4. Koningsveld's theory

For some oligomer mixtures the cloud point curves frequently appear to have an unusual shape such as a shoulder or two peaks. In order to explain this phenomenon Koningsveld<sup>8</sup> starts from the original lattice model expression of Flory and Huggins.

$$\Delta G_m/RT = \phi_1 m_1^{-1} \ln \phi_1 + \phi_2 m_2^{-1} \ln \phi_2 + \Gamma(T, \phi_2) \quad (121)$$

where the  $\Gamma$  function is used to include any correction needed for fitting the experimental data. Usually  $\Gamma(T, \phi_2)$  is a van Laar type function.

$$\Gamma = g(T) \phi_1 \phi_2 \quad (122)$$

Koningsveld assumes that  $g(T)$  is a complex function of the concentration  $g = g_0 + g_1 \phi_2 + g_2 \phi_2^2$ , with  $g_1 < 0$ ,  $g_2 > 0$  and  $|g_2| \geq |g_1|$ . With this expression for the free energy of mixing the calculated spinodal is markedly bimodal (Figure 2). He further shows (Figure 3) that the  $\Delta G_m(\phi_2)$  curve is not smooth but has slight ripples. In order to explain the form of  $g(T)$ , he uses Huggins' new treatment. Huggins expresses  $g$  as

$$g = \beta [1 - (1 - \rho) \phi_2]^{-1} = \beta Q^{-1} \quad (123)$$

where  $\rho = (\sigma_2/\sigma_1)/(v_2/v_1)$ , and  $\sigma_k$  and  $v_k$  are the contact area and molecular volume, respectively, of the segments of polymer  $k$ , and  $\beta = \sigma_2 \Delta \epsilon / 2RT$ , with  $\Delta \epsilon$  = the interchange energy. Huggins, like Flory, introduces the interacting surfaces of the segment in order to

explain the concentration dependence of the interaction parameter. Huggins then considers the influence of the immediate surroundings of a segment on its average orientation with respect to the preceding segment in the chain molecule. Setting the average allowed number of orientations of the segment equal to  $\nu^0$  when it is at infinite dilution in the second polymer, and correcting it to a value  $\nu^0(1-k_s)$  for a segment in the undiluted polymer, he calculates two orientational contributions to the entropy of mixing. Now  $\Delta G_m$  has the form

$$\begin{aligned} \Delta G_m/RT = & \phi_1 m_1^{-1} \ln \phi_1 + \phi_2 m_2^{-1} \ln \phi_2 + g \phi_1 \phi_2 - \phi_1 \ln(1+k_1 \rho \phi_2 Q^{-1}) \\ & - \phi_2 \ln(1+k_2 \phi_1 Q^{-1}) \end{aligned} \quad (124)$$

Two parameters  $k_{s1}$  and  $k_{s2}$  are related to  $k_1$  and  $k_2$  by  $k_{si} = k_i / (1+k_i)$  and considered as empirical parameters.  $Q = 1 - \gamma \phi_2$ ,  $\gamma = 1 - s_2/s_1$ ,  $s_i =$  interacting surface of segment  $i$  per unit volume. Eq.124 can be used to describe the double peaked spinodals observed in some oligomer mixtures if it is assumed that  $k_1$  is negative while  $k_2$  is positive.

Further study shows that the Huggins  $k$ -parameters are connected with the polymer coil expansion factor  $\alpha_1$  and  $\alpha_2$ ,

$$\alpha_1^3 = (\bar{r}_1^2 / \bar{r}_{1,0}^2)^{3/2} = 1 + k_1 (1 - r) \phi_2 Q^{-1} \quad (125)$$

$$\alpha_2^3 = (\bar{r}_2^2 / \bar{r}_{2,0}^2)^{3/2} = 1 + k_2 \phi_1 Q^{-1} \quad (126)$$

where  $r_k$  and  $r_{k,0}$  are the radii of gyration of polymer coils  $k$  under actual and unperturbed conditions, respectively. At infinite dilution the preceding equations (Eqs.125 and 126) become

$$(\alpha_1^3)_d = 1 + k_1 \quad (\phi_1 = 0, \phi_2 = 1) \quad (127)$$

$$(\alpha_2^3)_d = 1 + k_2 \quad (\phi_2 = 0, \phi_1 = 1) \quad (128)$$

A negative  $k_1$  and a positive  $k_2$  indicate contraction of coils 1 embedded in pure 2, and expansion of coils 2 in pure 1.

Another possible reason for the bimodality of spinodals is the

nonuniformity of segment density. The polymer mixture can be divided into three regions provided the mixture is compatible over the whole concentration range. In two of these the concentration of one polymer in the other is relatively small and the situation is quite similar to that of the dilute polymer solution. Between these two concentration ranges we can consider that the segments of both polymers are homogeneously mixed and the segment densities may both be assumed to be uniform. The boundary between these ranges depends primarily on the coil dimensions. Koningsveld suggests a correction for  $g$  of the form

$$g = g^c(1 - P_1 - P_2) + g_1^d P_1 + g_2^d P_2 \quad (129)$$

where  $g^c$ ,  $g_1^d$  and  $g_2^d$  are the  $g$ -values for the concentrated and for the two dilute concentration ranges, respectively. The probability  $P_k$  that a given volume element in the mixture does not fall within any coil domain  $k$  is given by

$$P_k = \exp(-\rho_k v_k) = \exp(-\lambda_k \phi_k) \quad (130)$$

where  $\rho_k$  is the number of coils  $k$  per unit volume and  $v_k$  their domain. The latter is related to the radius of gyration which can be expressed in a proportionality to  $\phi_k$ . The nonuniformity of segment density may lead to bimodal spinodals.

In conclusion, there are two possible reasons for the peculiar shape of the spinodal. One is the influence a second component exerts on the chain flexibility of the first, the other is the effect of nonuniform segment density on the thermodynamic properties of the mixture. It may well be that both mechanisms are operative.

Koningsveld's theory explains the bimodality of spinodals of oligomer mixtures and concludes that one coil may shrink in such mixtures. The theory however needs experimental verification.

## 2.5. The interaction parameter $\chi$ in Flory's theory

The last two terms of Eq.83 are the residual chemical potential of the solvent  $\Delta\mu_1^R$ , from which the interaction parameter  $\chi$  of the Flory-Huggins theory can be calculated.

$$\chi = \Delta\mu_1^R / RT\phi_2^2 = (P_1^* V_1^* / RT\phi_2^2) \{ 3\tilde{T}_1 \ln [(\tilde{v}_1^{\frac{1}{3}} - 1) / (\tilde{v}^{\frac{1}{3}} - 1)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + \tilde{P}_1 (\tilde{v} - \tilde{v}_1) \} + (X_{12} - TQ_{12} \tilde{v}) V_1^* \theta_2^2 / RT\tilde{v}\phi_2^2 \quad (131)$$

For simplicity  $\chi$  can be rewritten as

$$\chi = (P_1^* V_1^* / RT\phi_2^2) \{ 3\tilde{T}_1 \ln [(\tilde{v}_1^{\frac{1}{3}} - 1) / (\tilde{v}^{\frac{1}{3}} - 1)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + X_{12} V_1^* \theta_2^2 / RT\tilde{v}\phi_2^2 \} \quad (132)$$

if the situation where  $p$ =atmospheric pressure (approximately zero) and  $Q_{12}=0$  is considered.

Owing to the equation of state contribution,  $\chi$  is non zero even for an athermal polymer solution. The concentration dependence of  $\chi$  is decided by the equation of state contribution as well as the ratio  $s_2/s_1$ . In some cases this dependence is very sensitive to changes in  $s_2/s_1$ .

If, however,  $\chi'$  is calculated from the residual chemical potential of the solute, still assuming  $P=0$  and  $Q_{12}=0$ , a second equation results.

$$\chi' = (\Delta\mu_2^R / RT\phi_1^2) (V_1^* / V_2^*) = \{ P_2^* V_1^* (3\tilde{T}_2 \ln [(\tilde{v}_2^{\frac{1}{3}} - 1) / (\tilde{v}^{\frac{1}{3}} - 1)] + (\tilde{v}_2^{-1} - \tilde{v}^{-1}) + V_1^* X_{12} (s_2/s_1) \theta_1^2 / \tilde{v} \} / RT\phi_1^2 \quad (133)$$

Theoretically  $\chi'$  should be equal to  $\chi$ , but as shown in the following they are not equal. This is because the interaction term gives a large and dominant contribution to the values of  $\chi$  and  $\chi'$ . Ignoring the equation of state contribution, the ratio of the two  $\chi$  values will be

$$\chi'/\chi \approx (V_1^* X_{12} (s_2/s_1) \theta_1^2 / RT\tilde{v}\phi_1^2) / (V_1^* X_{12} \theta_2^2 / RT\tilde{v}\phi_2^2) = s_1/s_2 \quad (134)$$

Here we need to remember Eq.73, the definition of  $\theta$ .

Flory and colleagues<sup>7,52</sup> used Eqs. 131 and 132 for calculating

$\chi$  of seven polymer solutions including one athermal solution and one solution which showed an LCST behaviour. The agreement between theory and experiment is good. If, however, the theoretical  $\chi'$  is calculated from Eq.133 a second  $\chi'(\phi_2)$  curve results as shown in Figure 4. The parameters for the calculation are adopted from the related references. Figure 5 shows the ratio  $\chi'/\chi$  against  $\phi_2$ . In Table 1 the limiting values of  $\chi'/\chi$  at both  $\phi_2=0$  and  $\phi_2=1$  limits are listed together with the ratio  $s_1/s_2$  as given by Flory.

Table 1  $\chi'/\chi$  at  $\phi_2=0$  and  $\phi_2=1$  and  $s_1/s_2$  for polymer solutions

| systems                               | $\chi'/\chi(\phi_2=0)$ | $\chi'/\chi(\phi_2=1)$ | $s_1/s_2$ |
|---------------------------------------|------------------------|------------------------|-----------|
| 1. natural rubber/benzene             | 1.25                   | 1.25                   | 1.11      |
| 2. polyisobutylene/benzene            | 1.82                   | 1.79                   | 1.72      |
| 3. polyisobutylene/cyclohexane        | 1.38                   | 1.45                   | 1.61      |
| 4. polyisobutylene/n-pentane          | 1.12                   | 1.40                   | 1.89      |
| 5. polydimethylsiloxane/benzene       | 1.32                   | 1.44                   | 1.32      |
| 6. polydimethylsiloxane/cyclohexane   | 1.25                   | 1.31                   | 1.20      |
| 7. polydimethylsiloxane/chlorobenzene | 1.36                   | 1.44                   | 1.40      |

It can be seen that except for polyisobutylene/cyclohexane which is an athermal solution and polyisobutylene/n-pentane which shows an LCST behaviour Eq.134 holds quite well. In the two systems mentioned the equation of state contribution is large and Eq.134 becomes less accurate.

For polymer solutions  $s_1/s_2$  is greater than unity. As  $\phi_2$  increases from 0 to 1, the interaction part of the  $\chi$  value increases by  $(s_1/s_2)^2$ . The role of  $s$  in the concentration dependence of  $\chi$  is apparent. But if  $s_1 \neq s_2$  an anomalous result is obtained, which gives two different curves when  $\chi(\phi_2)$  is calculated from either the solvent or the solute residual chemical potentials.

This is because now  $\chi$  has concentration dependence, one more term  $RTn_1\phi_2\partial\chi/\partial n_1$  (or  $RTn_1\phi_2\partial\chi/\partial n_2$ ) must be added in Eq.40 (or Eq.41), hence

$$\Delta\mu_1^R/RT\phi_2^2 = \chi + \phi_1\partial\chi/\partial\phi_1$$

$$\Delta\mu_2^R/RT\phi_1^2(v_1^*/v_2^*) = \chi - \phi_2\partial\chi/\partial\phi_1$$

We cannot use Eqs.131 and 133 to calculate the interaction parameter  $\chi$ .

## 2.6. A comparison between Flory's treatment and McMaster's treatment

A comparison between the original form and McMaster's modified form of the Flory equation of state theory has been made. The parameters suggested in McMaster's paper<sup>6</sup> and listed in Table 2 were used for simulation of phase boundaries. The results are as follows.

Table 2 McMaster's data, base case parameters of polymer mixtures

| component | M | d(g/ml) | $\alpha \times 10^4 (K^{-1})$ | $\gamma$ (atm/K) | T(°C) |
|-----------|---|---------|-------------------------------|------------------|-------|
|-----------|---|---------|-------------------------------|------------------|-------|

a) pure component properties:

|   |       |       |      |      |     |
|---|-------|-------|------|------|-----|
| 1 | 50000 | 1.005 | 5.80 | 8.47 | 135 |
| 2 | 4000  | 1.055 | 7.23 | 7.24 | 135 |

mixture properties:  $X_{12}=0$ ,  $Q_{12}=0$  and  $s_1/s_2=1.56$

b) pure component properties:

|   |        |       |      |      |     |
|---|--------|-------|------|------|-----|
| 1 | 100000 | 1.005 | 5.80 | 8.47 | 135 |
| 2 | 100000 | 1.005 | 6.15 | 8.47 | 135 |

mixture properties:  $X_{12}=0$ ,  $Q_{12}=0$  and  $s_1/s_2=1.00$

a) The effect of molecular weight

Systems of high molecular weight which predicted to be incompatible by McMaster are now predicted to be compatible. Both calculations predict a large molecular weight dependence. For example if the molecular weight of component 1 changes from  $3 \times 10^4$  to  $5 \times 10^4$

while the molecular weight of component 2 is fixed at 4000, the phase boundary will move about  $150^{\circ}\text{C}$ , as seen in Figure 6.

b) The effect of the thermal expansion coefficient

McMaster's calculation predicts that two polymers having molecular weights of  $2 \times 10^5$  (chain length  $\sim 2000$  segments) require a difference in the thermal expansion coefficients of 4% or less in order to have significant mutual solubility. Even at molecular weights as low as  $5 \times 10^4$ , a difference of 10% in the thermal expansion coefficients can lead to virtually complete immiscibility. The calculation using the original form of the theory shows that the effect of  $\alpha$  is not so large. The pair of molecular weights  $2 \times 10^5$  with a difference of 5% in  $\alpha$  is still miscible. For the pair of molecular weights  $5 \times 10^4$ , 10% difference in  $\alpha$  does not affect miscibility at room temperature. The results are shown in Figure 7.

c) The effect of thermal pressure coefficient

Calculation shows that when  $\gamma_1$  or  $\gamma_2$  changes, the phase boundary will move in an opposite direction as predicted by McMaster. The discrepancy may come from the calculation of  $(\partial \tilde{v} / \partial n_1)_{T, V, n_2}$ . The role of  $\gamma$  in determining the phase boundary is complicated: in our calculation if either  $\alpha_1 < \alpha_2$  or  $\alpha_1 > \alpha_2$  (two  $\alpha$  values are  $5.80 \times 10^{-4}$  and  $7.23 \times 10^{-4}$ ) an increase of  $\gamma_2$  will increase miscibility. Thus it cannot be said that the equation of state difference caused by  $\alpha_1 < \alpha_2$  can be compensated by reducing  $\gamma_2$  in comparison to  $\gamma_1$  etc. as discussed by McMaster. The results are shown in Figure 8.

Compared to the thermal pressure coefficient, the effect of the thermal expansion coefficient is decisive in determining the equation of state difference between two polymers. When  $\alpha_1 = \alpha_2$ , all the model systems calculated here become completely miscible.

d) The effect of the interaction energy parameter  $X_{12}$

The calculation in this work predicts a larger influence than in McMaster's calculation. For instance, when  $X_{12}$  changes from 0 to  $-0.025$  cal/ml ( $-1$  atm) the phase boundary moves up  $100^{\circ}\text{C}$  instead of the  $15^{\circ}\text{C}$  in McMaster's calculation. The calculation shows that it is possible to find a polymer mixture which has both a UCST and an LCST if the system has a slightly positive  $X_{12}$ . The results are shown in Figure 9.

All the calculations here are based on the assumption that  $X_{12}=0$  and  $Q_{12}=0$ . In chapter 5 we will see that  $X_{12}\neq 0$  and  $Q_{12}\neq 0$  when the theory is applied to practical systems. Also we can see that  $Q_{12}$  is decisive in fitting the experimental phase boundaries.

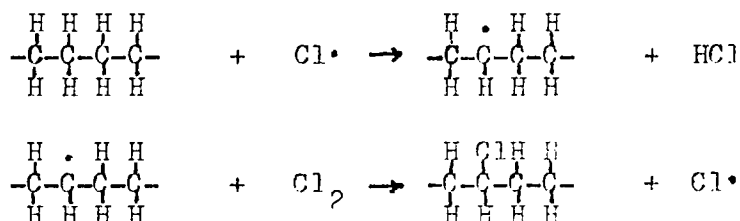
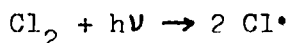
From the comparison it can be seen that the original Flory theory can give the same excellent description of the phase boundary behaviour. The theory shows that the LCST is a general phenomenon for polymer mixtures. The molecular weight has a large effect on the phase diagram, especially for low molecular weights. The difference in the thermal expansion coefficients is a reason for the LCST behaviour. The role of the thermal pressure coefficient is complicated. When mixing is accompanied by an exothermic process, i.e.  $X_{12}<0$ , the systems become more and more compatible. A small positive interaction will possibly cause a coexistence of an LCST and a UCST, or make an hourglass shaped phase boundary. Compared with McMaster's results, it seems that the introduction of equivalent translational degrees of freedom is not necessary. The Flory theory in the original form can give the same predictions in the study of polymer compatibility.

### 3. MATERIALS

#### 3.1. Preparation of polymers

##### 3.1.1. Chlorinated polyethylene (CPE)<sup>54</sup>

CPE samples were prepared by chlorination of polyethylene. Chlorination can be done in solution or in suspension. The reaction is a free radical reaction which is initiated by light or a free radical initiator.



High quantum yields show that the reaction has a considerable chain length. In this work high density polyethylene is preferred in order to avoid any branching in the molecule which will cause difficulty in the theoretical analysis. In order to obtain as homogeneous a product as possible solution chlorination was adopted in this work. Two improvements were made to the standard procedure: a) chlorobenzene was used as solvent to raise the reaction temperature, b) the light of an ordinary tungsten lamp initiated the reaction, without the necessity of ultraviolet or fluorescent lamps.

The reaction took place in a 3-necked flask in an oil bath. The flask was equipped with a stirrer, a reflux condenser and two gas inlet tubes (nitrogen and chlorine). Commercial high density polyethylene (10g, nominal  $M_n=10000$ ) was dissolved in chlorobenzene (200ml, AR) at 135°C. The solution was stirred during the reaction.

It was photochlorinated using light from a 60 watt tungsten lamp under a  $N_2$  atmosphere. Chlorine gas was bubbled into the flask with a flow rate of 28 ml/min. By adjusting the reaction time products with different chlorine contents were obtained. The reaction usually lasted from 2 to 10 hrs. The resulting products were cooled and precipitated into a 10 times excess of methanol (AR) and washed twice with methanol. The precipitate was soaked in methanol overnight to extract the residual chlorobenzene and dried in a vacuum oven at 1 mm Hg at 50°C for 2 weeks.

The properties of the CPEs are listed in Table 3.

Table 3 Properties of CPEs

| CPE | composition |       |       | molecular weights*                |                                   |                                | d, 25°C | $\alpha$ , 25-45°C                | T $\alpha$ |
|-----|-------------|-------|-------|-----------------------------------|-----------------------------------|--------------------------------|---------|-----------------------------------|------------|
|     | W %         |       |       |                                   |                                   |                                |         |                                   |            |
|     | C           | H     | Cl    | M <sub>w</sub> x 10 <sup>-5</sup> | M <sub>n</sub> x 10 <sup>-4</sup> | M <sub>w</sub> /M <sub>n</sub> | g/ml    | x 10 <sup>4</sup> K <sup>-1</sup> | °C         |
| 1   | 0.546       | 0.083 | 0.369 | 1.10                              | 1.58                              | 6.96                           | 1.159   | 6.25                              | -10        |
| 2   | 0.630       | 0.099 | 0.274 | 1.08                              | 1.52                              | 7.11                           | 1.071   | 13.24                             | - 8        |
| 3   | 0.454       | 0.062 | 0.480 | 1.20                              | 1.80                              | 6.67                           | 1.301   | 4.43                              | 27         |
| 4   |             |       | 0.357 | 1.15                              | 1.89                              | 6.08                           | 1.127   | 8.73                              | -10        |
| 5   | 0.641       | 0.101 | 0.245 |                                   |                                   |                                | 1.062   | 12.25                             | -10        |
| 8   | 0.712       | 0.115 | 0.165 |                                   |                                   |                                | 1.015   | 9.10                              |            |
| 11  |             |       | 0.224 |                                   |                                   |                                | 1.066   | 12.30                             | -12        |
| 12  |             |       | 0.210 |                                   |                                   |                                | 1.036   | 11.57                             |            |
| 15  |             |       | 0.447 | 1.70                              | 1.81                              | 9.38                           | 1.311   | 5.66                              | 27         |
| 16  |             |       | 0.516 | 1.98                              | 2.53                              | 7.83                           | 1.416   |                                   | 39         |
| 17  |             |       | 0.498 | 1.82                              | 2.08                              | 8.78                           | 1.365   | 3.85                              | 32         |
| 18  |             |       | 0.456 | 2.02                              | 2.29                              | 8.81                           | 1.319   | 4.93                              | 27         |
| 19  |             |       | 0.441 | 1.79                              | 2.09                              | 8.56                           | 1.304   | 5.47                              | 25         |
| 20  | 0.349       | 0.037 | 0.621 | 2.42                              | 2.58                              | 9.41                           | 1.487   | 3.72                              | 78         |

\* relative to polystyrene standards.

### 3.1.2. Chlorinated octadecane (COD) and cereclor

CODs were also prepared by photochlorination in chlorobenzene.

Because octadecane is a low molecular weight compound the concentration

of the reacting solution can be higher. *n*-Octadecane (25ml, Lab. R.) was mixed with chlorobenzene (200ml, AR) at 130°C. The reaction was initiated by irradiation from a 60 watt tungsten lamp. Chlorine was introduced into the flask at a rate of 25 ml/min. By controlling the reaction time different degrees of chlorination were obtained. The reaction usually lasted from 2 to 10 hrs. The products were separated by rotary evaporating the chlorobenzene at 50°C under a reduced pressure. They were then dried in a vacuum oven at 1 mm Hg at 50°C for two weeks.

Cereclor is a chlorinated paraffin (I.C.I.). It was dried under the same condition as for COD before use.

The properties of oligomeric samples are listed in Table 4.

Table 4 Properties of COD and cereclor

| sample   | chlorine<br>content,<br>weight<br>fraction | M<br>from<br>chlorine<br>content | M <sub>n</sub><br>from<br>VPO | d, g/ml |        | $\alpha$<br>$\times 10^{-4} \text{K}^{-1}$ | refractive index |         |
|----------|--------------------------------------------|----------------------------------|-------------------------------|---------|--------|--------------------------------------------|------------------|---------|
|          |                                            |                                  |                               | 25°C    | 70°C   |                                            | 24.5°C           | 69.5°C  |
| COD 1    | 0.173                                      | 306                              | 314                           | 0.8976  | 0.8651 | 8.20                                       | 1.45488          | 1.43685 |
| 2        | 0.246                                      | 334                              | 356                           | 0.9511  | 0.9180 | 7.87                                       | 1.46586          | 1.44723 |
| 3        | 0.334                                      | 376                              | 412                           | 1.0531  | 1.0167 | 7.82                                       | 1.48188          | 1.46401 |
| 3A       | 0.349                                      | 385                              | 421                           | 1.0807  | 1.0457 | 7.32                                       | 1.48430          | 1.46724 |
| 4        | 0.432                                      | 438                              | 467                           | 1.1417  | 1.1054 | 7.18                                       | 1.49508          | 1.47809 |
| 5        | 0.529                                      | 523                              | 546                           | 1.2579  | 1.2169 | 7.36                                       | 1.51301          | 1.49583 |
| cereclor |                                            |                                  |                               |         |        |                                            |                  |         |
| 45       | 0.457                                      |                                  | 395                           |         | 1.1319 | 6.79                                       |                  |         |
| 52       | 0.531                                      |                                  | 437                           |         | 1.2280 | 6.85                                       |                  |         |

### 3.1.3. Poly(methyl methacrylate)(PMMA)

Fractionation was used to obtain different molecular weight samples. The theory of fractionation was reviewed by Guzman<sup>55</sup>.

Using the binodal condition of a polymer solution, Eq.11, and also using the expression for  $\Delta\mu_2$  of the Flory-Huggins theory, Eq.41, we

can have

$$\phi_2/\phi'_2 = \exp[\sigma(r_2/r_1)] \quad 135)$$

$$\begin{aligned} \sigma &= (r_1/r_2) [(1-r_2/r_1)(\phi'_1 - \phi_1) + \chi(r_2/r_1)(\phi_1'^2 - \phi_1^2)] \\ &\approx -(\phi'_1 - \phi_1) + \chi(\phi_1'^2 - \phi_1^2) < 0 \end{aligned} \quad 136)$$

It can be seen that the ratio of the concentrations of polymer in two phases is an exponentially decreasing function of the chain length. This forms the foundation of fractionation. From the equation the inefficiency of fractionation can also be seen: a fraction of any molecular weight polymer will always remain in the dilute phase.

The analysis above refers to fractionation from a single solvent solution, the temperature being lowered to cause phase separation. In practice it is far more common to add a precipitant at constant temperature to a dilute solution of the polymer in a solvent. Similar relations can be obtained in this case.

A commercial product PMMA1.4 (Polysciences) was dissolved at 2% W/V in acetone (AR) and precipitated by addition of a large quantity of distilled water-acetone mixed precipitant (1:1 volume ratio). The precipitate was collected and dried in a vacuum oven at 1 mm Hg at 50°C for one week.

Another commercial product PMMA (I.C.I.) was used for fractionation. 30g of polymer was dissolved in acetone to form a 2% solution at 25°C. When adding distilled water-acetone (1:1 volume ratio) gradually the solution became turbid. To ensure the establishment of equilibrium, the turbid solution was warmed to 30°C to let the solution clear again and then allowed to cool slowly down to 25°C. The quantity of precipitate was controlled by the turbidity of solution. The precipitate, which formed a condensed layer at the bottom of flask, was collected after removing the remaining solution

through a siphon. The precipitate was redissolved and precipitated, as described in the previous paragraph. Four fractions were obtained in the experiment, by repeating this procedure, of which the middle two fractions F5 and F6 were used for this work.

The properties of the polymers are listed in Table 5.

Table 5 Properties of PMMA samples

| sample  | $M_w \times 10^{-4}$ | $M_n \times 10^{-4}$ | $M_w/M_n$ |
|---------|----------------------|----------------------|-----------|
| PMMA1.4 | 8.38                 | 3.46                 | 2.42      |
| F5      | 26.4                 | 15.4                 | 1.71      |
| F6      | 14.0                 | 7.17                 | 1.95      |

#### 3.1.4. Oligomeric PMMA (OMMA)

OMMA was prepared by chain transfer polymerization<sup>56</sup>. The Mayo equation for the molecular weight in telomerization where the solvent is used as a chain transfer reagent is

$$1/r_n = (1/r_n)_0 + C_s [S]/[M] \quad (137)$$

where  $r_n$  is the number average degree of polymerization.  $C_s$  is a constant, and  $[S]$  and  $[M]$  are the concentrations of solvent and monomer, respectively.

In our preparation the chain transfer reagent is iso-propyl alcohol (iso-PrOH). The reaction is a solution polymerization, in which iso-PrOH is also a solvent to dilute the reacting system. According to Mayo's equation different molecular weights can be obtained by adjusting the ratio  $[S]/[M]$ .

In an autoclave (volume content ~600 ml) were placed the distilled MMA, iso-PrOH (AR) and di-t-butyl peroxide ( $6 \times 10^{-3}$  mol/mol iso-PrOH). The ratios of monomer to solvent are given in Table 6. The mixture was degassed and kept at 130°C under a  $N_2$  atmosphere for 5 hrs. The lowest molecular weight oligomer product was evaporated

to dryness, redissolved in iso-PrOH, filtered and evaporated again to dryness. The higher polymers were solids and were reprecipitated into distilled water from an acetone solution. All the samples were dried in a vacuum oven at 1 mm Hg and 50°C for at least 2 weeks.

The properties of OMMA are listed in Table 6.

Table 6 Properties of OMMA samples

| OMMA   | MMA / iso-PrOH<br>molar ratio | $M_w$ | $M_n$ | $M_w/M_n$ | d, g/ml |        | $\alpha \times 10^{-4}$<br>K <sup>-1</sup> | refractive<br>index |         |
|--------|-------------------------------|-------|-------|-----------|---------|--------|--------------------------------------------|---------------------|---------|
|        |                               |       |       |           | 25°C    | 70°C   |                                            | 24.5°C              | 69.5°C  |
| 1      | 0.029                         |       | 502   |           |         |        |                                            |                     |         |
| PMMA16 | 0.479                         | 48800 | 12600 | 3.87      |         |        |                                            |                     |         |
| PMMA17 | 0.072                         | 14400 | 4270  | 3.37      |         |        |                                            |                     |         |
| 23     | 0.029                         |       | 434   |           | 1.1378  | 1.0889 | 9.76                                       | 1.47642             | 1.46077 |

### 3.1.5. Poly(ethyl methacrylate)(PEMA) and poly(butyl acrylate)(PBA)

PEMA is a commercial product (Polysciences). No further purification was carried out for this sample.

PBA is a commercial product, supplied in toluene solution (Polysciences). It was evaporated to dryness in a large petri dish and then dried in a vacuum oven at 1 mm Hg and 50°C for 2 weeks.

The molecular weights of PEMA and PBA are listed in Table 7.

Table 7 Molecular weights of PEMA and PBA \*

| polymer | $M_w \times 10^{-5}$ | $M_n \times 10^{-4}$ | $M_w/M_n$ |
|---------|----------------------|----------------------|-----------|
| PEMA    | 2.35                 | 7.07                 | 3.32      |
| PBA     | 1.19                 | 3.30                 | 3.61      |

\* relative to polystyrene standards

## 3.2. Characterization of polymers

The polymers listed in Tables 3-7 were characterized by following methods:

### 3.2.1. Microelemental analysis

The contents of C,H and Cl of CPE and COD samples were directly analysed. The results of chlorine content has a  $\pm 4\%$  accuracy by repeat measurements The results are shown in Tables 3 and 4.

### 3.2.2. Refractive index

The refractive indices of oligomers were determined using a Abbe "60" refractometer (Bellingham and Stanley Ltd.) using the sodium  $D_1$  line 5896 Å. The measurements were made at different temperatures (with an accuracy of  $\pm 0.2^\circ\text{C}$ ). The results are shown in Tables 4 and 6 and also in Figure 10.

### 3.2.3. Density and thermal expansion coefficient

The densities of oligomers were measured as ordinary liquids. A pycnometer of 4 ml capacity was first calibrated with twice-distilled water. The densities of oligomers were obtained by comparing their weights in the pycnometer. The data has an accuracy of  $\pm 0.0002$  g/ml at  $25^\circ\text{C}$  and  $\pm 0.0005$  g/ml at  $70^\circ\text{C}$ , respectively.

The densities of solid polymer or polyblends were determined by equal density titration<sup>57</sup>. 3-4 fine pieces of polymer film were placed in a flask containing twice-distilled water. The flask was kept at constant temperature in a bath maintained at  $25 \pm 0.1$  or  $70 \pm 0.5^\circ\text{C}$ . Through a syringe a saturated NaBr solution was titrated into the flask until the film pieces floated in the solution, without sinking to the bottom or floating to the surface for several minutes. The density of the NaBr solution in the flask was presumed to have an equal density to the polymer. The density of the liquid was then measured using a pycnometer. The accuracy was estimated as  $\pm 0.0005$  g/ml at  $25^\circ\text{C}$  and  $\pm 0.0015$  g/ml at  $70^\circ\text{C}$ , respectively, by repeat titrations.

The thermal expansion coefficient was calculated from the

densities at two different temperatures using the following equation

$$\alpha = (1 - d_1/d_2)/(T_1 - T_2) \quad 138)$$

The accuracy was estimated as  $\pm 0.15 \times 10^{-4}/K$  for oligomer and  $\pm 0.30 \times 10^{-4}/K$  for polymers.

### 3.2.4. Vapour pressure osmometry (VPO)<sup>58,59</sup>

VPO is a simple and rapid method for obtaining number average molecular weights in the range of  $100-2 \times 10^4$ . The solvent vapour in the saturated vapour chamber condenses onto a droplet of the solution. The heat of condensation thereby produced raises the temperature of the droplet, after compensating for the heat loss caused by conduction, convection and radiation. The working equation of VPO can be derived as

$$\Delta T/C_w = K/M_2 + (K/M_1)(1/2 - \chi)(d_1/d_2)^2 C_w + \dots \quad 139)$$

with

$$K = (1-f)RT^2 M_1 / Q^* \quad 140)$$

where  $\Delta T$  is the temperature difference between two droplets of solvent and solution,  $C_w$  is the concentration of polymer (g/ml),  $Q^*$  is the heat of condensation of solvent,  $f$  is a characteristic parameter for the heat loss of the apparatus. When  $f=0$  Eq.139 returns to the classical Clausius-Clapeyron equation for ebullioscopy where the thermodynamic equilibrium is reached.

In order to do the experiment we need to know the instrument constant  $K$ .  $K$  can be evaluated by extrapolating  $(\Delta T/C_w)$  against  $C_w$  using a known molecular weight standard sample.

A Knauer VPO apparatus was used for measurements. The experiment was run at  $37 \pm 0.1^\circ C$  with MEK (AR) as the solvent. The instrument was first calibrated with anthracene (AR,  $M=178.23$ ). The measured values have an accuracy of  $\pm 5\%$ .

Figure 11 shows some results of the measurements.

### 3.2.5. Gel permeation chromatography (GPC)

The appearance of GPC, especially high performance GPC, was a breakthrough for the measurement of molecular weight distributions<sup>60</sup>. The technique makes it possible to monitor this property of polymers in research and production. An important property of GPC is that the hydrodynamic volume calibration converts the calibration curves of the standard samples to that of the system investigated, which is based on a discovery that the molecules are separated according to their hydrodynamic volumes in solution if the molecular chain is not too stiff<sup>61</sup>. Thus we have

$$\log M_2 = \left[ \frac{1}{(\alpha_2 + 1)} \right] \log(K_1/K_2) + \left[ \frac{\alpha_1 + 1}{\alpha_2 + 1} \right] \log M_1 \quad 141)$$

where  $K$  and  $\alpha$  are the parameters in the Mark-Houwink equation.

$$[\eta] = KM^\alpha \quad 142)$$

The second property we need to know is the peak broadening which causes an error in the calculations. This is greatly suppressed in high performance GPC. It was estimated from the material balance equation theory<sup>62</sup> that if the column has a efficiency of 10000 plates, the calculation of molecular weights will give an error of  $\leq 19\%$ .

In this work the samples were measured on a high performance GPC(LC 750, Applied chromatography systems ltd.) at room temperature with THF (AR) as the solvent and polystyrene (narrow distribution) as the standards. The flow rate was 1 ml/min. The following intrinsic viscosity equations<sup>63</sup> were used to convert the calibration curve of the standard for use with PMMA.

$$[\eta] = 0.93 \times 10^{-4} M^{0.72} \quad \text{for PMMA, } 23^\circ \text{C} \quad 143)$$

$$[\eta] = 1.68 \times 10^{-4} M^{0.69} \quad \text{for polystyrene} \quad 144)$$

No such equations are available for CPE, PEMA and PBA. Only the relative values of molecular weight compared to polystyrene

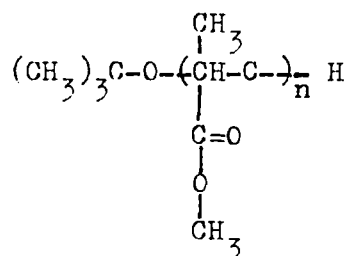
standards were obtained in these cases.

### 3.2.6. Infrared absorption spectroscopy (IR)<sup>64</sup>

IR was used to characterize the chemical structure of OMMA. In this analysis the useful information comes from the identification of the vibrations of functional groups. Our object is to find the end groups of the oligomer. The mechanism of chain initiation determines one of them. This can be a radical of initiator  $(\text{CH}_3)_3\text{CO}\cdot$  or solvent chain transfer reagent  $(\text{CH}_3)_2\text{C}(\text{OH})\cdot$ . Obviously the second situation is not preferred because a polar group  $(\text{OH})\cdot$  is in the structure.  $(\text{CH}_3)_3\text{CO}\cdot$  has an absorption at  $1255\text{ cm}^{-1}$  and the C-O-C ether group forming from the  $(\text{CH}_3)_3\text{CO}\cdot$  end group has an absorption at  $1080\text{ cm}^{-1}$ . The other end group is determined by the mechanism of chain termination. This can be known from detection of the  $\nu_{\text{C}=\text{C}}$  ( $1620\text{ cm}^{-1}$ ) absorption.

Two different molecular weights of OMMA were studied. Low molecular weight OMMA 23 was a viscous liquid and was spread as a thin layer onto a KBr plate. High molecular weight OMMA 16 was dissolved in MEK (AR) and cast onto the second KBr plate. The thickness of the films was shown to be in the proper range by the IR transmittance.

The spectra were obtained using a Perkin-Elmer 683 IR spectrophotometer. The results are shown in Figure 12. Two typical absorption bands at  $1080$  and  $1255\text{ cm}^{-1}$  were found for the  $(\text{CH}_3)_3\text{CO}\cdot$  end group. An absorption at  $1620\text{ cm}^{-1}$  was also found for the C=C group if the thickness of the sample films is increased. We did not find any absorption of  $(\text{OH})\cdot$  group at high frequency. This confirms that the oligomer prepared in this work has the same structure as in the literature<sup>56</sup>. The structure of OMMA is



### 3.3. Preparation of mixtures

One of the difficulties in the study of high molecular weight polyblends is that the techniques of preparing samples have a great influence on the phase state of the polyblend. The samples prepared are not always at thermodynamic equilibrium so that it is difficult to obtain repeatable data on samples prepared by different techniques or on temperature cycling. At best, a polyblend can be described as microheterogeneous, the size of the different phases and their interpenetration being limited by a host of factors among which are the extent of mixing, compatibility, molecular weight, clustering behaviour of the polymers, rheological, surface and interfacial properties.<sup>34</sup>

Mechanical mixing is an industrial method of preparing blends but it does not usually make a homogeneous mixture, and usually there is a certain particle size distribution in the blends. This is because the diffusion coefficient of a polymer in the bulk is very small and it is difficult to form a dispersion on a molecular scale in the limited mixing time, even at above the melting temperature. The LCST behaviour of polyblends eventually prevents molecular mixing if the attempted mixing temperature is above the LCST. Thus the blends often reflect the phase state at the mixing temperature rather than equilibrium at room temperature. This problem of quench-in structure is very severe in systems which are only just

compatible<sup>65</sup>. The principles of irreversible thermodynamics state that the rate of a particular process is proportional to the free energy difference between the initial and final states. Because this difference is small in such systems, the rate of approach to the final state is also small.

A second method is by mixing polymers in solution, which overcomes the difficulty of ~~the~~ extremely small diffusion coefficient of polymer molecules in the bulk state. It is usually assumed<sup>29</sup> that a mixed polymer film deposited from solution is more likely to be in it's equilibrium state than a mixed polymer sample prepared by mastication of the two polymer in the bulk. There are three ways to remove solvent:

a) by evaporation. This requires a careful selection of the solvent to make sure that no phase separation takes place during evaporation, because the phase state of the polymer mixture presumably reflects the detailed path from dilute solution to solid sample<sup>66</sup>. Some authors have reported<sup>67</sup> that clear films of polystyrene/poly(vinyl methyl ether) mixtures were obtained upon casting from toluene or benzene, while usually incompatible films resulted upon casting from trichloroethylene and chloroform. Also, the residual solvent, which sometimes bonds to polymers, is difficult to remove.

b) by freeze-drying. This is an alternative way to evaporate solvent. It is reported<sup>68</sup> that homogeneous blends of incompatible polymers PMMA/polystyrene have been prepared by rapid freezing of their co-solutions in naphthalene followed by room temperature sublimation of the solvent. The common solvent for freeze-drying are benzene, p-dichlorobenzene and naphthalene etc.

c) by coprecipitation. This is the quickest way to remove

solvent from dilute solution, hence the selection of solvent is not so important as we know that the role of solvent becomes critical only when the solution is concentrated. The problem is that the precipitate cannot always be used directly for physical or physicochemical measurements. It needs to be pressed into films in the molten state. The same problem as in mechanical mixing is imposed here as the moulded samples with different thermal histories are no longer the same as the original precipitate.

A third choice for making nolyblends is in-situ polymerization. This is a good method for obtaining a well mixed blend if no phase separation appears during polymerization.

In this work we used solvent casting and coprecipitation for preparing polymer mixtures. PMMA/CPE and PBA/CPE blend films were cast from MEK (AR) solution in petri dishes. The rate of evaporation was controlled by partial covering. It was discovered that fast evaporation and humid weather were often the reasons for forming turbid films. After evaporation of the solvent, the films were dried in a vacuum oven at 1mm Hg and 50°C for 1 week. Because the PBA used is very soft it was necessary to use liquid nitrogen to temporarily harden blends with high concentration of PBA during transfer. CPE/CPE blends at fixed weight fraction 0.5 were cast from chlorobenzene (AR) solutions. The procedure is same as for the previous two systems.

Some of the PMMA/CPE blends were prepared by coprecipitation. The polymers, in various proportions, were dissolved to a total 5% (W/V) in THF (AR). The solutions were then poured with stirring into a 20 times excess of distilled water. The precipitates were then dried in an oven for 72 hrs at 50°C. The samples were pressed at 140°C for 15 min to produce films of 0.3 to 0.6 mm thickness.

### 3.4. Microstructure of CPE

#### 3.4.1. Nuclear magnetic resonance (NMR)<sup>69</sup>

NMR spectroscopy is perhaps the most powerful technique available for studying the environment of individual atoms within a polymer chain. NMR yields qualitative as well as quantitative information which is most often unequivocal. We now know that sequences of carbon atoms as long as 5 in length (pentads) can be observed easily using  $^{13}\text{C}$ -NMR.

The  $^{13}\text{C}$ -NMR analysis of CPE in this work is composed of two aspects. The analysis follows the papers published by Keller and Kuege<sup>39</sup>.

a) Determination of the constitution, namely, the contents of  $-\text{CH}_2-$ ,  $-\text{CHCl}-$  and  $-\text{CCl}_2-$  groups (in mol%) of the CPE samples, which are designed as X, Y and Z, respectively.

$$X = F_0 / \sum_{i=0}^2 F_i \quad 145)$$

$$Y = F_1 / \sum_{i=0}^2 F_i \quad 146)$$

$$Z = F_2 / \sum_{i=0}^2 F_i \quad 147)$$

where  $F_0$ ,  $F_1$  and  $F_2$  are the corrected intensities (area) under  $-\text{CH}_2-$ ,  $-\text{CHCl}-$  and  $-\text{CCl}_2-$  resonances, respectively.  $F_0 = F_0(\text{expt})/N_0$ ,  $F_1 = F_1(\text{expt})/N_1$  and  $F_2 = F_2(\text{expt})$ .  $F_i(\text{expt})$  is the experimental value.  $N_i$  is the relative intensity factor.  $N_0 = N_1 = \bar{N} = 1.5 \pm 0.2$  obtained from the measurement of chlorinated poly(vinyl chloride). When the chlorine content is higher than 50% by weight,  $N_0 \neq N_1$  and we need to have a further correction for the intensities:

$$F_{0,\text{corr}} = (F_0 + F_1) / (I_{\text{corr}}^{-1} + 1) \quad 148)$$

$$F_{1,\text{corr}} = I_{\text{corr}}^{-1} (F_0 + F_1) / (I_{\text{corr}}^{-1} + 1) \quad 149)$$

where

$$I_{\text{corr}}^{-1} = 0.47 I^{-1} + 0.34 \quad 150)$$

In Eq.150  $I^{-1}=F_1/F_0$ . Eq.150 is obtained from calibrating the  $I^{-1}$  of the  $^{13}\text{C}$ -NMR spectra with that of the  $^1\text{H}$ -NMR spectra.

After obtaining X,Y and Z, the molar degree of chlorination can be calculated.

$$\bar{\alpha}=(Y+2Z)/2 \quad 151)$$

The original definition of  $\bar{\alpha}$  is

$$\bar{\alpha}=N_{\text{Cl}}/(N_{\text{Cl}}+N_{\text{H}}) \quad 152)$$

where  $N_{\text{Cl}}$  and  $N_{\text{H}}$  are the numbers of Cl and H atoms in the chain respectively.  $\bar{\alpha}$  should be between 0 and 1, and is connected with the weight degree of chlorination in wt%,  $G_{\alpha}$  :

$$G_{\alpha}=M_{\text{Cl}}\bar{\alpha}/[(M_{\text{Cl}}-M_{\text{H}})\bar{\alpha}+M_{\text{H}}+M_{\text{C}}/2]=g_{\alpha}\times 100\% \quad 153)$$

where  $M_{\text{Cl}}$ ,  $M_{\text{H}}$  and  $M_{\text{C}}$  are the atomic weights. Thus,  $\bar{\alpha}$  and  $G_{\alpha}$  can be determined from the NMR spectra.

$G_{\alpha}$  can also be determined from the chemical analysis. Thus,  $\bar{\alpha}$  can be calculated from  $G_{\alpha}$  if we rewrite Eq.153:

$$\bar{\alpha}=g_{\alpha}(M_{\text{H}}+M_{\text{C}}/2)/[M_{\text{Cl}}-g_{\alpha}(M_{\text{Cl}}-M_{\text{H}})] \quad 154)$$

The two series of results for  $\bar{\alpha}$  and  $G_{\alpha}$  can be compared.

b) Determination of chlorine distribution. From the statistics<sup>70</sup> the probabilities of finding  $-\text{CH}_2-$ ,  $-\text{CHCl}-$  and  $-\text{CCl}_2-$  groups in a random substitution are

$$\pi_0=x(\bar{\alpha})=(1-\bar{\alpha})^2 \quad 155)$$

$$\pi_1=y(\bar{\alpha})=2\bar{\alpha}(1-\bar{\alpha}) \quad 156)$$

$$\pi_2=z(\bar{\alpha})=\bar{\alpha}^2 \quad 157)$$

The conditional probabilities of finding the corresponding groups in the circumstances where the presence of a substituent on a given repeat unit affects the probability of a second substituent on the same repeat unit but not the substitution probability on any other repeat unit are

$$\pi_0 = X(\bar{\alpha}, \lambda) = (1-\lambda)^{-2} [1 + \lambda^2 - 2\bar{\alpha}(1-\lambda) - 2\lambda(1-\bar{\alpha} + 2\bar{\alpha}\lambda)^{\frac{1}{2}}] \quad 158)$$

$$\pi_1 = Y(\bar{\alpha}, \lambda) = (1-\lambda)^{-2} [-4\lambda + 2\bar{\alpha}(1-\lambda)(1+\lambda) + 4\lambda(1-2\bar{\alpha} + 2\bar{\alpha}\lambda)^{\frac{1}{2}}] \quad 159)$$

$$\pi_2 = Z(\bar{\alpha}, \lambda) = (1-\lambda)^{-2} [2\lambda - 2\bar{\alpha}\lambda(1-\lambda) - 2\lambda(1-2\bar{\alpha} + 2\bar{\alpha}\lambda)^{\frac{1}{2}}] \quad 160)$$

where  $\lambda < 1$  means that the reaction is a hindered substitution,  $\lambda = 0$  that the probability of finding  $-\text{CCl}_2-$  group is zero, and  $\lambda > 1$  means that the substituent Cl atom increases the chance for the second H atom on the same C atom to be substituted by another Cl atom. When  $\lambda = 1$  the reaction is a random substitution; Eqs. 158-160 reduce to Eqs. 155-157.

With  $^{13}\text{C}$ -NMR we are interested in analysing the sequence structure up to 5 repeat units (pentads). For example, the probabilities of finding some of them are listed in Table 8, where 0, 1 and 2 reflects  $-\text{CH}_2-$ ,  $-\text{CHCl}-$  and  $-\text{CCl}_2-$  groups, respectively.

Table 8 Probabilities of finding some pentads

| pentads  | random substitution                  | conditional substitution                                |
|----------|--------------------------------------|---------------------------------------------------------|
| 1. 00000 | $(1-\bar{\alpha})^8$                 | $X^4(\bar{\alpha}, \lambda)$                            |
| 2. 10000 | $4\bar{\alpha}(1-\bar{\alpha})^7$    | $2Y^3(\bar{\alpha}, \lambda)Y(\bar{\alpha}, \lambda)$   |
| 3. 01000 | $4\bar{\alpha}(1-\bar{\alpha})^7$    | $2X^3(\bar{\alpha}, \lambda)Y(\bar{\alpha}, \lambda)$   |
| 4. 10001 | $4\bar{\alpha}^2(1-\bar{\alpha})^6$  | $X^2(\bar{\alpha}, \lambda)Y^2(\bar{\alpha}, \lambda)$  |
| 5. 01010 | $4\bar{\alpha}^2(1-\bar{\alpha})^6$  | $X^2(\bar{\alpha}, \lambda)Y^2(\bar{\alpha}, \lambda)$  |
| 6. 11000 | $16\bar{\alpha}^2(1-\bar{\alpha})^6$ | $4X^2(\bar{\alpha}, \lambda)Y^2(\bar{\alpha}, \lambda)$ |
| 7. 11001 | $16\bar{\alpha}^3(1-\bar{\alpha})^5$ | $2X(\bar{\alpha}, \lambda)Y^3(\bar{\alpha}, \lambda)$   |

The middle 0 in Table 8 can be replaced by 1 or 2. Thus if we know  $\bar{\alpha}$  and  $\lambda$ , the theoretical probabilities of finding these pentads can be calculated and compared with the experimental results.

From the spectra of model compounds we know the correlation between the pentads and the related chemical shifts of CPE polymers, which are listed in Table 9 and have been reported in the literature<sup>39</sup>.

Table 9 Correlation between pentads and chemical shifts

| -CCl <sub>2</sub> - sequence |                         | -CHCl- sequence |                         | -CCl <sub>2</sub> - sequence |                         |
|------------------------------|-------------------------|-----------------|-------------------------|------------------------------|-------------------------|
| pentad                       | $\delta(^{13}\text{C})$ | pentad          | $\delta(^{13}\text{C})$ | pentad                       | $\delta(^{13}\text{C})$ |
| 11201                        | -88.5...-89.3           | 10101           | -54.4...-54.9           | 10001                        | -21.0                   |
| 10200                        | -89.9                   | 10100           | -58.1                   | 10000                        | -24.2                   |
| 01210                        | -96.6                   | 00100           | -61.3                   | 00000                        | -27.4                   |
|                              |                         | 01100           | -63.1                   | 11001                        | -29.8                   |
|                              |                         |                 |                         | 01001                        | -33.0                   |
|                              |                         |                 |                         | 01000                        | -36.2                   |
|                              |                         |                 |                         | 11010                        | -41.7                   |
|                              |                         |                 |                         | 01010                        | -44.9                   |

A Bruker WM 250 FT NMR Spectrometer was used to obtain the  $^{13}\text{C}$ -NMR spectra of the polymers. The resonance frequency for  $^{13}\text{C}$  is 62.9 MHz on the instrument.

Samples were dissolved in a 75/25 w/w ortho-dichlorobenzene/ $\text{d}_6$ -benzene mixture and hexamethyldisiloxane (HMDS) was added as an internal shift reference. Sample concentrations were normally around 15 wt %. The solvent system permitted an adequate polymer solubility and sufficient deuterium concentration to operate the spectrometer field lock system. All spectra were run at 80°C to improve solubility and resolution, by reducing the solution viscosity. Broad-band proton decoupling was used for all spectra.

The resulting spectra are shown in Figure 13.

#### 3.4.2. Microstructure of CPE

The molar degree of chlorination  $\bar{\alpha}$  and the weight degree of chlorination  $G_{\alpha}$  determined by  $^{13}\text{C}$ -NMR are seen in Table 10. They are compared with the values obtained from chemical analysis. It can be seen that the relative error  $\Delta$  between two methods is reasonable because each method was estimated to have a relative error of 5%.

$$\Delta = (G_{\alpha, \text{sp}} - G_{\alpha, \text{chem}}) / G_{\alpha, \text{chem}}$$

Table 10  $\bar{\alpha}$  and  $G_{\alpha}$  from  $^{13}\text{C}$ -NMR and chemical analysis

| sample | $\bar{\alpha}$ |        | $G_{\alpha}$ |      | $\Delta$ |
|--------|----------------|--------|--------------|------|----------|
|        | NMR            | chem   | NMR          | chem |          |
| CPE 1  | 0.1160         | 0.1138 | 37.4         | 36.9 | +0.01    |
| 2      | 0.0651         | 0.0739 | 24.9         | 27.4 | -0.09    |
| 3      | 0.1641         | 0.1779 | 45.9         | 48.0 | -0.04    |
| 4      | 0.0958         | 0.1081 | 32.9         | 35.7 | -0.08    |
| 20     | 0.3084         | 0.3097 | 62.0         | 62.1 | 0        |

The molar fraction contents of  $-\text{CH}_2-$ ,  $-\text{CHCl}-$  and  $-\text{CCl}_2-$  groups (X, Y and Z) determined from spectra are plotted against  $\bar{\alpha}$  in Figure 14. Also plotted are the theoretical curves from Eqs.155-160. Our data at low chlorine contents are close to the theoretical curves of hindered-type substitution.

The sequence distribution was also determined. Three pentad fractions  $F_{00000}$ ,  $F_{01000}$  and  $F_{10000}$  with higher accuracy are plotted in Figures 15 and 16 and compared with the theoretical curves calculated from the equations in Table 8. The results also show the characteristics of hindered-type substitution of our chlorination when the chlorine content is lower than 50% by weight. The theoretical curves cannot fit the experimental data even at  $\lambda=0$ , where the probability of finding  $-\text{CCl}_2-$  group is zero. We considered the model that the intimate neighbour is influenced by the  $\mu$ -parameter<sup>70</sup>, but this does not improve the discrepancy.

Comparing the results of  $F_{00000}$  with the literature<sup>39,40</sup>, we can draw the conclusion that our sample has a more homogeneous chlorine distribution along the chain because  $F_{00000}$  decreases rapidly with  $\bar{\alpha}$ . Calculation shows that  $F_{00000}$  should be zero at  $\bar{\alpha}=0.100$  ( $G \approx 34.0$ ) if chlorine is homogeneously distributed along the chain.

DTA results support our conclusion. Figure 17 shows the DTA thermograms of some chlorinated polyethylenes ( the experimental details will be discussed in chapter 4). It can be seen that for CPE 3 (48.0% Cl) a normal  $T_g$  transition occurs at  $10^{\circ}\text{C}$  while for CPE 4 (35.7% Cl) and CPE 2 (27.4% Cl) after the  $T_g$  transitions there are endothermic peaks at  $0^{\circ}$  and  $40^{\circ}\text{C}$ , respectively. These can be considered as the melting points of the residual crystalline parts in CPE, which correspond to the paraffins with 14 and 21 carbons, respectively. Similar phenomenon was reported for CPE polymers<sup>41</sup>, however, there is a difference between them. One can see that when suspension CPE samples with different degrees of chlorination were used the endothermic peaks occurred over the same temperature range ( $\sim 95^{\circ}\text{C}$ ) which corresponded to the melting point of a certain length of paraffin segments (about 54 carbons). Crystallinity persisted in suspension CPE until the chlorine content reached 56% by weight, which corresponded to the chlorine content of poly(vinyl chloride). Thus the result reflects that suspension chlorination is indeed quite inhomogeneous along the chain, it can leave a long length of  $\text{CH}_2$  groups without chlorination. In this work the endothermic peak temperature changes with the degree of chlorination, this reflects the fact that solution chlorination is a more homogeneous process.

## 4. DETERMINATION OF THE PHASE BOUNDARY AND THE INTERACTION PARAMETER

### 4.1. Introduction

This chapter contains a discussion of some methods for determination of the phase boundary and interaction parameter of amorphous polymer mixtures. For the measurement of phase boundaries one can use light scattering turbidity, DTA, electronmicroscopy, dynamic mechanical relaxation and dielectric relaxation. In chapter 1 their roles in the measurement of phase boundaries have already been discussed. In this chapter the backgrounds and the experimental details will be described. For the measurement of interaction parameters one can use heats of mixing, density measurements and IGC. The backgrounds and the experimental details will be described. The stress will be placed on IGC which will be studied from the viewpoint of methodology. All the experimental results except for those from IGC will be discussed along with the practical systems in chapter 5.

Many methods have been developed in the literature for measuring phase boundaries but none of them can be said to be universally applicable. The dominating factor influencing our choice of method is the rate of phase separation and growth of separated phases. We can divide polymer mixtures into three types:

a) Oligomer mixtures.

Such mixtures phase-separate very fast and the phase separation can be observed visually by turbidity. Phase volume can also be measured easily.

b) Polyblends with at least one component having a low  $T_g$

or low  $T_m$  and low molecular weight (usually smaller than  $10^5$ ).

In this case the phase separation is also fast. For example, poly(vinyl methyl ether)/polystyrene is a blend in which polystyrene is mobile above its  $T_g$  transition (although the  $T_g$  is high), the phase boundary can be observed visually using a microscope<sup>71</sup>.

c) Polyblends with high  $T_g$  components.

In such cases the phase separation takes place at a slow speed to produce small domain sizes and is difficult to detect at the early stage.

Thus, the measured phase boundary, which is in principle an equilibrium thermodynamic property, is often influenced by the kinetics of phase demixing.

## 4.2. Light scattering turbidity

### 4.2.1. Theory

There are two light scattering theories relating to the phase separation of polymeric liquid mixtures. The first is the well developed fluctuation theory for polymer solutions<sup>2,72</sup>, in which the intensity of scattered light  $I$  is derived to be proportional to the reciprocal of the differentiation of the chemical potential of the solvent with respect to the concentration of polymer.

$$I \propto (-d\mu_1/dc)^{-1} \quad 162)$$

Thus Gordon<sup>12</sup> suggests that if  $I$  is measured near the critical temperature in the one phase region, the spinodal can be obtained by extrapolating  $I^{-1}$  as a function of temperature to zero, because the condition for the spinodal is  $d\mu_1/dc=0$ . This method was used to measure the spinodal of polymer solutions and oligomer mixtures<sup>73</sup>.

The second theory was originally developed for a polymer solution undergoing spinodal decomposition by van Aartsen and

Smolders<sup>74</sup> and was adapted for polymer mixtures.<sup>75</sup> The main conclusion of the theory is that scattering can be described as a reflection of incident beam on planes perpendicular to the frequency vectors with a spacing  $D_m$  for which the Bragg reflection condition Eq.163 is obeyed.

$$D_m = \lambda_0 / 2 \sin(\theta_m / 2) \quad 163)$$

where  $\lambda_0$  is the wavelength of incident light,  $\theta_m$  is the angle of the intensity maximum. Thus, the blend after phase separation may be regarded as having a periodic structure.

For polymer mixtures we cannot use Eq.162 for measuring the spinodal since a large scale of fluctuations in these systems at the critical temperature is impossible because of high viscosity. According to Eq.163 the intensity maximum of scattered light moves to small angle continuously during the course of phase separation. The scattering intensity at a fixed angle is therefore a complex quantity and a judgement of the cloud point from the recorded intensity at one angle can only be made empirically.

#### 4.2.2. Experimental

The phase boundaries of PBA/CPE blends were examined by measuring scattered light from the sample using a specially designed light scattering photometer<sup>11</sup>. The films were supported in a sample holder located in a thermostatically controlled aluminium block. Light from a tungsten lamp was focussed onto the sample and the intensity of light scattered at  $45^\circ$  was measured using a photodiode. The temperature of the block was altered at a controlled rate and a plot of scattered light intensity against temperature was obtained. At the cloud point the intensity increases rapidly. The point of intersection of the two tangents which reflect the trends of intensity increasing before and after phase separation was taken as the cloud point, as shown

in Figure 18.

Measurements of light scattering turbidity were also carried out for PMMA/CPE blends with chlorine content of CPE changing from 27.4 to 51.6% by weight.

The phase boundaries of OMMA/COD mixtures were also determined. Mixtures of oligomers were weighed in different proportions into glass tubes. The experiment was carried out in a silicone oil bath for mixtures of COD1/OMMA23 and COD2/OMMA23. The samples were heated to at least  $10^{\circ}\text{C}$  above the cloud point and mixed thoroughly with a glass rod. On cooling the mixture at  $0.1^{\circ}\text{C}/\text{min}$ , the cloud point was detected by the appearance of turbidity in the mixture. The measurements were each repeated twice. Mixtures of COD3/OMMA23 were also studied and for this a methanol bath was cooled by a stream of nitrogen from a liquid nitrogen container. The cooling rate was controlled at  $0.1^{\circ}\text{C}/\text{min}$  by adjusting the nitrogen stream. It was not possible to measure the phase boundaries of systems containing COD with higher chlorine contents since the mixtures became viscous or solidified before any change was apparent. The accuracy of the phase boundary was estimated as  $\pm 0.2^{\circ}\text{C}$  for COD1/OMMA23 and COD2/OMMA23, and  $\pm 2^{\circ}\text{C}$  for COD3/OMMA23 mixtures.

#### 4.3. Differential thermal analysis (DTA)

##### 4.3.1. Theory

A generalized theory of DTA has been reported by Gray<sup>76,77</sup> and is considered here. The model used is shown in Figure 19. The thermal analysis cell consists of the sample and its container at temperature  $T_s$ , a source of thermal energy at temperature  $T_b$ , and a path having a thermal resistance  $R$ , through which the thermal energy flows to or from the sample at a rate  $dq/dt$ . The total heat capacity of the

sample plus container is designated  $C_s$ , which, together with  $R$ , is assumed constant over the range of interest. At any instant the sample is generating energy at a rate  $dH/dt$  which can either increase the sample temperature or be lost to the surroundings. As energy must be conserved, the sum of the two effects must equal, so that

$$dH/dt = C_s (dT_s/dt) - dq/dt \quad 164)$$

However,

$$dq/dt = (T_b - T_s)/R \quad 165)$$

so that Eq.164 can be rewritten as

$$dH/dt = C_s (dT_s/dt) + (T_s - T_b)/R \quad 166)$$

By writing a similar equation to Eq.164 for the reference cell where  $dH/dt=0$  and subtracting it from Eq.164, it may be shown that the instantaneous rate of heat generation by the sample in DTA is

$$R(dH/dt) = (T_s - T_r) + R(C_s - C_r) dT_r/dt + R C_s d(T_s - T_r)/dt \quad 167)$$

Transformations in polymers may be classified into three basic types: endothermic, with heat absorption; exothermic, with heat evolution; and the so-called second-order or glass transition, in which not the enthalpy but the specific heat undergoes a sudden change. Schematic presentations for the enthalpy, specific heat and temperature differential vs temperature are shown in Figure 20 for the three types of transformations. The temperature differential  $(T_s - T_r)$  can be obtained by solving Eq.167 using the conditions of transformations for enthalpy and specific heat. It can be seen that the thermograms are only reversed with respect to the specific heat curves.

#### 4.3.2. Experimental

Thermograms of CPE samples with different degrees of chlorination were studied using DTA. Measurements were made on a Du Pont 990 instrument using a sample weight of around 10 mg. The sample was

scanned from  $-100^{\circ}$  to  $100^{\circ}\text{C}$  at  $10^{\circ}\text{C}/\text{min}$  heating rate. Figure 17 shows the thermograms of the CPE samples.

The phase boundaries of PMMA/CPE blends were also determined by DTA. DTA (and DSC) has been widely used in the study of polymer compatibility. The advantages of the method are: a) a small quantity of sample is needed ( $\sim 10\text{mg}$ ), b) any form of sample (solid or liquid, powder or film) can be used, c) there is an accurate control of the thermal history through programmed heating and cooling cycles, d) One can use a rapid temperature scan in a broad range ( $-150^{\circ}$  to  $300^{\circ}\text{C}$ ), which makes the measurement of heat sensitive polymer such as CPE possible, and e) It is possible to make a quantitative determination of the composition from the measured  $T_g$  and  $\Delta T$  values.<sup>78</sup>

The measurements were made using a sample weight of around 10 mg. The sample was heated at  $100^{\circ}\text{C}/\text{min}$  and held at the upper temperature for 10 min and then quenched to  $-20^{\circ}\text{C}$ . The sample was then scanned at a rate of  $10^{\circ}\text{C}/\text{min}$ . The upper temperature of fast heating was changed by  $10^{\circ}\text{C}$  intervals. Phase separation was determined by the first appearance of new transitions in a subsequent scan, as illustrated in Figure 21.

#### 4.4. Electronmicroscopy

Electronmicroscopy is widely used in the study of polymer mixtures. The homogeneity of a blend is directly observed in a micrograph. McMaster<sup>79</sup> observed phase separation by both nucleation and growth and spinodal decomposition mechanisms in mixtures of PMMA and styrene/acrylonitrile copolymer according to the composition of the blend and the temperature. Matsuo<sup>80</sup> and Kaplan<sup>81</sup> compared dynamic mechanical studies with electronmicroscopy and concluded that two transitions would be apparent in blends where the level of

heterogeneity is greater than  $\sim 1000 \text{ \AA}$ . Between 200 and  $1000 \text{ \AA}$  two transitions would appear but would be broadened, while for less than  $150 \text{ \AA}$  the blend would exhibit only one glass transition. Studies on phase morphology by microscopy can explain many of the properties of polymer mixtures.

For a study using microscopy the problem always exists that the image may not be a perfect reconstruction of the object. The reasons for this come from preparation of the sample, replication methods and damage due to the electron beam. Sometimes samples need to be observed at gradually changing temperatures if the corresponding phase structures are to be known. This is particularly important for systems where phase transformations proceed rapidly. For systems with two components having a  $T_g$  higher than room temperature, quenched samples after treatment at high temperatures can be used for observation since they preserve the corresponding structures. The quality of the image in microscopy is judged by resolution and visibility (contrast). A good instrument has a resolution of higher than  $10 \text{ \AA}$ , which meets the needs for polyblend studies if an ultrafine film (several hundred  $\text{\AA}$ ) is used as object. Staining techniques using osmium tetroxide create a high contrast in systems containing double bonds because metallic osmium is deposited onto the double bond. In this work the contrast of the image comes from the chlorine in CPE, which appears as a dark phase, while PMMA is relatively transparent to the electron beam.

In order to check the measured phase boundary a PMMA1.4/CPE16 mixture was studied by transmission electron microscopy (TEM). The blend had a weight fraction of 0.263 CPE and the cloud point was  $140^\circ \text{C}$  as measured by DTA (see chapter 5). Several strips of the blend

were heated at 110°, 130°, 150° and 170°C for 15 min and then quenched before TEM observation. One strip of the blend without heat treatment was used as a reference.

The samples were sectioned using an LKB ultramicrotome to 400-800 Å. Because the samples were hard at room temperature, they were easily sectioned without the need for cooling as is required for low  $T_g$  systems. The fine sections were floated onto water and collected on a copper grid for microscopy.

Observations were made on a JEM 100B machine, which has a maximum resolution of 2.6 Å. The results will be discussed in chapter 5.

#### 4.5. Dynamic mechanical relaxation

##### 4.5.1. Theory

###### a) The dissipation factor $\tan \delta$

The characteristic of the mechanical response of a polymer is that it is not a simple Hookean spring, nor a Newtonian fluid. It is a viscoelastic body which can be simply simulated by a series combination of a spring and a dashpot, known as the Maxwell model<sup>82</sup>. If a stress  $\sigma$  is applied to this model the strain  $\epsilon$  will be given by

$$d\epsilon/dt = (1/E)d\sigma/dt + \sigma/\eta \quad 168)$$

with

$$\tau = \eta/E \quad 169)$$

where  $t$  is the time,  $E$  is the Young's modulus of the spring,  $\eta$  is the viscosity of the fluid in the dashpot,  $\tau$  is the relaxation time of the model defined by Eq.169. The right hand side of Eq.168 is composed of two terms: the first term is a term for a Hookean elastomer, the second is a term for a Newtonian fluid.

If  $\sigma$  is a sinusoidal stress with frequency  $\omega$ ,

$$\sigma(t) = \sigma_0 e^{i\omega t} \quad (170)$$

We can define the complex dynamic modulus  $E^*$  as

$$\begin{aligned} E^* &= d\sigma(t)/d\varepsilon(t) = \tau\omega E/(\tau\omega - i) \\ &= E\tau^2\omega^2/(1+\omega^2\tau^2) + i\tau\omega E/(1+\omega^2\tau^2) = E' + iE'' \end{aligned} \quad (171)$$

with

$$E' = E\tau^2\omega^2/(1+\omega^2\tau^2) \quad (172)$$

$$E'' = E\tau\omega/(1+\omega^2\tau^2) \quad (173)$$

Eq. 171 shows that for a viscoelastomer the response (strain) is also a sinusoidal function but with a phase angle of  $\delta$  delay. The tangent of the phase angle  $\delta$  between stress and strain is

$$\tan\delta = E''/E' = 1/\tau\omega \quad (174)$$

When  $\tau\omega \sim 1$ ,  $\tan\delta$  will reach a maximum. This point corresponds to the glass transition. At this point the segmental motion of the chain molecules starts, but with a large phase angle delay to the stress, which causes the maximum mechanical damping.

The model described here is a rather simplified model which only has a single relaxation time. For a practical polymer we should have a relaxation time spectra to characterize the different units of molecular motion such as segment, sub-segment and side group etc. Thus we will obtain a series of transitions in the dynamic measurements.

b) The glass transition temperature  $T_g$  of homogeneous polyblend

Polymer compatibility can be detected by consideration of the number of  $T_g$  transitions in the blend. If only one  $T_g$  is found intermediate between the two  $T_g$  temperatures of the pure components, the blend is miscible. If the loss peak in  $\tan\delta$  is broad, the blend is not perfectly homogeneous.

For miscible polyblends, a plot of  $T_g$  against composition is

not always a linear function. There may be positive deviations from linearity if there are strong specific interactions in the blends, or there may be negative deviations from linearity in blends having weak interactions. The systems for these three cases (positive, negative and no deviations) are summarized in a book by Olabisi and others<sup>83</sup>. The following equations are used to express the negative deviations from the linearity:

The Fox equation<sup>84</sup>,

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (175)$$

the Gordon-Taylor equation<sup>85</sup>,

$$T_g = [w_1 T_{g1} + k(1-w_1) T_{g2}] / [w_1 + k(1-w_1)] \quad (176)$$

and the Kelley-Bueche equation<sup>86</sup>,

$$T_g = [\phi_1 T_{g1} + k(1-\phi_1) T_{g2}] / [\phi_1 + k(1-\phi_1)] \quad (177)$$

In the three equations  $w_i$  and  $\phi_i$  are the weight fraction and volume fraction of component  $i$ .  $k$  is the ratio of the thermal expansion coefficients between the rubber and glass states of the component polymers.

$$k = (\alpha_{12} - \alpha_{g2}) / (\alpha_{11} - \alpha_{g1}) \quad (178)$$

When  $k=1$  Eqs. 176 and 177 reduce to the linear form

$$T_g = w_1 T_{g1} + w_2 T_{g2} \quad (179)$$

$$T_g = \phi_1 T_{g1} + \phi_2 T_{g2} \quad (180)$$

Couchman<sup>87</sup> developed a thermodynamic theory to explain these equations. He started from expressing the molar entropy  $S$  of the mixed system.

$$S = n_1 S_1 + n_2 S_2 + \Delta S_m \quad (181)$$

where  $n_i$  is mole fraction,  $S_i$  is molar entropy of the pure component  $i$ , and  $\Delta S_m$  is the excess entropy of mixing. If  $S$  is referred to the glass transition temperature and the value is denoted as  $S^0$ ,

by introducing the heat capacity  $C_{pi}$ , Eq.181 can be rewritten as

$$S = n_1 \left\{ S_1^0 + \int_{T_{g1}}^T C_{p1} d \ln T \right\} + n_2 \left\{ S_2^0 + \int_{T_{g2}}^T C_{p2} d \ln T \right\} + \Delta S_m \quad (182)$$

Using the characteristic continuity of extensive thermodynamic parameters at the glass transition temperatures (see Figure 20 for enthalpy):

$$S_i^0(\text{glass}) = S_i^0(\text{liquid}) \quad (183)$$

We have

$$n_1 \left\{ \int_{T_{g1}}^T (C_{p1}^g - C_{p1}^l) d \ln T \right\} + n_2 \left\{ \int_{T_{g2}}^T (C_{p2}^g - C_{p2}^l) d \ln T \right\} + \Delta S_m^g - \Delta S_m^l = 0 \quad (184)$$

For ideal and regular solutions,

$$\Delta S_m^g = \Delta S_m^l \quad (185)$$

and Eq.184 reduces to

$$n_1 \int_{T_{g1}}^T \Delta C_{p1} d \ln T + n_2 \int_{T_{g2}}^T \Delta C_{p2} d \ln T = 0 \quad (186)$$

where  $\Delta$  denotes transition increments. Noting  $\Delta C_{pi}$  is constant and intergrating Eq.186, we obtain

$$n_1 \Delta C_{p1} \ln(T_g/T_{g1}) + n_2 \Delta C_{p2} \ln(T_g/T_{g2}) = 0 \quad (187)$$

For later convenience  $n_i$  is exchanged for the weight fraction  $w_i$  and  $\Delta C_{pi}$  is then taken as per unit weight. Eq.187 can then be rewritten as

$$\ln T_g = (w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}) / (w_1 \Delta C_{p1} + w_2 \Delta C_{p2}) \quad (188)$$

If  $T_{g1} \sim T_{g2}$ , Eq.188 reduces to the Wood equation<sup>88</sup>

$$T_g = (w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}) / (w_1 \Delta C_{p1} + w_2 \Delta C_{p2}) \quad (189)$$

If  $T_{g1} \sim T_{g2}$  and  $\Delta C_{p1} T_{g1} \sim \Delta C_{p2} T_{g2}$ , Eq.188 reduces to the Fox equation (Eq.175). If  $\Delta C_{p1} \sim \Delta C_{p2}$ , Eq.188 reduces to the Pochan, Beatty and Hinman equation<sup>89</sup>

$$T_g = w_1 \ln T_{g1} + w_2 \ln T_{g2} \quad (190)$$

If  $T_{g1} \sim T_{g2}$  and  $\Delta C_{p1} \sim \Delta C_{p2}$ , Eq.188 reduces to Eq.179.

Starting from the continuity of total volume of mixture, with similar derivations as used for the entropy continuity, Couchman's

theory also explained Eq.177, the Kelley-Bueche equation.

#### 4.5.2. Experimental

Measurements were carried out on a Rheovibron (Model DDV-2, Toyo Measuring Instrument Co. Ltd.). A strip of the sample (20x5x0.2 mm) was subjected to an imposed oscillatory frequency of 11 Hz. A temperature range from  $-60^{\circ}$  to  $170^{\circ}\text{C}$  was scanned at  $1^{\circ}\text{C}/\text{min}$  heating rate and a plot of  $\tan\delta$  against temperature obtained. A maximum in  $\tan\delta$  was taken as a measure of  $T_g$ .

The experiments consisted of 4 groups: a) pure CPE samples, b) PMMA/CPE blends, c) PBA/CPE blends and d) CPE/CPE blends. Here the results for the pure CPE samples are presented. The remainder will be discussed in the following chapter.

Pure CPE samples with different chlorine contents were used. Figure 22 is a plot of the  $T_g$  measured against chlorine content in CPE. It shows that at low chlorine content the chlorine destroys the crystallinity of polyethylene and brings about a rubber state. Because the polymer still has  $-\text{CH}_2-$  blocks in the chain, the loss peak has a smaller value (the maximum of  $\tan\delta$  is around 0.4 as compared with 1.5 of the sample of higher chlorine content). CPE with the same chlorine content as poly(vinyl chloride) has a lower  $T_g$ , which reflects a random distribution of chlorine along the chain in CPE.

#### 4.6. Dielectric relaxation

Dielectric relaxation is a similar technique to dynamic mechanical relaxation for the study of molecular motion in polymers. Unlike dynamic mechanical measurements, a wide and continuous range of frequencies can be readily used. This permits the dynamic dielectric constants and the dielectric dissipation factor  $\tan\delta$  to be

determined either as a function of temperature (temperature-plane measurements) over many frequencies or as a function of frequency (frequency-plane measurements) at selected temperatures. Frequency-plane measurements are particularly important because blend compatibility may be studied at temperature above or below  $T_g$  permitting a study of phase separation at lower or upper critical solution temperatures<sup>67</sup>.

Compared with DTA (DSC) and dynamic mechanical measurements, the use of dielectric techniques in the study of polymer blends has been limited. This is in part due to the greater experimental difficulties inherent in this method and in part due to the lack of sensitivity of dielectric measurements to blends of nonpolar polymers. Some studies in this field have been summarized in the literature<sup>90</sup>.

The theory describing the response of a viscoelastic body to a electric field is quite similar to that of dynamic mechanical relaxation. The Maxwell model has been used to simulate the behaviour of a polymer under a sinusoidal stress. This simple model has an electrical analogue, as shown in Figure 23<sup>91</sup>. One can write for the electrical model

$$de/dt = C(dV/dt) + (1/R)V \quad 191)$$

where  $de/dt$  is the current,  $C$  the capacity,  $R$  the resistivity, and  $V$  the electrical potential. Comparing Eq.191 with Eq.168, it is clearly seen that within the two models the resistance is equivalent to the dashpot and the capacitor is equivalent to the spring. While the two parts are connected in series in the mechanical model, the two corresponding parts should be connected in parallel in the electrical model. If a periodic electrical field is applied, a similar equation

for the electrical dissipation factor  $\tan \delta$  can be derived.

In this work some PMMA/CPE blends were studied using dielectric measurements.  $\tan \delta$  was measured on a film sample with a 1621 Precision Capacitance Measurement System (General Radio). An oscillation frequency was chosen and a temperature range from  $-40^{\circ}$  to  $170^{\circ}\text{C}$  was scanned at  $1^{\circ}\text{C}/\text{min}$  heating rate.

The results will be discussed in chapter 5.

#### 4.7. Heats of mixing

##### 4.7.1. Introduction

Calorimetry is a classical method for studying the thermodynamics of polymer solutions. Both the Flory-Huggins theory and the Flory equation of state theory developed equations which connect the heat of mixing ( $\Delta H_m$ ) with the interaction parameter between two components. The difficulty in measuring  $\Delta H_m$  is that the extremely low rates of solution of polymers and the high viscosities of their solutions prevent high accuracy. Hence the heat change on diluting a solution of the polymer with an additional amount of solvent may sometimes be measured in preference to the mixing of pure polymer with solvent<sup>2</sup>.

In oligomer mixtures the viscosity is greatly reduced so that the measurements can be made directly.<sup>5,18</sup>

Pouchly and Biros<sup>92</sup> reported calorimetry data on model compounds designed to explain the solvating power of cyclic ethers and ketones for poly(vinyl chloride). Heats of mixing were measured for various singly and doubly chlorinated hydrocarbons (4-6 carbons) and poly(vinyl chloride) with THF and for hexane with cyclohexane. The specific interactions detected explained the many examples of miscibility or partial miscibility among halogenated polymers and

those containing oxygen (e.g. ester groups).

The heat of mixing for two polymers can be calculated from mixing in a solvent by Hess's law with the aid of the following thermochemical equations:

$$\left. \begin{array}{l} m_1 \text{ g of polymer 1 + solvent} = \text{solution 1} + Q_1 \\ m_2 \text{ g of polymer 2 + solvent} = \text{solution 2} + Q_2 \\ \text{solution 1} + \text{solution 2} = \text{solution 4} + Q_4 \end{array} \right\} \quad 192)$$

or alternatively,

$$\left. \begin{array}{l} m_1 \text{ g of polymer 1} + m_2 \text{ g polymer 2} = \text{solution 3} + \Delta H_m \\ \text{solution 3} + \text{solvent} = \text{solution 4} + Q_3 \end{array} \right\} \quad 193)$$

Eq.192 describes a cycle that solution 4 (two polymers in one solvent) can be prepared by dissolving two polymers separately into the solvent and then mixing the two polymer solutions together, or alternatively it can be prepared by blending two polymers first and then dissolving the polyblend into solvent (as described in Eq.193).

The total heat effect should be same, we can write

$$Q_1 + Q_2 + Q_4 = \Delta H_m + Q_3 \quad 194)$$

Hence, the heat of mixing of polymers can be found as

$$\Delta H_m = Q_1 + Q_2 - Q_3 + Q_4 \quad 195)$$

In this work the heats of mixing were measured for 4 pairs of oligomers: OMMA/COD, OMMA/cereclor, PBA/cereclor and COD/COD. these are taken as model compounds for the related high molecular weight polymer pairs.

#### 4.7.2. Experimental

The heats of mixing were measured using a modified NBS batch type calorimeter<sup>11</sup>. The machine has an accuracy of  $\pm 0.02$  J/g as determined by an acid base reaction. However the viscosity of the oligomers made mixing difficult and we estimate an error of  $\pm 0.1$  J/g

for our systems.

The machine was calibrated using a heating coil immersed in the particular systems under investigation. The calibration constant  $F$  is calculated by

$$F=Q/A \quad 196)$$

with

$$Q=I^2Rt \quad 197)$$

where the current  $I$  was fed into the resistor  $R$  for time  $t$ . The chart recorder showed a peak whose area  $A$  was proportional to the heat  $Q$ , generated by the resistor. With different time  $t$  a plot of  $Q$  vs  $A$  was obtained, hence  $F$  was calculated.

Figure 24 shows examples of the calibrations. The  $F$  values for the systems investigated are shown in Table 11. It can be seen that  $F$  changes little with chlorine content and temperature.

Table 11  $F$  values

| mixture          | temperature        | chart recorder | $F$                    |
|------------------|--------------------|----------------|------------------------|
|                  | $^{\circ}\text{C}$ | f.s.d.         | $\text{J}/\text{cm}^2$ |
| OMMA23/COD2      | 70                 | 3mV            | 0.2143                 |
| OMMA23/COD3      | 70                 | 1mV            | 0.0680                 |
| OMMA23/COD3A     | 70                 | 1mV            | 0.0680                 |
| OMMA23/COD4      | 70                 | 1mV            | 0.0704                 |
| OMMA23/COD5      | 70                 | 1mV            | 0.0715                 |
| OMMA1/cereclor45 | 70                 | 300 V          | 0.0226                 |
| OMMA1/cereclor45 | 85                 | 300 V          | 0.0239                 |
| PBA/cereclor45   | 70                 | 300 V          | 0.0399                 |
| PBA/cereclor52   | 70                 | 300 V          | 0.0399                 |
| COD/COD          | 70                 | 300 V          | 0.0447                 |

#### 4.8. Density

The prediction of the excess volume of mixing is one of the great successes of the Flory equation of state theory. In chapter 2

we have discussed the details of the theory. Owing to the interaction between two components or the disparity of the equation of state coefficients between them, the volume of a mixture may not be additive. For polymer mixtures the differences of the equation of state parameters are not large and the interaction term is decisive in determining the sign and magnitude of the excess volume of mixing. Flory calculated the interaction energy parameter  $X_{12}$  from measurements of the excess volume of mixing<sup>7</sup>.

From Eq.118 we can see that if  $\Delta V_m = 0$  during mixing, then

$$1/d_m = w_1/d_1 + w_2/d_2 \quad (198)$$

or, more conveniently

$$v_m = w_1 v_1 + w_2 v_2 \quad (199)$$

where  $v_i$  is the specific volume ( $v_i = 1/d_i$ ). Calculation using the equation of state (Eq.55) shows that the negative deviation of  $d_m$  or the positive deviation of  $v_m$  from linearity is a result of strong molecular interactions favouring better packing between molecules<sup>19</sup>.

In this work the densities of PMMA/CPE16 blends were measured by equal density titration as described in chapter 3. The results will be discussed in chapter 5.

#### 4.9. Inverse gas chromatography (IGC) of one-phase and two-phase blends

##### 4.9.1. The theory for one-phase blends

The theory of IGC for the study of polymer compatibility is based on two assumptions:

a) The activity of the solvent probe  $a_1$  at the limit of  $w_1 \rightarrow 0$  is related to the specific retention volume  $V_g^0$  as follows

$$\ln(a_1/w_1)^\infty = \ln(273.2R/P_1^0 V_g^0 M_1) - (P_1^0/RT)(B_{11} - V_1) \quad (200)$$

where  $w_1$  is the weight fraction of solvent in the polymer (liquid phase),  $M_1$  is the molecular weight,  $P_1^0$  the saturated vapour pressure,

$V_1$  the molar volume and  $B_{11}$  the second virial coefficient of the solvent vapour. The first term on the right hand side of the equation is the definition of the activity of an ideal gas in equilibrium with the liquid phase in the gas chromatographic column. The second term is the correction for imperfect gas behaviour. Eq.200 is assumed to be true for both the homopolymer and blend coatings.

b) The activity of the solvent,  $a_1$ , can be related to the interaction parameter  $\chi$  through conventional polymer solution theories when the limiting case of  $\phi_2 \rightarrow 1$  is approached. Based on the framework of the Flory-Huggins theory, for a single polymer

$$\ln(a_1/w_1)_{23}^{\infty} = \ln(v_1/v_2) + 1 + \chi_{12} \quad (201)$$

and for a blend

$$\ln(a_1/w_1)_{23}^{\infty} = \ln[v_1/(w_2v_2 + w_3v_3)] + 1 + \phi_2\chi_{12} + \phi_3\chi_{13} - \chi'_{23}\phi_2\phi_3 \quad (202)$$

where  $v_i$  and  $\phi_i$  are the specific volume and the volume fraction of component  $i$ , respectively.  $\chi'_{23} = \chi_{23}/r_2$ , and  $r_2$  is the number of segments in the polymer molecule.  $\chi_{23}$  is the usual parameter defined in Flory's terminology ( $\chi_{23} = Zr\Delta\omega_{23}/kT$ , in which  $Z$  is the lattice coordination number and  $\Delta\omega_{23}$  is the change in energy for the formation of an unlike contact pair).

Combining Eqs.200-202, we have

$$\ln[v_{g23}^0/(w_2v_2 + w_3v_3)] - \phi_2\ln(v_{g2}^0/v_2) - \phi_3\ln(v_{g3}^0/v_3) = \chi'_{23}\phi_2\phi_3 \quad (203)$$

where  $v_{g23}^0$  is the specific retention volume of the homogeneous blend.

This equation can also be rewritten in a logarithmic form as in the literature<sup>93</sup>.

$$\ln\left\{v_2^{\phi_2}v_3^{\phi_3}v_{g23}^0/[(w_2v_2 + w_3v_3)(v_{g2}^0)^{\phi_2}(v_{g3}^0)^{\phi_3}]\right\} = \chi'_{23}\phi_2\phi_3 \quad (204)$$

In high polymer blends when the number of molecules is very small in the combinatorial entropy term, the free energy of mixing ( $\Delta G_m$ ) is determined by the interaction between the polymers.

$$\lim(r_2, r_3 \rightarrow \infty) \Delta G_m / RT = \chi'_{23} n_2 r_2 \phi_3 = (w_2 / \phi_2 m_2) \chi'_{23} \phi_2 \phi_3 \quad (205)$$

where  $n_2$  is the number of moles of polymer 2 and  $m_2$  the molecular weight per segment. Therefore, from Eq.203 the algebraic difference of the logarithm of the retention volume per unit volume between the pure components and the blend depends on the free energy of mixing.

Unlike most experiments, in IGC the systems are studied at very high concentration of polymers. An injection of solvent is only 0.1  $\mu$ l in quantity. If, for example, a 2 metre column is used, the peak retention volume is 50 ml, and the half width of the peak is 10 ml, then the solvent will spread over a zone of about 0.4 metres in length, as shown in Figure 25. If, for example, the diameter of the column is 0.4 cm and 1 gram of polymer is loaded on the support, the concentration of solvent in solution would be only about 0.1  $\mu$ l / 0.2g  $\approx$  0.0005 volume fraction, or the concentration of polymer is around 0.9995 volume fraction. At high concentration of polymer the analysis of activity by the Flory-Huggins theory leads to

$$a_1 \approx \phi_1 e^{1+\chi_1} \quad (206)$$

or

$$P_1 \approx P_1^0 \phi_1 e^{1+\chi_1} \quad (207)$$

Eqs.206 and 207 are Henry's law with  $e^{1+\chi_1}$  as the limiting constant, when the concentration of the diluent is expressed by its volume fraction<sup>2</sup>. Eq.206 was required to derive Eqs.201 and 202 and is also therefore the basis for any consideration of phase separated systems.

#### 4.9.2. Calculation of the retention volume for a phase separated blend

If two pure polymers are in equilibrium with a common solvent vapour in a small region, the activity of the solvent can be expressed as

$$\ln(a_1) = \ln\phi_1^2 + 1 + \chi_{12} = \ln\phi_1^3 + 1 + \chi_{13} \quad (208)$$

where  $\phi_1^2$  and  $\phi_1^3$  are the volume fractions of solvent in polymer 2 and 3, respectively. This is a logarithmic form of Eq.206, Henry's law. Based on Eq.208, multiplying the first expression for  $\ln(a_1)$  by  $\phi_2$  and the second by  $\phi_3$  and adding the two expressions, we obtain an expression,

$$\ln(a_1) = \phi_2 \ln\phi_1^2 + \phi_3 \ln\phi_1^3 + 1 + \phi_2 \chi_{12} + \phi_3 \chi_{13} \quad (209)$$

If we introduce  $w_1^m$ , the weight fraction of solvent in the liquid phase (consisting of two pure polymers)

$$w_1^m = V_1 d_1 / (V_2 d_2 + V_3 d_3) \quad (210)$$

where  $V_i$  and  $d_i$  are the volume and density of component  $i$ , respectively, then Eq.209 can be put in the form

$$\ln(a_1/w_1^m) = \phi_2 \ln(\phi_1^2/w_1^m) + \phi_3 \ln(\phi_1^3/w_1^m) + 1 + \phi_2 \chi_{12} + \phi_3 \chi_{13} \quad (211)$$

Using Eq.208 and noting that

$$\phi_1^i = V_1^i / V_i \quad (212)$$

and

$$V_1 = V_1^2 + V_1^3 \quad (213)$$

where  $V_1^i$  is the volume of solvent in polymer  $i$ . The limiting form of Eq.211 becomes

$$\begin{aligned} \ln(a_1/w_1^m)^\infty = & \ln[V_1 / (w_2 v_2 + w_3 v_3)] + 1 + \phi_2 \chi_{12} + \phi_3 \chi_{13} \\ & - \ln[(\phi_2 + \phi_3 e^{\chi_{12} - \chi_{13}}) \phi_2 (\phi_3 + \phi_2 e^{\chi_{13} - \chi_{12}}) \phi_3] \end{aligned} \quad (214)$$

Eq.214 gives the activity of solvent in equilibrium with two separated pure polymers at the limit  $w_1^m \rightarrow 0$ .

If Eq.201 is used to eliminate  $\chi_{12}$  and  $\chi_{13}$  in Eq.214 and the logarithm of the activity term of Eq.201 is substituted into Eq.200, the final equation becomes

$$V_{gm}^0 / (w_2 v_2 + w_3 v_3) = \phi_2 (V_{g2}^0 / v_2) + \phi_3 (V_{g3}^0 / v_3) \quad (215)$$

This is equivalent to

$$V_{gm}^0 = w_2 V_{g2}^0 + w_3 V_{g3}^0 \quad 216)$$

In Eqs. 215 and 216  $V_g^0$  is the retention volume per unit weight of polymer and  $V_g^0/v$  can be regarded as the retention volume per unit volume of polymer, hence the dependence on weight fraction and volume fraction results, respectively. From the analysis of the activity of the solvent it is shown that the retention volume of a phase separated blend is a linear function of composition if the blend is separated into two pure polymers.

#### 4.9.3. Experimental

The apparatus consisted of a Pye Unicam GCD chromatograph. It contained a 2 metre coiled pyrex column packed with a Teflon support (Phase Separation, 30/60 mesh) on which the polymer was deposited as a thin film. A uniform flow of nitrogen carrier gas was passed through the column which was kept at constant temperature in an air circulating oven. A pulse of solvent was injected at one end and detected at the exit by a flame ionization detector.

The packing was prepared by coating from solution. The polymer (1.2 g) was dissolved in MEK (AR) and the solution added to 15 g of the support which had been washed with MEK and dried in an oven at 100°C prior to use. The volatile solvent was evaporated slowly with heating and frequent stirring to prevent coagulation of the particles. The powder was then sieved (30/60 mesh) to remove any large particles (though none was found). The packing was packed into the glass column, applying a vacuum to one end. The columns were packed in three ways as described in chapter 1 and shown in Figure 25: column 1 was filled with packings having polymer blend coatings, column 2 was packed with two mixed packings, each coated with a single polymer,

and column 3 was packed in series with two single packings.

The packed columns were loaded into the g.l.c. oven and conditioned for 12 hrs at 100°C, while nitrogen was flushed through the column in order that it should come to equilibrium. The retention volumes were measured for several solvents (pentane, MEK, THF and chloroform). Samples of solvent (0.1  $\mu$ l) were injected using a 1  $\mu$ l Hamilton syringe. The retention time was recorded using a stopwatch or was calculated from the distance from injection on a well calibrated chart recorder. The dead volume was measured by injecting a sample of methane. The measurements were repeated three times and an average was taken. The flowrates of carrier gas were taken from 5 -15 ml/min and the net retention volume extrapolated to zero flowrate. Figure 26 shows the extrapolations for CPE20 at different temperatures from 80°C-160°C using chloroform as the probe solvent.

The specific retention volume is calculated by

$$V_g^0 = (t_r - t_{gas})Q(273.2f_p/TW) \quad (217)$$

where  $V_g^0$  is the retention volume at 0°C,  $t_r$  is the retention time of solvent,  $t_{gas}$  is the retention time for a non-interacting methane sample,  $Q$  is the volume flowrate of carrier gas,  $T$  is the operating temperature of the column,  $W$  is the weight of stationary phase, and  $f_p$  is a correction for the pressure drop along the column given by

$$f_p = 3[(P_i/P_0)^2 - 1]/2[(P_i/P_0)^3 - 1] \quad (218)$$

where  $P_i$  is the inlet pressure and  $P_0$  is the outlet pressure.  $V_g^0$  has a relative error of  $\pm 5\%$  by repeat measurements on different columns.

The mixtures studied are PMMA/CPE20, PEMA/CPE20 and PBA/CPE20. The details of the polymers can be seen in chapter 3.

For the measurements of interaction parameter it is recommended that the polymer should be in the molten state. This temperature is

usually taken as  $T_g + 50^\circ\text{C}$ . For the PMMA/CPE system when the weight fraction of CPE is greater than 0.5,  $T_g + 50^\circ\text{C}$  will be below  $120^\circ\text{C}$ , the experimental temperature. For the PEMA/CPE system this requirement is fulfilled at  $120^\circ\text{C}$ , but the retention volumes of pure PEMA shows that this temperature could be lower because the retention volume decreases at above  $80^\circ\text{C}$ . For the PBA/CPE system only bulk adsorption is observed in all the measurements except for the pure CPE at  $80^\circ\text{C}$ . From the retention volume-temperature relation we can see that CPE20 reaches the molten state at around  $100^\circ\text{C}$  (Figure 26).

The choice of loading of polymer on the inert support is another problem for IGC. At low loadings the contribution of surface adsorption is relatively large, this causes the specific retention volume  $V_g^0$  to increase sharply. At high coverage the coated film becomes so thick that solvent vapour cannot reach equilibrium in a limited sweep time. For example, under the conditions discussed previously the sweep time would be about 120 seconds for a 0.4 m zone to pass a section of packing if the flowrate is 5 ml/min. Nonequilibrium adsorption will cause  $V_g^0$  to drop rapidly because all the stationary phase does not come into equilibrium with the solvent. Hence the suitable loading depends on the surface area of support, the density of polymer and the diffusion coefficient of the solvent in the stationary phase. Owing to the fact that solvents have quite different diffusion coefficients, it is difficult to find a common polymer loading for use with all solvents. In this work 8% w/w coverage was used in accordance with previous usage<sup>30</sup>.

#### 4.9.4. Results and discussion

##### a) Results on mixed packings

In the previous section we derived Eq.216 for the retention

volume of a phase separated blend. With mixed polystyrene and polybutadiene packings Klein, Widdecke and Wolter<sup>94</sup> verified this equation. They further showed that if this incompatible polyblend was coated onto the support,  $V_g^0$  also obeyed Eq.216. Dipaoba-Baranyi and Degre<sup>95</sup>, and Galin and Rupprecht<sup>38</sup> confirmed the last observation using high molecular weight polystyrene/poly(n-butyl methacrylate) and polystyrene/poly(dimethyl siloxane), respectively. Both are incompatible pairs. Thus the conclusion can be drawn that the retention volume of an immiscible polyblend is the same as that of mixed packings.

In this work mixed packings are examined as a model of phase separated blends. As shown in Figure 27-29, in all the cases the experimental  $V_g^0$  values for mixed packings are in agreement with Eq.216. It was observed that for PBA and PEMA columns the retention volumes at low temperatures (80° or 100°C) are a little smaller than required by the linear relationship. The data are just beyond the experimental error. This may be due to the relatively larger thickness considering that the same weight percentage coverage were used for coating polymers in all experiments.

As expected, the retention volume of the column with packings in series also obeys Eq.216. The experimental values are purely due to additivity of the column.

#### b) Results on PBA/CPE and PMMA/CPE blends

The retention volumes of these two systems are also found to be linear functions of composition, as shown in Figures 27 and 29. This casts some doubts on the homogeneity of blend coatings. The conclusion can be drawn from Eq.203 that  $V_{g23}^0$  must be smaller than the corresponding algebraic average even when the homogeneous

polyblend reaches the phase separation temperature, i.e.  $\chi'_{23}=0$ . After phase separation the retention volume will follow Eq.216. There is a gap between these two retention volumes and the magnitude of the gap depends on the difference between  $V_{g2}^0$  and  $V_{g3}^0$ , i.e. between the interactions of the pure polymers with the solvent. For example, for a homogeneous blend of  $w_2=0.5$  in the PBA/CPE system at  $80^\circ\text{C}$  the specific retention volume ought to be smaller than 35 ml (where  $\chi'_{23}=0$ ), while the additive value is 55 ml (after separating into two pure polymers). The gap is 20 ml which is far beyond the experimental error.

If the retention volume of the polyblend is linearly dependent on composition as in Eq.215, a positive  $\chi'_{23}$  will be calculated from Eq.203, because  $\ln[\phi_2(V_{g2}^0/v_2)+\phi_3(V_{g3}^0/v_3)]$  is no longer a linear function of  $\phi_2$ . For PBA/CPE such a positive  $\chi'_{23}$  is calculated. The value decreases with temperature, as shown in Figure 30. We can see that both the sign and the trend of change with temperature of  $\chi'_{23}$  is contrary to the thermodynamics of polymer compatibility. Polymer compatibility needs  $\chi'_{23}$  to have a negative or very small positive value. The LCST behaviour suggests that  $\chi'_{23}$  should increase with temperature.

The unusual  $\chi'_{23}$  is assumed to arise as a result of phase separation of the polyblend during casting onto the support or during heating. Experience on casting blend films shows that phase separation may take place during evaporation of a solvent. This will depend on the conditions under which the solvent is evaporated and the nature of the polymer/polymer/solvent three component phase diagram. Incompatibility in the presence of a solvent is often observed for compatible polymers. For example, if blends of poly(vinyl

chloride) with various polyacrylates are cast from THF two phase systems result whereas if they are cast from MEK one phase systems result<sup>30</sup>.

If phase separation does take place then Eq.203 cannot be used because the equation is strictly applicable to a homogeneous ternary system. Instead, we need the analysis of phase separated blends as discussed above.

### c) Results on PEMA/CPE blends

As seen in Figure 28, the retention volumes of the PEMA/CPE blends are below the linear relationship. The difference between them tends towards zero as the temperature increases. Table 12 lists the interaction parameters calculated from Eq.203 with an accuracy of  $\pm 0.20$ . This error in  $\chi'_{23}$  results from an error of  $\pm 5\%$  in  $v_g^0$ . However, it can be seen that the system is more compatible at higher concentrations of CPE as a larger negative  $\chi'_{23}$  is found. With increasing temperature  $\chi'_{23}$  tends towards zero as would be expected.

Table 12  $v_g^0$  and  $\chi'_{23}$  of PEMA/CPE blends

| $v_g^0$ and $\chi'_{23}$ | $v_g^0(\text{ml/g})$ | $v_g^0(\text{ml/g})\chi'_{23}$ | $v_g^0(\text{ml/g})\chi'_{23}$ | $v_g^0(\text{ml/g})\chi'_{23}$ | $v_g^0(\text{ml/g})\chi'_{23}$ | $v_g^0(\text{ml/g})$ |
|--------------------------|----------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|----------------------|
| $w_{\text{CPE}}$         | 0                    | 0.2547                         | 0.5011                         | 0.7451                         | 1                              |                      |
| 1.chloroform             |                      |                                |                                |                                |                                |                      |
| 80°C                     | 37.5                 | 24.2 -1.15                     | 14.9 -0.99                     | 8.5 -1.58                      | 6.9                            |                      |
| 100°C                    | 28.8                 | 23.2 -0.50                     | 15.9 -0.86                     | 12.0 -1.00                     | 10.8                           |                      |
| 120°C                    | 18.7                 | 18.1 0.81                      | 12.0 -0.41                     | 10.0 -0.37                     | 8.5                            |                      |
| 2.MEK                    |                      |                                |                                |                                |                                |                      |
| 80°C                     | 35.0                 | 27.1 -0.64                     | 20.5 -0.88                     | 14.5 -1.65                     | 16.5                           |                      |
| 100°C                    | 20.3                 | 19.2 -0.24                     | 17.4 -0.53                     | 16.8 -0.74                     | 20.0                           |                      |
| 120°C                    | 13.0                 | 13.8 -0.31                     | 12.0 -0.49                     | 11.4 -0.41                     | 11.6                           |                      |

## 5. ANALYSIS OF PRACTICAL SYSTEMS

### 5.1. Introduction

In this chapter we will discuss the origins of polymer compatibility in terms of four systems: PMMA/CPE, PBA/CPE, CPE/CPE and PEGM/PPGM. The data of the last system are quoted from two Ph.D. theses<sup>11,32</sup>.

We will also simulate the phase boundaries for the four systems investigated. The idea that the compatibility behaviour of polymer mixtures can be simulated by studying oligomer mixtures<sup>5</sup> will be tested in quantitative calculations. The thermodynamic parameters obtained from the heats of mixing and phase boundaries of oligomer mixtures will be used as reference values to calculate the phase boundaries of polymer mixtures.

### 5.2. The PMMA/CPE system

#### 5.2.1. Oligomeric analogues

##### a) Heats of mixing and phase boundaries

Figure 31 shows the experimental heats of mixing of OMMA/COD. The theoretical curves of  $\Delta H_m$  also shown were calculated using Eq.80. With all the parameters fixed it was possible to adjust  $X_{12}$  to obtain a best  $\Delta H_m$  curve to fit the experimental results. Table 13 shows the parameters used for the calculation.  $M_n$  and  $d$  are the experimental results given in chapter 3. The expansion coefficient  $\alpha$  was estimated from the density measurements at two different temperatures with an accuracy of  $\pm 0.15 \times 10^{-4}/K$ . The thermal pressure coefficient  $\gamma$  was not available in the literature. It is known from the literature<sup>96</sup> that the isothermal compressibility coefficient  $k$  of tetradecane at  $20^\circ C$  is  $0.895 \times 10^{-4}/atm$ , and the  $k$  value of dichloroethane at  $20^\circ C$  is

$0.80 \times 10^{-4}/\text{atm}$ . Hence  $k$  for COD was set as  $0.85 \times 10^{-4}/\text{atm}$ .  $k$  of OMMA was set as  $1.00 \times 10^{-4}/\text{atm}$  after considering the  $k$  value of PMMA<sup>97</sup>.

$\gamma$  was then calculated by Eq.98. It was found that  $\gamma$  has little influence on the calculation. Changing  $\gamma$  of OMMA from 2 to 10 atm/K changes the value of  $\Delta H_m$  calculated by about 2% and has virtually no effect on the phase boundaries. The value of  $s_1/s_2$  was estimated by Bondi's technique<sup>51</sup>, in which the correction for the case when the group is not attached to carbon is not considered.  $X_{12}$  was also calculated using Eq.114. The value so obtained was within 5% of that from Eq.80.

Table 13 Parameters of oligomer mixtures

|          | $M_n$ | $d, \text{g/ml}$ |        | $\alpha \times 10^4$ | $\gamma$ | $s_1/s_2$ | $X_{12}$ | $Q_{12}$ |
|----------|-------|------------------|--------|----------------------|----------|-----------|----------|----------|
|          |       | 25°C             | 70°C   | $\text{K}^{-1}$      | atm/K    |           | atm      | atm/K    |
| 1.COD1   | 314   | 0.8976           | 0.8651 | 8.20                 | 9.64     | 0.97      | 210      | -0.14    |
| COD2     | 356   | 0.9511           | 0.9180 | 7.87                 | 9.26     | 0.96      | 170      | -0.13    |
| COD3     | 412   | 1.0531           | 1.0167 | 7.82                 | 9.20     | 0.96      | 105      | -0.12    |
| COD3A    | 421   | 1.0807           | 1.0457 | 7.32                 | 8.61     | 0.96      | 75       |          |
| COD4     | 467   | 1.1417           | 1.1054 | 7.18                 | 8.45     | 0.95      | 30       |          |
| COD5     | 546   | 1.2579           | 1.2167 | 7.36                 | 8.66     | 0.94      | -35      |          |
| 2.OMMA23 | 434   | 1.1378           | 1.0889 | 9.76                 | 9.76     |           |          |          |

\*  $1\text{atm}=0.1013\text{J/ml}=0.02422\text{cal/ml}$

Figure 32 shows the heats of mixing for OMMA with cereclor. Cereclor52 shows a favourable heat of mixing and cereclor45 very close to zero. The asymmetric dependence on composition for cereclor 45 cannot be explained by the experimental error.

Figure 33 shows the experimental phase boundaries of OMMA/COD. The spinodals were simulated using Eq.84 with  $X_{12}$  evaluated from the heats of mixing using Eq.80. The value of  $X_{12}$  for COD1/OMMA23 was an extrapolated value. It was found that if  $Q_{12}$  was set to zero the

three systems discussed here would be miscible in the temperature range of interest. With  $Q_{12}$  as in Table 13 the spinodals simulated were in the right temperature range, but the experimental phase boundaries were asymmetric and the UCST was towards higher concentrations of COD.

b) The variation of  $X_{12}$  and  $Q_{12}$  with chlorine content

$X_{12}$  and  $Q_{12}$  were plotted against the degree of chlorination of COD. The results are shown in Figure 34.  $X_{12}$  decreases linearly with increasing chlorine content of COD. Thus  $X_{12}$  can be separated into two terms as discussed by Paul<sup>98</sup>.

$$X_{12} = X_{12,\text{dis}} + w_{\text{Cl}} X_{12,\text{sp}} \quad (219)$$

The dispersion force  $X_{12,\text{dis}}$  is around 340 atm, the specific interaction  $X_{12,\text{sp}}$  is about -710 atm. With increasing chlorine content the heat of mixing from endothermic to exothermic.  $Q_{12}$  is negative which suggests that the mixture has a more ordered structure compared to the pure substances. This could be caused by specific interactions between the two components in the mixture.  $Q_{12}$  also seems to have a dependence on the chlorine content in COD.

c) The shape of theoretical spinodals

It is impossible to move the theoretical UCST to the side of higher concentrations of COD by adjusting  $Q_{12}$ . Several other factors may influence our calculation:

1) The molecular weights of the oligomers used for the calculation are number average values. In fact, the weight average value is a better measure for predicting the cloud point curve of polydisperse polymers<sup>71</sup>. We can assume that COD has a narrow molecular weight distribution because it was prepared by chlorination of octadecane. The molecular weights calculated according to their chlorine contents

are in agreement with the values measured by VPO (see Table 4). This suggests that no disruption or extension of the basic chain structure occurs during chlorination. OMMA23 was prepared by polymerization in the presence of a chain transfer agent. This produces a broad molecular weight distribution and probably a much higher  $M_w$  for this oligomer. If a larger  $M_w$  is used in the calculation the theoretical phase boundary will move to higher concentration of COD because COD has a relatively low molecular weight.

2) There can be irregular asymmetry in the phase boundary<sup>33</sup>. This phenomenon has been discussed in chapter 1. Some authors<sup>34,9</sup> tried to explain the phenomenon using the equation of state theory. They concluded that if  $x_{12} < 0$  and  $s_1/s_2 < 1$ , or  $c_{12} > 0$  and  $m_1/m_2 < 1$ , an irregular asymmetric phase boundary will result. For OMMA/COD the condition  $x_{12} < 0$  and  $c_{12} > 0$  holds because of specific interactions. The condition  $s_1/s_2 < 1$  and  $m_1/m_2 < 1$  also holds from the geometry of the chain molecules.

#### 5.2.2. PMMA/CPE16 (51.6% Cl) blends

a) The experimental phase boundaries

Figure 35 shows the phase boundaries, which were determined from DTA measurements.

Figure 36 is an electronmicroscopy result which verifies the phase boundary measured by DTA. It can be seen that the sample treated at 110°C was still as homogeneous as the reference. When it was treated at 130°C dark areas appeared. The dimensions of the areas are a little smaller than 0.1  $\mu$ , which is much larger than the dimensions of a CPE molecule (~100 Å). With increasing temperature, the separated two phases are clearly observed.

It is possible that the spinodal is far above the binodal in

the blend investigated as the micrography shows disconnected spots at 150° and 170°C, which is a strong indication of a nucleation and growth mechanism of phase separation.

It was found that exposure under the electron beam increased contrast between two phases and induced further phase separation in the sample which had already phase separated, as the dark spots increased their sizes. A similar phenomenon has been reported in the literature<sup>79</sup>.

The system was studied using dynamic mechanical measurements.

Figures 37-39 show plots of  $\tan\delta(T)$  of CPE16 blends with PMMA of different molecular weights which confirm that the mixtures are compatible. The plots of  $T_g$  measured against compositions are also shown in the corresponding figures. The  $T_g$  forms a linear relationship with composition. No efforts were made to measure samples with a low concentration of CPE of the system in Figure 37 because they are too brittle.

Figure 40 shows the influence of temperature on compatibility. The same blends in Figure 39 were treated at 140°C for 15 minutes. We can see that the  $T_g$  of sample 218 is far above the linear relationship, which suggests that phase separation has already taken place in the sample.

The system was also studied using dielectric measurements.

Figures 41 and 42 show the dielectric  $\tan\delta(T)$  results of CPE16 blends with PMMA of different molecular weights which confirm that the systems are compatible.  $T_g$  results as determined by the peak values of  $\tan\delta$  are also plotted against composition. The  $T_g$  also has a linear relationship with composition.

b) The simulated spinodals

Figure 43 shows the simulated spinodals of the system. Table 14 shows the parameters used for the simulation. Because the temperature range of interest is above  $100^{\circ}\text{C}$ ,  $\alpha$  values for  $T > T_g$  were used.  $\gamma$  of PMMA was also chosen to be the value when  $T > T_g$ .  $\alpha$  and  $\gamma$  for PMMA were taken from the literature<sup>97</sup>.  $\alpha$  for CPE16 was evaluated from the densities observed at two temperatures and has an accuracy of  $\pm 0.15 \times 10^{-4}/\text{K}$ .  $\gamma$  of CPE is not available in the literature, it was arbitrarily set as  $10 \text{ atm/K}$ . This parameter has little influence on the simulation. For example, when  $\gamma$  changes from 8 to  $14 \text{ atm/K}$  (a range which covers most polymers), the phase boundary only changes  $2^{\circ}\text{C}$ . The value of  $s_1/s_2$  of the oligomeric analogue was also used for high molecular systems.  $X_{12}$  was chosen as  $-30 \text{ atm}$ , the value required to fit  $\Delta H_m$  values of the oligomeric analogue with the same chlorine content as CPE16.  $Q_{12}$  was similarly chosen to be  $-0.095 \text{ atm/K}$ . It was found that the LCST so calculated for PMMA1.4/CPE16 was  $10^{\circ}\text{C}$ , which was low compared to the experimental observation. Both  $X_{12}$  and  $Q_{12}$  have a large effect on the results. Since  $Q_{12}$  is an empirical parameter we adjust  $Q_{12}$  to fit the experimental phase boundary. When  $Q_{12} = -0.06 \text{ atm/K}$  a satisfactory result is obtained. Considering that both  $X_{12}$  and  $Q_{12}$  may have molecular weight dependence, the adjustment of  $Q_{12}$  is acceptable. Another reason for accepting a less negative  $Q_{12}$  value in high polymer mixtures is that the values of  $Q_{12}$  from oligomeric analogues may be small because  $M_n$  was used for simulation of the phase boundary. If  $M_w$  values were used the  $Q_{12}$  values would be larger, and the value extrapolated to high chlorine content would also be higher.

Table 14 Parameters of PMMA/CPE16 blends

|       | $M_w$              | $d, g/ml$<br>30°C | $\alpha$<br>$\times 10^4/K$ | $\gamma$<br>atm/K | $s_1/s_2$ | $X_{12}$<br>atm | $Q_{12}$<br>atm/K |
|-------|--------------------|-------------------|-----------------------------|-------------------|-----------|-----------------|-------------------|
| CPE16 | $1.98 \times 10^5$ | 1.400             | 5.45                        | 10.00             | 0.94      | -30             | -0.06             |
| PMMA  | *                  | 1.200             | 5.74                        | 11.56             |           |                 |                   |

\*  $M_w$  of PMMA samples are  $1.44 \times 10^4$ ,  $4.88 \times 10^4$ ,  $8.38 \times 10^4$ ,  $1.40 \times 10^5$  and  $2.64 \times 10^5$  for PMMA 17, 16, 1.4, F6 and F5, respectively.

The phase boundary simulated for high molecular weight polymer mixtures is flat bottomed. The measurement of the LCST of the polymer mixture must therefore be done with great care, considering the inherent difficulty arising from the kinetic influence on phase separation in the system. In our experiment two polymers with high glass transition temperatures were studied, the phase separation thus proceeded slowly and gave only small phase sizes (about  $\sim 10^3$  Å by TEM). The method for phase boundary measurement is DTA, which is not an accurate method for  $T_g$  measurements. For these two reasons the error in our phase boundary measurement is  $\pm 10^\circ C$ , which is not accurate enough to locate the position of an LCST.

It was found that the calculated molecular weight dependence of the phase boundary confirmed the experimental observation. For example, when the molecular weight of PMMA increased from  $1.44 \times 10^4$  to  $2.64 \times 10^5$ , the LCST decreased by about  $50^\circ C$ , while the simulated spinodal decreased about  $30^\circ C$ . Compared to the large molecular weight dependence predicted by McMaster<sup>6</sup>, where  $X_{12}=0$  and  $Q_{12}=0$  were assumed, the improvement is apparent. From Eq.84 for the spinodal we can see that in our system  $X_{12}$  and  $Q_{12}$  counterbalance each other and suppress the combinatorial entropy term. Since they are less molecular weight dependent than the combinatorial entropy

term, and we effectively ignored any possible molecular weight dependence in our discussion, the resultant phase boundary has less dependence on molecular weights.

### c) Volume changes on mixing

The volume change of mixing was calculated using Eq.117. The theoretical  $\Delta V_m/V^0$  is very small for PMMA/CPE16 blends. The maximum value of  $\Delta V_m/V^0$  is around  $6 \times 10^{-5}$  at weight fraction 0.5. This is in agreement with the density measurement. To an accuracy of  $5 \times 10^{-4}$  the specific volume was found to be a linear function of concentration. Therefore  $\Delta V_m/V^0$  must be smaller than  $5 \times 10^{-4}$ , showing that a very weak interaction exists in the mixture. The experimental results for the specific volume of polyblends are shown in Figure 44.

### 5.2.3. Blends of PMMA with other CPE samples

a) Solvent cast PMMA/CPE17 (49.8% Cl) films are transparent except for those with  $M_w$  of PMMA  $> 1 \times 10^5$  at weight fraction 0.5. The phase boundaries determined by DTA are shown in Figure 45. Dynamic mechanical measurements show that a single composition dependent  $T_g$  but the loss peaks are broad and possibly even composed of two adjacent peaks. It is possible that this system is homogeneous at large scale ( $> 10^3$  Å) but heterogeneous at small scale ( $\sim 100$  Å).

Figure 46 shows the  $\tan \delta(T)$  values of PMMA/CPE17. Sample 243 with low molecular weight PMMA ( $M_w = 14400$ ) is transparent, but the loss curve is already composed of two peaks. Sample with higher molecular weights are turbid, the loss peaks are quite broad.

Figure 47 shows the  $\tan \delta(T)$  value of PMMA1.4 ( $M_w = 83800$ )/CPE17 over the complete concentration range. We can see that the loss peaks are quite broad at high concentration of PMMA. A plot of  $T_g$  against weight fraction of CPE is also given which shows a linear

relationship except at the middle point ( $w_{\text{CPE}}=0.4828$ ) where phase separation may occur in the sample. The sample was turbid at this concentration.

Figure 48 shows that when the same blends as in Figure 47 were heated at 200°C for 15 min, all the samples phase separated.

b) Blends of PMMA with all other CPE samples of low chlorine contents were incompatible as the films were turbid and two  $\tan\delta$  peaks appeared in dynamic mechanical measurements.

Figure 49 shows  $\tan\delta(T)$  of PMMA/CPE3 (48.0% Cl). Samples cast from THF, MEK and chlorobenzene all showed two phases.

Figure 50 shows  $\tan\delta(T)$  of PMMA/CPE15 (44.7% Cl). Samples were moulded after coprecipitation or cast from THF solution. Both show two phases.

c) One particular system, PMMA/CPE2 (27.4% Cl), shows a transparent gap between 65 and 90°C by light scattering turbidity and an intermediate loss peak by both the dynamic mechanical and dielectric measurements. The system was thought to be compatible in that temperature range<sup>99</sup> but it was later shown to be incompatible<sup>100</sup>.

Figure 51 shows the turbid and transparent regions measured on PMMA/CPE2. The film is turbid at room temperature. When heating up the film becomes clear and then turbid again. There is a temperature gap between the two turbid regions.

Figure 52 shows  $\tan\delta(T)$  of PMMA/CPE2. The samples are moulded coprecipitates. For the blend with 15.1 wt% CPE2 (curve 1) only the loss peak of PMMA at 155°C can be seen, for the blend with 25.0 wt% CPE2 (curve 2) there is a new peak at 60°C, while for high content of CPE2 sample (curve 3) a peak at -10°C appears which is the loss peak of CPE2.

Figure 53 shows the dielectric  $\tan\delta(T)$  of PMMA/CPE2 blends at an oscillation frequency 1.01 KHz. The peak at 80°C has been identified as the  $\beta$  transition of PMMA, the  $T_g$  transition was higher than 180°C, the peak at 133°C could be considered as a new peak. When the content of CPE2 was greater than 15.1% a rise in the dissipation curve appeared at 90°C, which was believed to be a result of dipole polarization in the polymers.

The reasons for considering the system to be incompatible are:

- 1) The "phase boundary" by light scattering has no molecular weight dependence even when the  $M_w$  of PMMA is as low as  $1.44 \times 10^4$ .
- 2) The film changes its transparency with temperature with a very high speed, faster than even for a PBA/CPE film, which is known as having a fast phase separation process.
- 3) The refractive index of oligomers (Figure 10) shows that the transparent gap by light scattering could be a result of similar refractive index and different temperature coefficient of refractive index of the two polymers.
- 4) The heat of mixing of oligomeric analogues suggests that compatibility can only be found with high chlorine content CPE and it is difficult to understand how compatibility can only occur at 27.4% chlorination (CPE2) and 51.6% chlorination (CPE16) but not between.

The results of dynamic mechanical and dielectric measurements still however remain unexplained. The intermediate peak in the mechanical experiment is unlikely to be due to a one-phase  $T_g$  because the temperature of the peak (60°C) is far below the value expected by additivity (103°C). This peak could be a result of a cooperative motion of the  $\beta$  transition in PMMA and the melting process of local crystallinity in CPE2. The literature<sup>101</sup> reported a  $\beta$  transition of

PMMA at 50°C and our DTA shows that CPE2 has a melting point at 40°C (Figure 17). A similar phenomenon may also occur in the dielectric measurements.

### 5.3. The PBA/CPE system

#### 5.3.1. The miscibility of polymers

PBA/CPE20 and PBA/CPE17 were found to be miscible. This was verified by dynamic mechanical measurements. Figure 54 shows single sharp composition-dependent loss peaks for the PBA/CPE20 blends. The samples with weight fraction of CPE in the blends smaller than 0.5 are too soft to hold in the clamps of machine and were not therefore measured. A plot of  $T_g$  against the weight fraction of CPE shows that the measured  $T_g$  is far above the linear relationship. This indicates that there are strong interactions in the blends. PBA/CPE3 films were turbid and the dynamic mechanical results also show that the samples were phase separated.

The phase diagrams were determined using light scattering as shown in Figure 55. The phase boundaries were obtained with reproducibility of  $\pm 3^\circ\text{C}$ . With increasing the chlorine content in CPE the phase boundary moves towards the higher temperatures.

Figure 56 shows the results for the heat of mixing. In the experiment a sample of PBA with molecular weights  $M_w = 1.19 \times 10^5$ ,  $M_n = 3.90 \times 10^4$  (relative to polystyrene standards) was mixed with cereclor45 and cereclor52 in various proportions. A large negative heat of mixing was observed. We cannot, however, say that the polymer pair must be miscible solely because the heat of mixing of their oligomeric analogues is negative. For example, the heat of mixing of PBA with cereclor45 (45.7% Cl) is exothermic but the corresponding polymer pair PBA/CPE3 (48.0% Cl) is incompatible.

### 5.3.2. Simulation of the phase boundaries

A thermodynamic explanation of the phase diagrams using the Flory equation of state theory was attempted for the systems, following the same procedure as in the previous section. The heat of mixing  $\Delta H_m$  was used to evaluate  $X_{12}$ , the interaction energy parameter in the theory using Eq.80. The parameters used in the calculation are listed in Table 15. With  $d, \alpha, \gamma$  and  $s_1/s_2$  fixed, a value for  $X_{12}$  can be selected to obtain a best fit of the  $\Delta H_m$  curve. In Table 15, the  $d, \alpha$  and  $\gamma$  for PBA were obtained from Van Krevlin<sup>102</sup>, the densities of other materials were measured values,  $\alpha$  was calculated from the densities of two temperatures (45° and 70°C) and  $\gamma$  was arbitrarily set as 10 atm/K. The value of  $\gamma$  is difficult to measure, but, fortunately, has little influence in the calculation. For instance, calculation shows when  $\gamma$  of cereclor or CPE changes from 10 to 20 atm/K  $\Delta H_m$  only changes by 0.7% and the phase boundary has a negligible change. This range of  $\gamma$  covers most of polymeric materials.  $s_1/s_2$  was evaluated by Bondi's technique<sup>51</sup>.

Table 15 Parameters for calculation at 70°C

|            | $M_w$ relative<br>to polystyrene | $d$<br>g/ml | $\alpha$<br>$\times 10^4/K$ | $\gamma$<br>atm/K | $s_1/s_2$ | $X_{12}$<br>atm | $Q_{12}$<br>atm/K |
|------------|----------------------------------|-------------|-----------------------------|-------------------|-----------|-----------------|-------------------|
| PBA        | 119000                           | 1.050       | 5.47                        | 15.36             |           |                 |                   |
| cereclor52 | 437*                             | 1.228       | 6.85                        | 10.00             | 0.97      | -110            |                   |
| cereclor45 | 395                              | 1.132       | 6.48                        | 10.00             | 0.98      | -75             |                   |
| CPE20      | 242000                           | 1.458       | 4.57                        | 10.00             | 0.96      | -152            | -0.305            |
| CPE17      | 182000                           | 1.333       | 5.66                        | 10.00             | 0.98      | -94             | -0.235            |

\*  $M_n$  by VPO.

Values for  $X_{12}$  of -110 and -75 atm for PBA/cereclor52 and PBA/cereclor45, respectively, were evaluated from  $\Delta H_m$ . If it is

assumed that  $X_{12}$  has a linear dependence on the chlorine content as found in the OMMA/COD system (Figure 34) and the molecular weight dependence of  $X_{12}$  can be neglected,  $X_{12}$  values of -152 and -94 atm would be found for PBA/CPE20 and PBA/CPE17, respectively. We adjusted  $Q_{12}$ , the interaction entropy parameter, to counterbalance  $X_{12}$  for calculating the spinodals. Figure 57 shows the  $X_{12}$  and  $Q_{12}$  values used for the calculation.

Eq.84 is the equation for the spinodal. The theoretical curves calculated are plotted together with the experimental phase boundaries in Figure 55 for comparison. It can be seen that for the two systems the experimental phase boundaries are far above the calculated curves when the weight fractions of CPE are lower than 0.5. Also the two theoretical spinodals seem to be too flat bottomed. There may be two reasons for this:

a) Irregular asymmetry of the phase boundary, which often appears in strongly interacting systems ( this phenomenon was discussed in section 5.2.1.).

b) In choosing the  $X_{12}$  for oligomers for the polymers, we neglected the possible molecular weight dependence of  $X_{12}$ . It was reported<sup>103</sup> that this dependence was large in systems where the dispersion force was dominant. If the  $X_{12}$  values for the polymers have smaller negative values,  $Q_{12}$  will also have smaller negative values. The spinodala simulated will then have a more sensitive temperature dependence on composition. This can be observed in section 2.6, where calculations were carried out for  $X_{12}=0$  and  $Q_{12}=0$ , the spinodals then had a sharp curvature with temperature.

The interaction parameter  $\chi$  of the Flory-Huggins theory can be expressed as in Eq.131. Figure 58 shows the results calculated

from Eq.131 at 70°C. It can be seen that PBA/CPE20 is a stable homogeneous blend at this temperature as  $\chi$  has a large negative value. For PBA/CPE17 a small positive  $\chi$  is obtained as the blend reaches the critical state at this temperature. The critical value  $\chi_c$  can be calculated from Eq.43.

$$\chi_c/v_1^* = (1/2) [1/v_1^{*\frac{1}{2}} + 1/v_2^{*\frac{1}{2}}]^2 \approx 10^{-4} \quad (220)$$

The calculation shows that the empirical parameter  $Q_{12}$  plays an important role in adjusting the theoretical phase boundaries to fit the experimental results. This is reflected in the calculation of  $\chi$ . For example, in the PBA/CPE17 blend  $Q_{12}$  must counterbalance  $X_{12}$  in the term  $(X_{12} - TQ_{12}\tilde{v})$  (see Eq.131) in order to make  $\chi$  reach the critical value.

#### 5.4. The CPE/CPE system

##### 5.4.1. Compatibility among CPE samples having different chlorine contents

Compatibility between different CPE samples was determined visually by the transparency of films. The blends of transparent films were taken as compatible while the blends of turbid or translucent films were taken as incompatible. Out of 78 possible pairs 55 pairs of CPE were observed at room temperature. The results are shown in Figure 59, where "+" means the pair is immiscible while "-" is miscible. The phase boundaries for these blends were not determined.

Figure 59 can be divided into 4 regions. A is a "polar plastic" region where the polymers mix with each other because of the similarity of their equation of state properties. B is a "rubber" region where the polymers also mix with each other because they also have similar equation of state parameters. In region C the "polar

plastics" do not mix with the corresponding "rubber" components. The D region is also a "rubber" region (cf. B), but the polymers cannot mix with each other because of the large differences in their equation of state properties. The CPE of very low chlorine content, a crystalline material, has not been discussed here because the crystallinity in the polymer makes the problem complicated.

Transparent films of CPE/CPE 20/18, 20/15, 20/19, 18/19 and 15/19 blends (in region A) at 0.5 weight fraction were measured by dynamic mechanical analysis and show an intermediate loss peak which suggests compatibility. A complete concentration range was measured for CPE20 (62.1% Cl)/CPE19 (44.1% Cl) blends as shown in Figure 60, the system has the greatest difference of chlorine content between the two pure components in region A of Figure 59. The fact that the  $T_g$  of the blend is a linear function of weight fraction suggests that there are no specific interactions in the system. The films in region B were not measured because their  $T_g$  temperatures are too close to each other.

#### 5.4.2. The interaction energy parameter $X_{12}$

Heats of mixing of the various COD's were measured at weight fraction 0.5 as shown in Figure 61 and one system was measured over the complete concentration range as shown in Figure 62. An endothermic effect was found for all the oligomer pairs.

$X_{12}$  can be evaluated from Eq.80 and one of the simulated curves is shown in Figure 62 for the COD3/COD5 system. For other mixtures  $X_{12}$  was estimated from the values of  $\Delta H_m$  at 0.5 weight fraction. The  $X_{12}$  values are positive. They are plotted as a function of the difference between chlorine contents of the mixed oligomers, as shown in Figure 63. The curve has a shape similar to the  $(\delta_1 - \delta_2)^2$

function, which is characteristic for mixtures in which the dispersion forces dominate, where  $\delta_i$  is the solubility parameter of polymer i.

Some of the parameters for the COD's used in the calculation are seen in Table 4. The thermal pressure coefficients,  $\gamma$ , were set as 10 atm/K, this parameter had little influence on the final results.  $s_1/s_2$  values were calculated from Bondi's technique<sup>51</sup>, they ran from 0.97 to 1.02 according to the difference in chlorine contents of the mixed oligomers.

#### 5.4.3. The thermodynamic mixing functions

The free energies of mixing, heats of mixing and entropies of mixing were calculated for the CPE/CPE mixtures from Eqs. 82, 80 and 81 at 25°C. The results for 20 polymer pairs are shown in Figure 64. Some of the parameters used in the calculation are seen in Table 3. The weight average molecular weights were used. The  $M_w$  for CPE8 and CPE12 were not available because they would not dissolve in THF for GPC measurements.  $M_w$  was set as  $1 \times 10^5$  in both cases. It is apparent that the thermal expansion coefficient  $\alpha$  decreases significantly when the polymer changes from a rubber at low chlorine content to a glass at high chlorine content, as shown in Figure 65. The thermal pressure coefficients,  $\gamma$ , were set as 10 atm/K. It was found that the role of  $\gamma$  in the calculation depended on the difference between the  $\alpha$  values of CPE. The larger this difference, the greater influence of  $\gamma$  on the thermodynamic mixing functions. Calculation for the cases where  $\gamma_1 = \gamma_2 = 10$  atm/K, or  $\gamma_1 = 20$  atm/K while  $\gamma_2 = 10$  atm/K, or  $\gamma_1 = \gamma_2 = 20$  atm/K showed that  $\Delta G_m$  could increase 50% with increase of  $\gamma$  for the pairs in which  $\alpha_1 \approx 2\alpha_2$  or  $2\alpha_1 \approx \alpha_2$ . For most of compatible pairs such as CPE/CPE 15/19, 3/18, 3/19, 3/2 and 20/17  $\Delta G_m$  had almost no change

with such an increase of  $\chi$ . One can confidently say that the  $\chi$  values so set will not influence the conclusions appearing in the following discussion, and that these  $\chi$  values cover most polymers.  $X_{12}$  values were determined by the difference of chlorine contents between the two polymers from Figure 63.  $X_{12}$  is molecular weight dependent. As reported by Flory<sup>102</sup>,  $X_{12}$  decreases with molecular weight for the polyisobutylene/n-alkanes system in which the dispersion forces are dominant. Hence the thermodynamic functions were calculated in the case of  $X_{12}=0$  as well as  $X_{12}\neq 0$  for comparison, as will be discussed later.  $s_1/s_2$  values were evaluated by Bondi's technique<sup>51</sup>, they ran from 0.97 to 1.00 according to the differences of the chlorine contents of the two polymers.

It can be seen from Figure 64 that the  $\Delta G_m$  values are positive for all the 20 polymer pairs. The spinodals (Eq.84) have also been calculated and show that the polymer pairs are immiscible at 25°C. Thus, if we assume that the  $X_{12}$  of oligomers can be used for polymers, all the polymer pairs should be immiscible according to calculation. As discussed above, the  $X_{12}$  values of polymer mixtures in which the dispersion forces dominate may be smaller than that of oligomers. The situation for  $X_{12}=0$  has been calculated for comparison. The results are not much improved: out of 7 compatible polymer pairs only 2 pairs (CPE/CPE 15/19 and 20/17) have a negative  $\Delta G_m$ , and the third pair (CPE/CPE 3/18) has a nearly zero  $\Delta G_m$ . All the rest still have positive  $\Delta G_m$  values. The spinodals calculated also confirm these results. As can be seen in Figure 64,  $\Delta H_m$  is not important when the difference of chlorine contents of the polymers in the mixtures is large. It is the large negative entropy term from the

disparity of the equation of state properties of polymers that determines the positive  $\Delta G_m$ . The calculation using  $X_{12}=0$  does not change the  $\Delta G_m$  values of these systems very much.

An analysis of some compatible and incompatible pairs may be interesting:

a) CPE20/CPE19

This compatible pair is in region A. Because the chlorine difference reaches 18 wt%, the  $\Delta H_m$  is relatively large (+0.519 J/g). Owing to the difference in their thermal expansion coefficient,  $-T\Delta S_m$  is positive (+0.276 J/g). Hence the  $\Delta G_m$  of the pair is +0.795 J/g. This pair should be immiscible by calculation.

b) CPE4/CPE2

This compatible pair is in region B. Their chlorine contents are similar and the dispersion forces between the two species is small. According to calculation, the great difference in the thermal expansion coefficients makes  $\Delta H_m$  small and negative (-0.108 J/g). However, this difference makes a large positive  $-T\Delta S_m$  (+0.761 J/g). The resultant  $\Delta G_m$  (+0.653 J/g) is still unfavourable for mixing.

c) CPE/CPE 15/1 and 3/1

These two pairs are incompatible in region C. The immiscibility comes from the disparity of two polymers: CPE3 and CPE15 are glassy whereas CPE1 is a rubber. The two pairs have similar chlorine contents and the  $\Delta H_m$  are nearly zero in both cases.

d) CPE/CPE 12/8, 4/12 and 4/8

The three incompatible pairs are in region D. The polymers in this region are rubbers. The chlorine content range in this region is quite similar to region A. Hence the polymer pairs are expected to be miscible. The immiscibility arises from a moderate difference

in the thermal expansion coefficients. In CPE12/CPE8 mixtures the chlorine content difference is so small that  $\Delta H_m$  is  $-0.015$  J/g. With  $\alpha_1/\alpha_2=1.27$ , this leads to  $-T\Delta S_m=+0.252$  J/g. A small positive  $\Delta G_m$  ( $+0.237$  J/g) results in incompatibility for the pair. With increasing difference of chlorine content, the unfavourable  $\Delta H_m$  increases and reaches equal magnitude as  $-T\Delta S_m$  in the CPE4/CPE12 mixtures. CPE4/CPE8 is an interesting mixture, because the polymers have nearly equal thermal expansion coefficients,  $-T\Delta S_m$  is negative ( $-0.176$  J/g), but the moderate dispersion forces give a  $\Delta H_m$  of  $+0.803$  J/g. The resultant  $\Delta G_m$  ( $+0.627$  J/g) leads to incompatibility of the pair.

In conclusion, it seems that we can draw a dotted line for  $\Delta G_m$  in Figure 64. Above the line the polymer pairs are immiscible, otherwise the possibility exists that these pairs are miscible. Considering that  $X_{12}$  should be smaller than that for oligomers, the slope of the line may be smaller. The line represents the inefficiency of the theory (without  $Q_{12}$ ): it cannot generate a negative  $\Delta G_m$ , hence fails to predict the compatibility.

One way to remedy this inefficiency within the scope of theory is by introducing the empirical parameter  $Q_{12}$ .  $Q_{12}$  is expected to be positive and proportional to the difference in the chlorine contents of the two polymers in the mixture.

## 5.5. The PEGM/PPGM system

### 5.5.1. Heats of mixing and phase boundaries

These oligomer mixtures have endothermic heats of mixing and give a UCST behaviour. In this work we first calculate the theoretical  $\Delta H_m$  and the phase boundary. The parameters used for the calculation are quoted from references<sup>18,50</sup> and listed in Table 16.

Table 16 Parameters of PEGM and PPGM at 30°C

|                | M    | d      | $\alpha$               | $\gamma$ | $X_{12}^{\text{atm}}$ |     | $Q_{12}$ | $\chi_h^o$ | $\chi_s^o$ |       |
|----------------|------|--------|------------------------|----------|-----------------------|-----|----------|------------|------------|-------|
|                |      |        |                        |          | 1.                    | 2.  |          |            | 3.         | 4.    |
|                |      | g/ml   | $\times 10^4/\text{K}$ | atm/K    |                       |     | atm/K    |            |            |       |
| PEGM 600       | 600  | 1.0718 | 7.8                    | 15.35    |                       |     |          |            |            |       |
| PPGM 400       | 400  | 0.9551 | 8.7                    | 9.97     | 112                   | 130 | -0.062   | 2.11       | -0.34      | -0.04 |
| 1000           | 1000 | 0.9775 | 8.5                    | 10.17    | 107                   | 130 | 0.079    | 2.12       | -0.36      | -0.74 |
| 1500           | 1500 | 0.9852 | 8.15                   | 10.76    | 106                   | 115 | 0.073    | 1.89       | -0.34      | -0.70 |
| 2000           | 2000 | 0.9881 | 7.8                    | 11.36    | 97                    | 105 | 0.065    | 1.73       | -0.33      | -0.64 |
| $s_1/s_2=1.08$ |      |        |                        |          |                       |     |          |            |            |       |

\* 1. from Eq.114, 2. from Eq.80, 3. from Eq.225 and 4. from Eq.225+the  $Q_{12}$  term

$X_{12}$  was firstly evaluated by Eq.114 and  $\Delta H_m$  was simulated by Eq.80 using the  $X_{12}$  values obtained. It was found that the  $X_{12}$  values calculated from Eq.114 were small. Thus  $X_{12}$  was recalculated by fitting the  $\Delta H_m$  curve over the whole range of concentration (Eq.80). The new  $X_{12}$  values are about 10 % larger. The calculations were carried out for  $\Delta H_m$  at 30°, 50°, and 70°C as shown in Figures 66-68. The  $X_{12}$  values so evaluated including those at 30°C are listed in Table 17.

Table 17  $X_{12}$  values

| $X_{12}(\text{atm})$ of | PEGM600/PPGM1000 | PEGM600/PPGM1500 | PEGM600/PPGM2000 |
|-------------------------|------------------|------------------|------------------|
| 30°C                    | 130              | 115              | 105              |
| 50°C                    | 115              | 105              | 95               |
| 70°C                    | 80               | 75               | 70               |

$\Delta G_m$  was then calculated from Eq.82 with  $Q_{12}=0$  and the results are shown in Figures 69-71. This predicted that all the oligomer pairs were immiscible at 30 and 50°C except the PEGM600/PPGM400 pair, although all the  $\Delta G_m$  values are negative. In order to make the phase boundaries calculated fit the experimental measurements the

interaction entropy parameter  $Q_{12}$  was introduced as in the previous sections. With the values of  $Q_{12}$  in Table 16 the calculated phase boundaries have a best fit with the experimental cloud points, one example is shown in Figure 72.

#### 5.5.2. $X_{12}$ and $Q_{12}$

$X_{12}$  is a measure of the intensity of the interaction energy between the two components in the mixture. In the literature<sup>103</sup>  $X_{12}$  was reported to have a molecular weight dependence. Calculation shows that  $X_{12}$  also has a temperature dependence, as shown in Figure 73. Plots of  $X_{12}$  and  $Q_{12}$  against  $1/M$ , where  $M$  is the molecular weight of PPGM, show that both  $X_{12}$  and  $Q_{12}$  are decreasing functions of molecular weight when  $M > 1000$  (Figure 74). The observation that  $X_{12}$  depends on  $M$  is in agreement with the literature<sup>103</sup>. Cooper and Booth<sup>18</sup> found that the heat of mixing increased with molecular weight for the same system, which is opposite to the quoted data even after considering correction for the density. Thus they found that  $X_{12}$  increased with molecular weight.

$Q_{12}$  was introduced for calculating the phase boundary. Except in the case of PEGM600/PPGM400  $Q_{12}$  was found to be positive. Friday, Cooper and Booth<sup>31</sup> interpreted the phase boundary in terms of the Flory-Huggins theory with  $\chi = \chi_0 + \chi_1 \phi_1$ , where  $\phi_1$  is the volume fraction of PEGM. They found the critical value  $\chi_c$  to be about 0.1 and  $\chi_1$  to be -0.02, i.e.  $\chi$  is a decreasing function of the concentration of PEGM. This was attributed to the ratio  $s_1/s_2$  by the authors. From Eq.132 the same conclusion would be drawn if the contribution of the equation of state terms is negligible. But the  $\chi$  obtained directly from the heat of mixing is much higher than  $\chi_c$ : the phase separation occurs at elevated temperature. Only when a positive  $Q_{12}$

is introduced can the system be understood from both  $\Delta H_m$  and phase boundary measurements.  $Q_{12}$  introduced in this way is plausible. A third independent experiment is needed to verify it's reliability.

### 5.5.3. $\chi$ of the Flory-Huggins theory

$\chi$  at weight fraction 0.5 was calculated as a function of temperature using Eq.132 and the results are shown in Figure 75. It decreases with temperature, hence the system gives a UCST behaviour. It is shown that the contribution of the equation of state terms to  $\chi$  is small, although it indeed increases with temperature. This excludes the possibility of finding an LCST at an elevated temperature.

$\chi$  can also be divided into enthalpy and entropy terms.

$$\chi = \chi_h + \chi_s \quad (221)$$

where

$$\begin{aligned} \chi_h &= (\partial \Delta H_m / \partial N_1)_{T,P,N_2} / RT \phi_2^2 \\ &= \{ P_1^* V_1^* [(\tilde{v}_1^{-1} - \tilde{v}^{-1}) + (\alpha T / \tilde{v})(\tilde{T}_1 - \tilde{T}) / \tilde{T}] + (V_1^* X_{12} / \tilde{v})(1 + \alpha T) \theta_2^2 \} / RT \phi_2^2 \end{aligned} \quad (222)$$

$$\begin{aligned} \chi_s &= \chi - \chi_h \\ &= \{ P_1^* V_1^* [3T_1 \ln((\tilde{v}_1^{1/3} - 1) / (\tilde{v}^{1/3} - 1)) - (\alpha T / \tilde{v})(\tilde{T}_1 - \tilde{T}) / \tilde{T}] \\ &\quad - (V_1^* X_{12} / \tilde{v}) \alpha T \theta_2^2 - T Q_{12} V_1^* \theta_2^2 / RT \phi_2^2 \} \end{aligned} \quad (223)$$

In deriving Eq.223, Eq.131 was used for  $\chi$  with the assumption that  $P=0$ . The difficulty in using Eqs.222 and 223 is in evaluation of the expansion coefficient  $\alpha$  of the mixture. An example is given here for PEGM600/PPGM2000 where both  $\alpha$  values are equivalent. The calculations are shown in Figure 76.

By a series expansion of Eqs.222 and 223 with  $Q_{12}=0$ ,

$$\chi_h = (P_1^* V_1^* / \tilde{v}_1 RT) [Y_{12}(1 + \alpha_1 T) - (2/3)(\alpha_1 T)^2(1 + \alpha_1 T)] + O(\phi_2) \quad (224)$$

$$\chi_s = (P_1^* V_1^* / \tilde{v}_1 RT) \{ Y_{12} \alpha_1 T - (\alpha_1^2 T / 2) [1 + (4\alpha_1 T / 3)(1 + \alpha_1 T)] \} + O(\phi_2) \quad (225)$$

where

$$A = (1 - T_1^*/T_2^*)(P_2^*/P_1^*) - (s_2/s_1)X_{12}/P_1^* \quad 226)$$

$$Y_{12} = (s_2/s_1)^2 X_{12}/P_1^* \quad 227)$$

The limiting values of  $\chi_h^o$  and  $\chi_s^o$  at  $\phi_2=0$  can be calculated. It can be seen from Table 16 that  $\chi_s^o$  at  $Q_{12}=0$  (Eq.225) has a negative contribution to  $\chi$  (which increases compatibility), it's magnitude is about 15% of  $\chi_h$ . Thus  $\chi_s$  is not negligible in this system although the disparity of the pure components is not large. If  $Q_{12} \neq 0$  is considered a term  $-Q_{12}V_1^*(s_2/s_1)^2/R$  should be included in Eq.225. From Table 16 we can see that except for PEGM600/PPGM400  $\chi_s^o$  becomes more negative as the interaction entropy parameter  $Q_{12}$  is favourable for mixing.

## 6. CONCLUSIONS

This work concentrates on some basic problems in the thermodynamic study of polymer compatibility. A critical assessment of the Flory equation of state theory has been made, some characteristics of applying the equation of state theory to practical systems has been explored, the origins of compatibility in polymer mixtures has been discussed, a theoretical explanation of the IGC behaviour of two-phase polyblends has been developed. Finally, the microstructure of CPE which has been prepared by a modified method of photochlorination has been analysed.

The conclusions are:

### 6.1. On the Flory equation of state theory

The theory produces two different curves for the concentration dependence of the interaction parameter  $\chi$  when calculated from the solvent and solute residual chemical potentials, respectively. This shows that the conventional equations (Eqs.131 and 133) cannot be used to calculate the interaction parameter  $\chi$ .

The theory is especially rewritten for the purpose of studying polymer compatibility. The functional relationship of the equation of state parameters on pressure and temperature are also given.

The theory can give the same qualitative descriptions of the compatibility behaviour of polymer mixtures as McMaster's modified treatment.

### 6.2. The simulation of phase boundaries

The Flory equation of state theory has been applied to simulate the phase boundaries of polymer mixtures. The interaction

energy parameters  $X_{12}$  obtained from the measured  $\Delta H_m$  of oligomer models are used for the polymers. By adjusting the interaction entropy parameter  $Q_{12}$  the spinodals are calculated to fit the experimental data.

The spinodals so generated are less molecular weight dependent as expected and in better agreement with the experimental observations.

$Q_{12}$  plays an important role in the calculation. In the systems such as PMMA/CPE, OMMA/COD and PBA/CPE, where there are the specific interactions,  $Q_{12}$  is negative which means that some ordered structure may exist in the mixture. In the systems such as CPE/CPE and PEGM/PPGM, where the dispersion forces dominate,  $Q_{12}$  is positive which indicates that some ordered structure may exist in the pure components or the mixture has a more random structure. This conclusion is quite similar to that reported for polymer solutions<sup>104</sup>. The report has summarised all the data in the literature.

Further improvement can be made by considering the molecular weight and temperature dependences of  $X_{12}$  and  $Q_{12}$  in the calculation. Such dependences have been found in PEGM/PPGM mixtures.

The results show that simulation of a polymer mixture by oligomeric analogues is a valuable method in the thermodynamic study of polymer compatibility.

### 6.3. The origins of polymer compatibility

Investigation of the effect of chlorine content on the heats of mixing of OMMA/COD shows that there are two kinds of interactions in the mixture: dispersion forces and specific interactions. In PMMA/CPE and PBA/CPE systems only when chlorine content reaches a certain limit, where the specific interactions dominate in the

mixture, is compatibility possible. In the CPE/CPE system where only the dispersion forces exist, the compatibility is determined by similarity of the properties of the equation of state parameters of the pure components.

A strong exothermic heat of mixing of the oligomeric analogues usually predicts compatibility for the polymer mixture. But this is not always true. PBA/cereclor45(45.7% Cl) has a negative heat of mixing whereas the corresponding PBA/CPE3(48.0% Cl) is incompatible.

Similarly, a positive heat of mixing of oligomeric analogues does not always result in incompatibility for polymer mixtures. All the COD/COD pairs have positive heats of mixing, but we still find two regions among the CPE/CPE blends in which all the polymer pairs are miscible.

#### 6.4. On IGC of one-phase and two-phase blends

A calculation of the activity of a solvent in contact with phase separated blends shows that the specific retention volume is a linear function of composition if the blend is separated into two pure polymers. The measurements on mixed packings have verified this analysis.

It is further predicted that there is a gap between the retention volumes of homogeneous and phase separated polyblends. When phase separation takes place during heating, the retention volume will have a sudden increase.

The results on the PBA/CPE and the PMMA/CPE systems show that phase separation may occur during coating onto the support as the retention volume follow the expression for a two-phase blend.

The results on the PEMA/CPE system show it to be homogeneous as coated and the interaction parameter tends towards zero with

increasing temperature as expected.

#### 6.5. The microstructure of CPE

CPE has been prepared by photochlorination in solution at 135°C in which chlorobenzene is used as solvent and the light of a tungsten lamp is used as an initiator.

$^{13}\text{C}$ -NMR and DTA analyses show that the prepared polymer has a more homogeneous chlorine distribution than reported in the literature.

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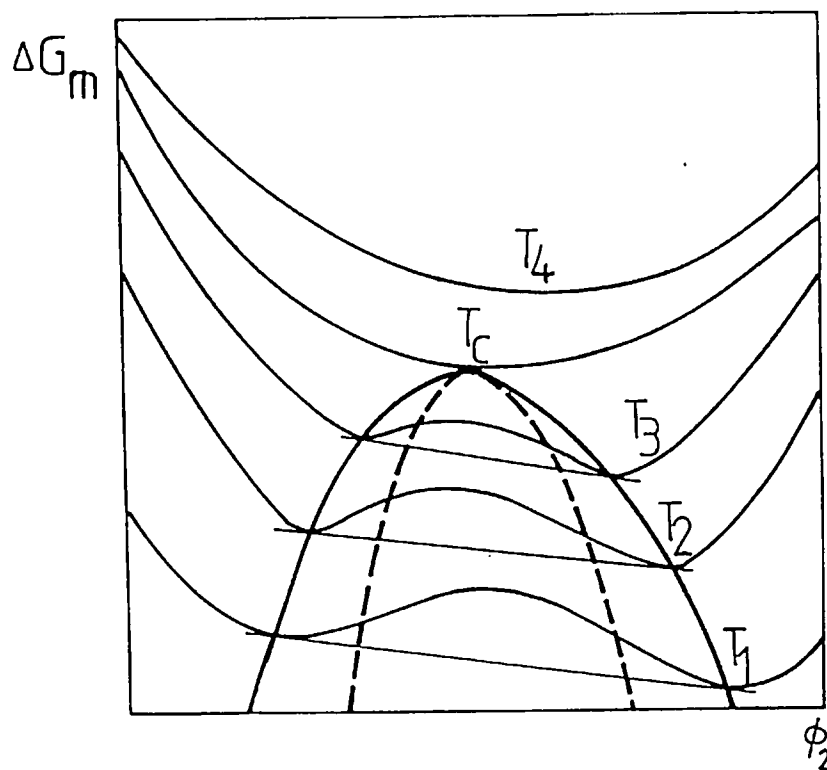


Figure 1. Free energy of mixing  $\Delta G_m$  as a function of temperature and composition.

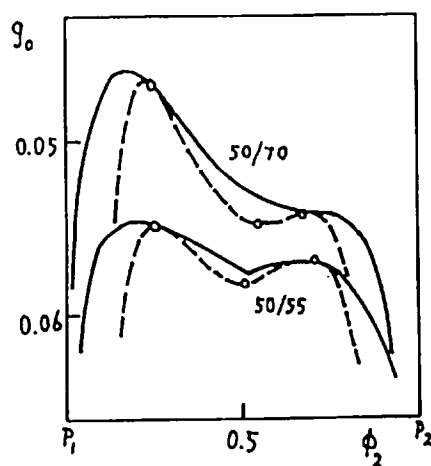


Figure 2. Cloud point curves(—), spinodals(---) and critical points(  $\bullet$  ) calculated from Eqs.121 and 122 with  $g_1=-0.04$  and  $g_2=+0.04$  for indicated  $m_{w1}/m_{w2}$  values.

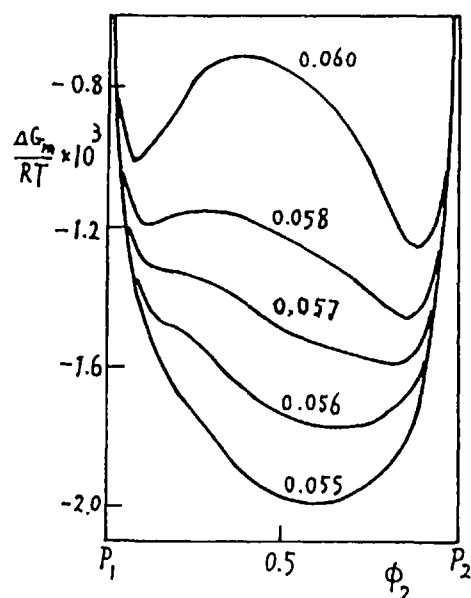


Figure 3.  $\Delta G_m(\phi_2)$  curves calculated for a binary 50/50 mixture for indicated  $g_0$  values (see Figure 2).

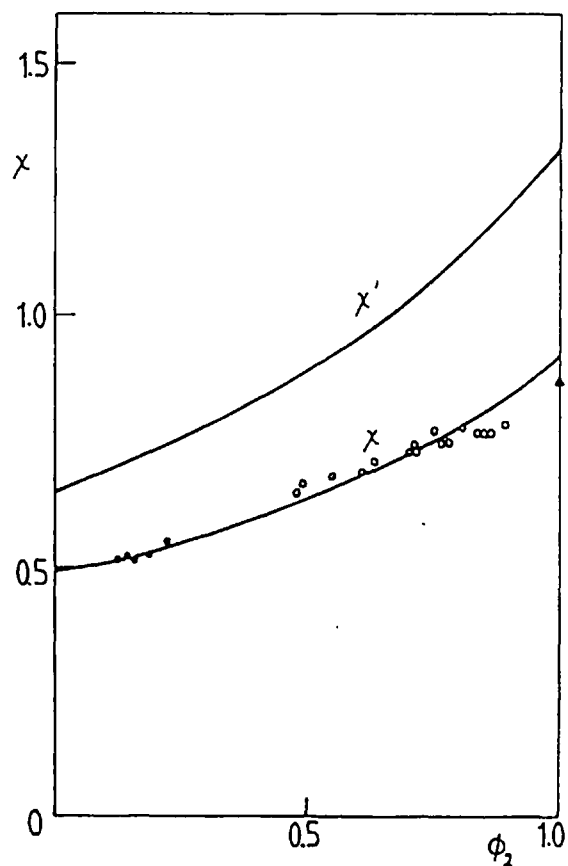


Figure 4.  $\chi$  and  $\chi'$  of polydimethylsiloxane-benzene solution at 25°C. The experimental points are quoted from Flory's paper(52). ● osmometric results, ○ vapour pressure results, ▲ inverse gas chromatographic result.

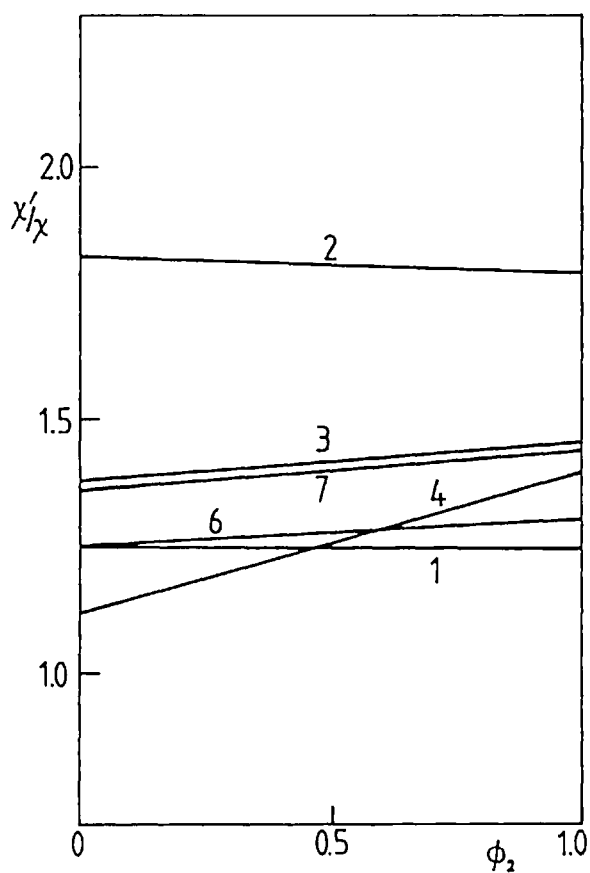


Figure 5.  $\bar{n}/n$  of polymer solutions. The number represents the related solution seen in Table 1.

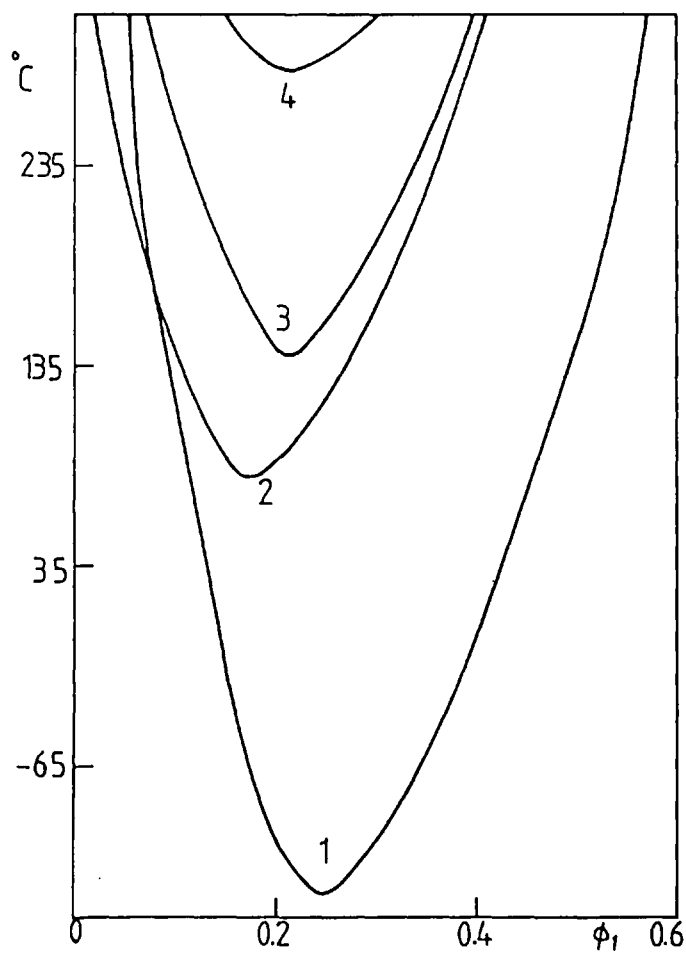


Figure 6. Spinodal curves illustrating molecular weight effects. Phase diagram 1 in Table 2. Molecular weight: 1. 50000/6000, 2. 80000/4000, 3. 50000/4000 and 4. 30000/4000.

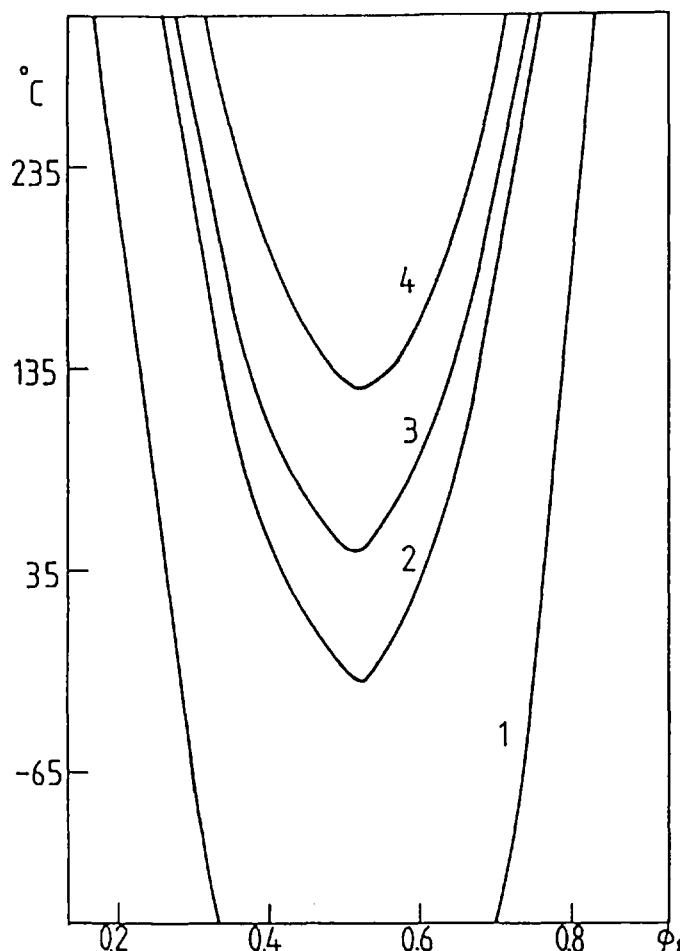


Figure 7. Effects of molecular weight and the thermal expansion coefficient. Phase diagram 2 in Table 2. Molecular weight and  $\alpha \times 10^3 / K$ : 1. 100000/100000 and 0.580/0.630, 2. 200000/200000 and 0.580/0.610, 3. 50000/50000 and 0.580/0.640 and 4. 100000/100000 and 0.580/0.620.

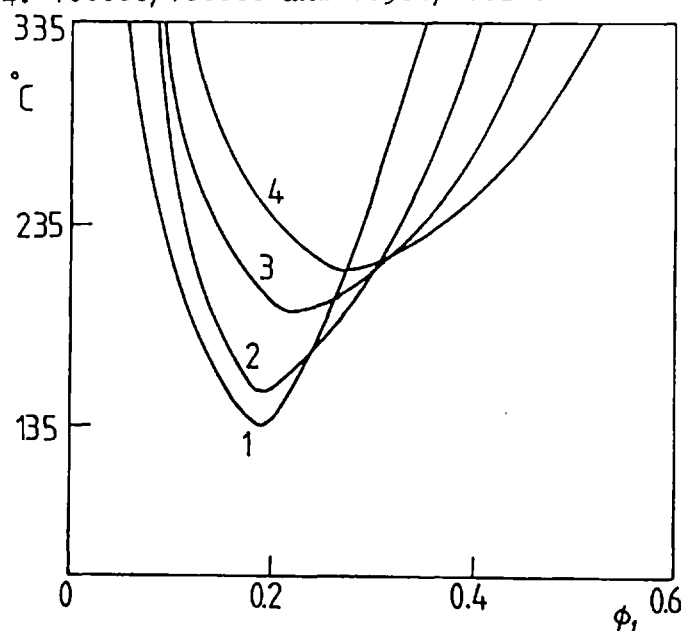


Figure 8. Effect of the thermal pressure coefficient. Phase diagram 1 in Table 2.  $\gamma$  atm/K: 1. 8.47/6.50, 2. 8.47/7.24, 3. 8.47/8.47 and 4. 8.47/10.00.

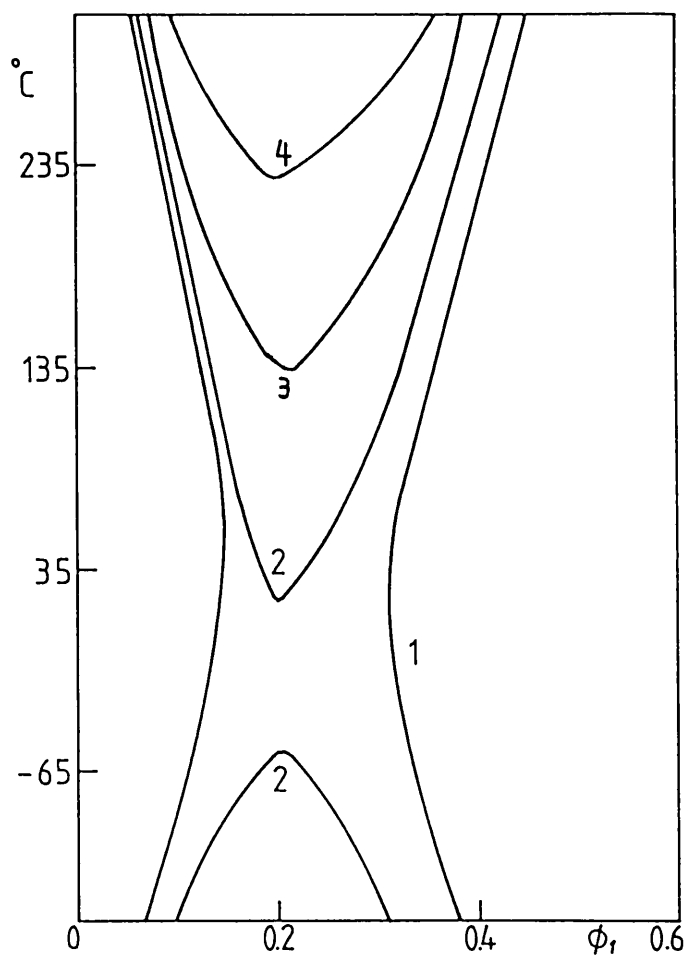


Figure 9. Effect of the interaction energy parameter . Phase diagram 1 in Table 2.  $X_{12}$  atm: 1. 1.5, 2. 1.0, 3. 0 and 4. -1.0.

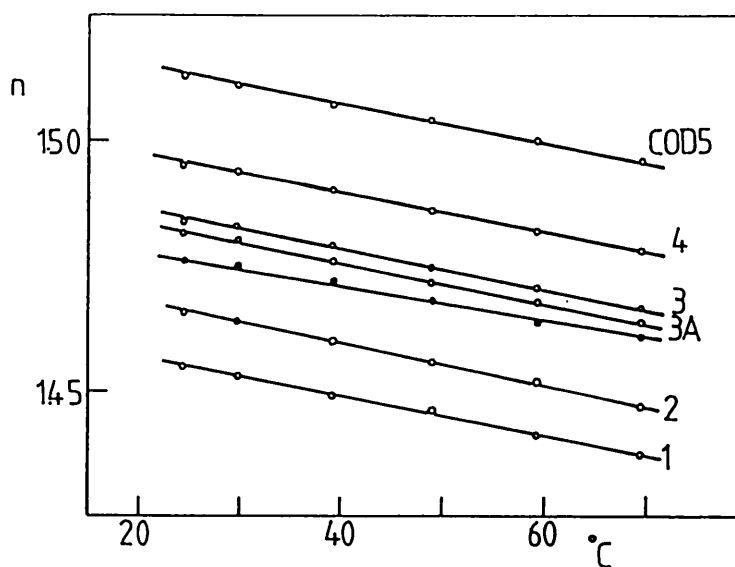


Figure 10. Plots of refractive index against temperature for COD(  $\circ$  ) and OMMA(  $\bullet$  ).

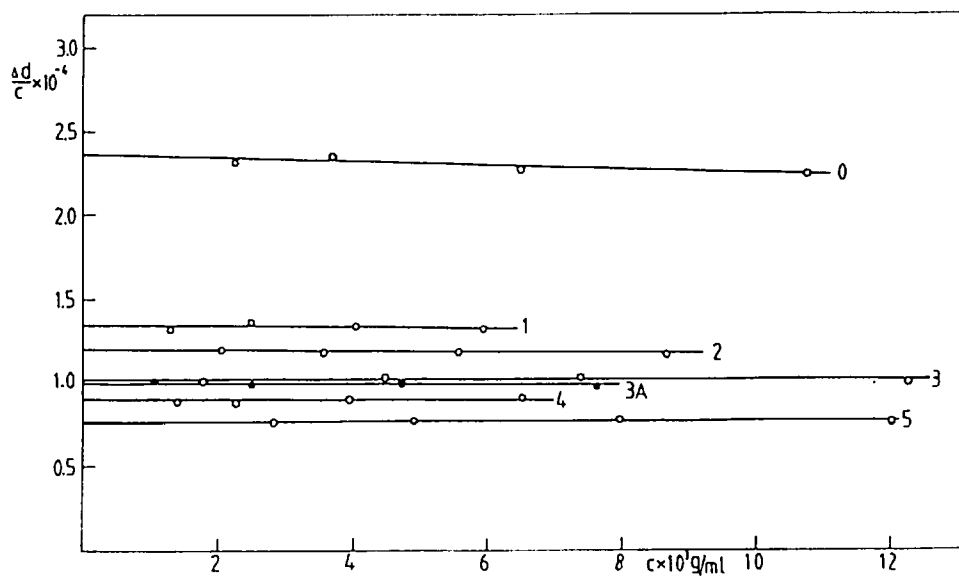


Figure 11. Plots of  $\Delta d/C$  against concentration in VPO.  $\Delta d$  is proportional to the temperature difference. O—standard sample, others are COD samples.

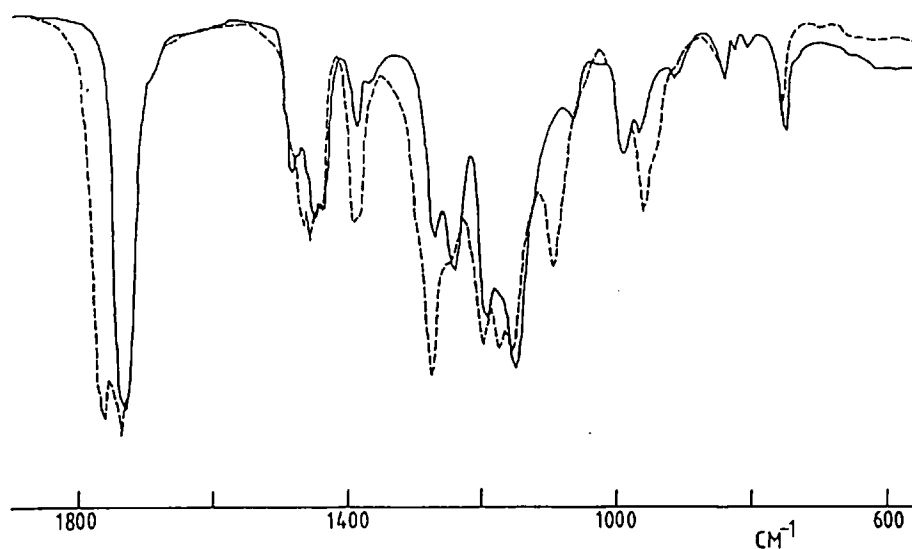


Figure 12. IR spectra of OMMA16(—) and OMMA23(---).

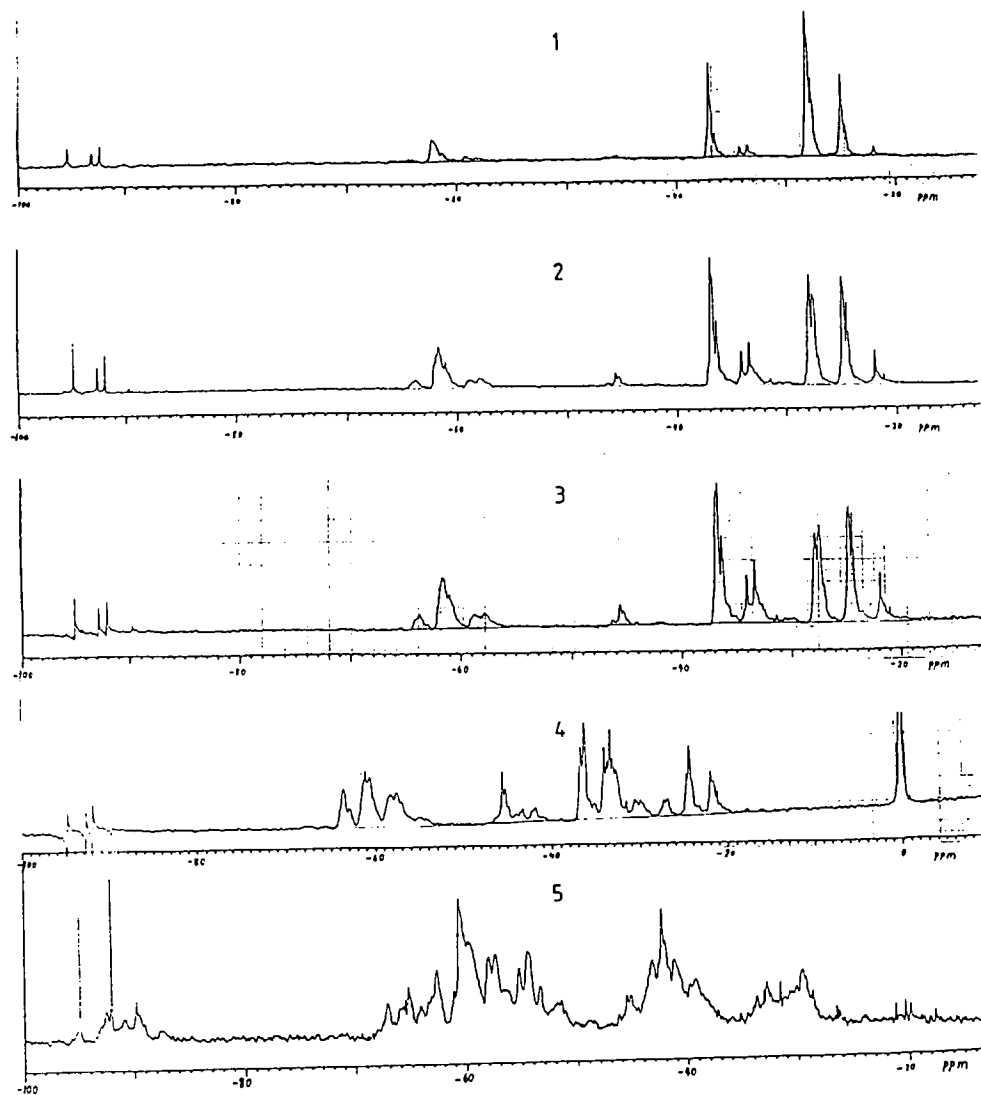


Figure 13.  $^{13}\text{C}$ -NMR spectra of CPE samples. 1. CPE2, 2. CPE4, 3. CPE1, 4. CPE3 and 5. CPE20.

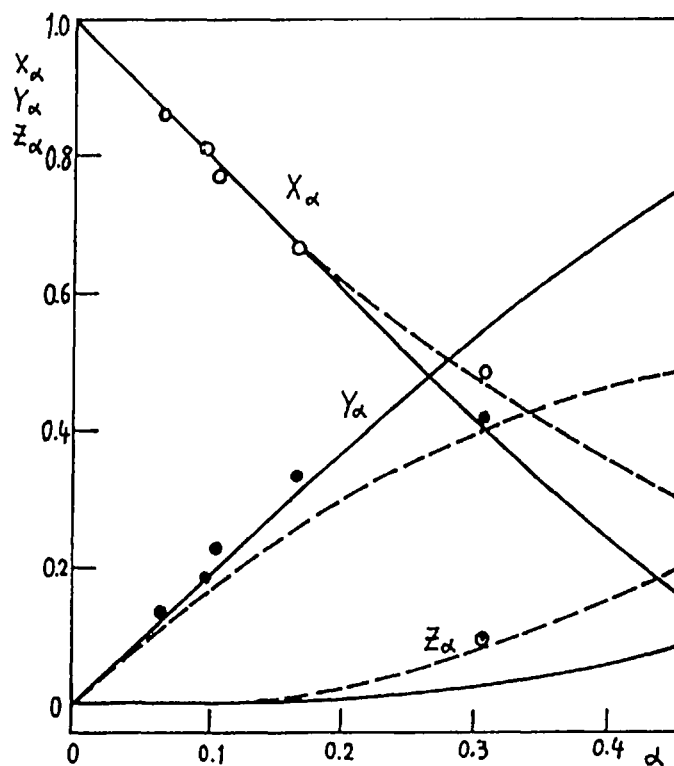


Figure 14. Experimental values of  $X_\alpha$ ,  $Y_\alpha$  and  $Z_\alpha$  as a function of the molar degree of chlorination  $\alpha$ . The theoretical curves: — random substitution, ---- hindered substitution with  $\lambda=0.2$ .

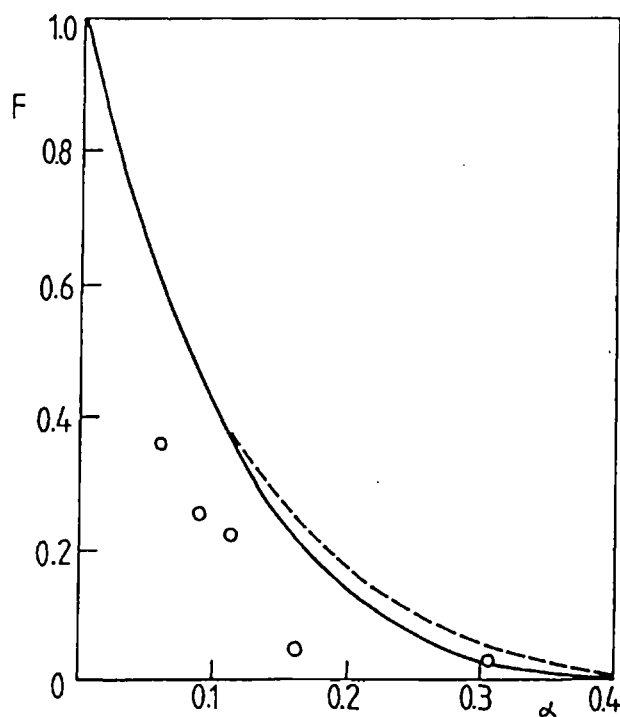


Figure 15. Molar fraction of pentad 00000 determined by  $^{13}\text{C}$ -NMR. Theoretical curves seen Figure 14.

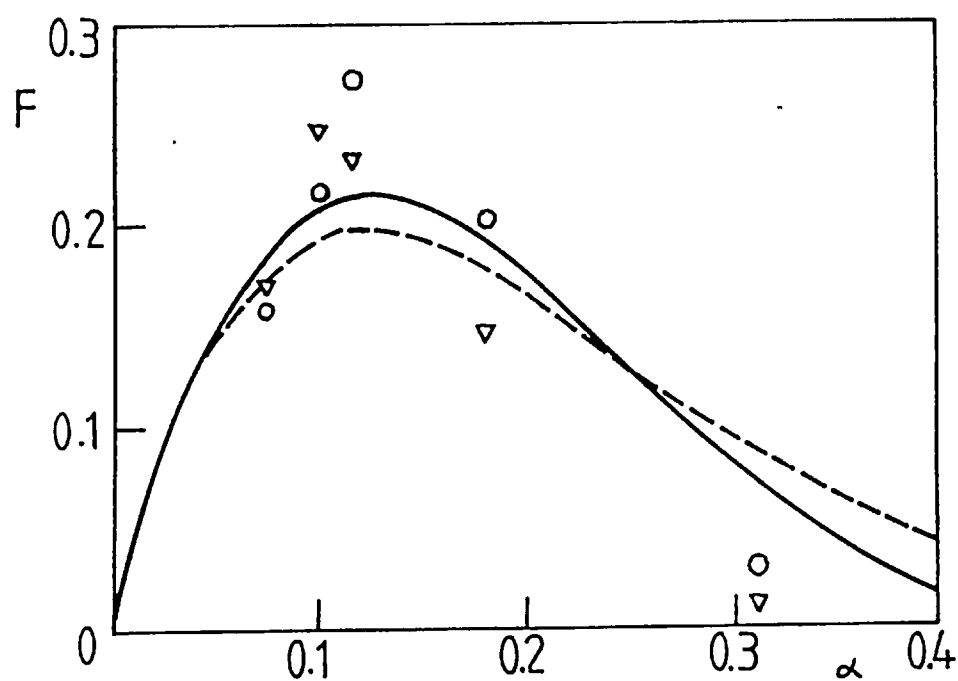


Figure 16. Molar fractions of pentads 01000(○) and 10000(▽) determined by  $^{13}\text{C}$ -NMR. Theoretical curves seen Figure 14.

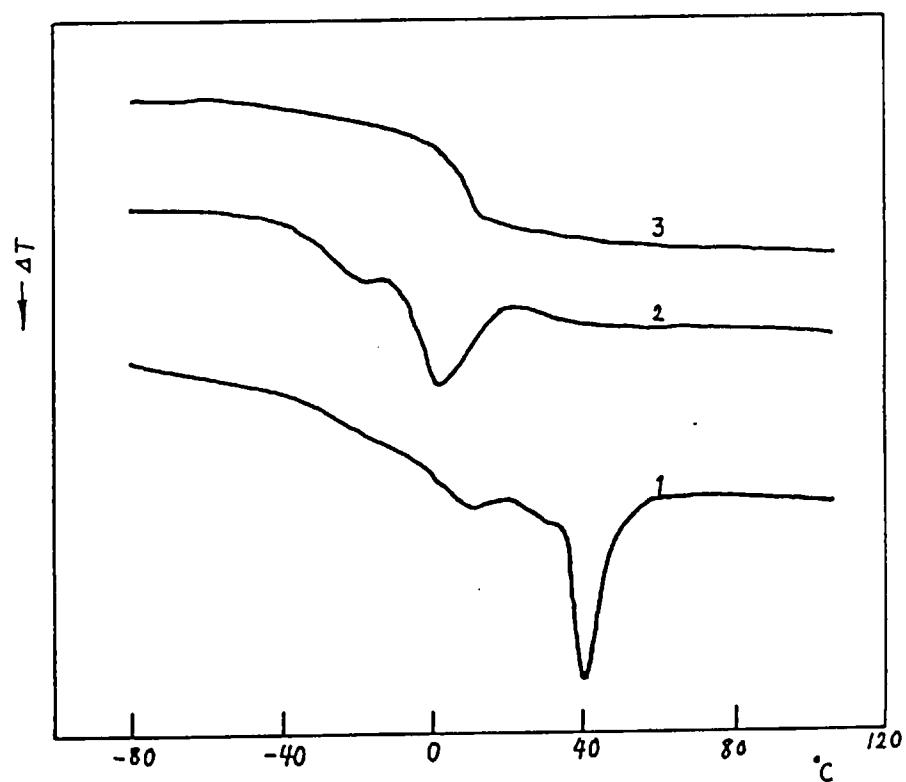


Figure 17. DTA of CPE samples. 1. CPE2, 2. CPE4 and 3. CPE3.

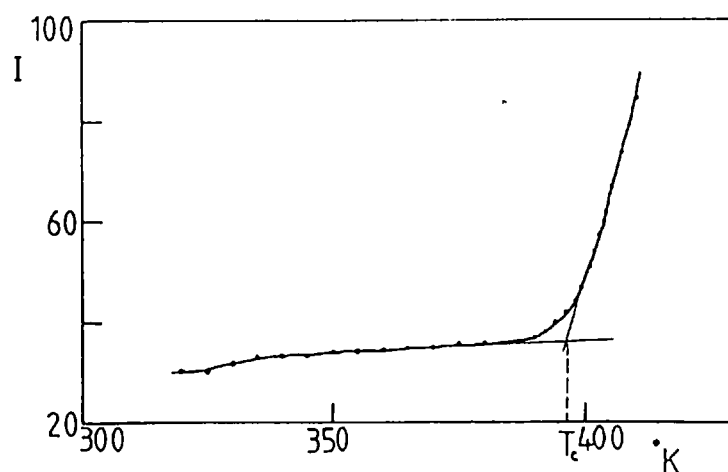


Figure 18. Intensity of scattered light as a function of temperature. The cross point is the cloud point temperature.

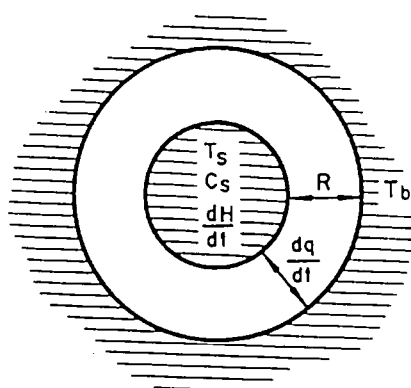


Figure 19. Thermal analysis cell schematic.

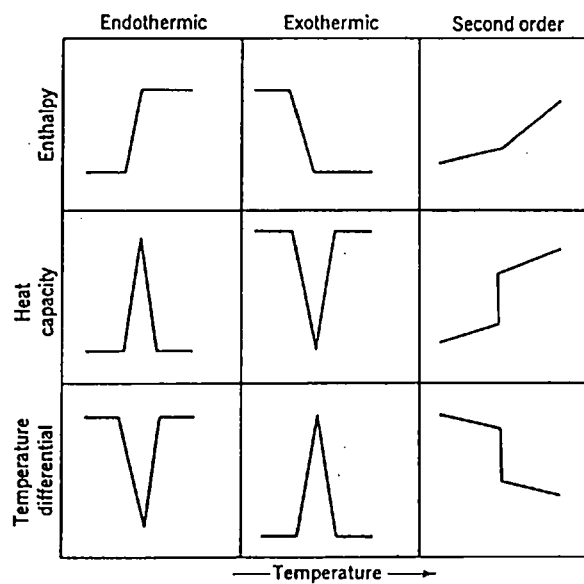


Figure 20. Changes in enthalpy, heat capacity and temperature for the first and second transitions.

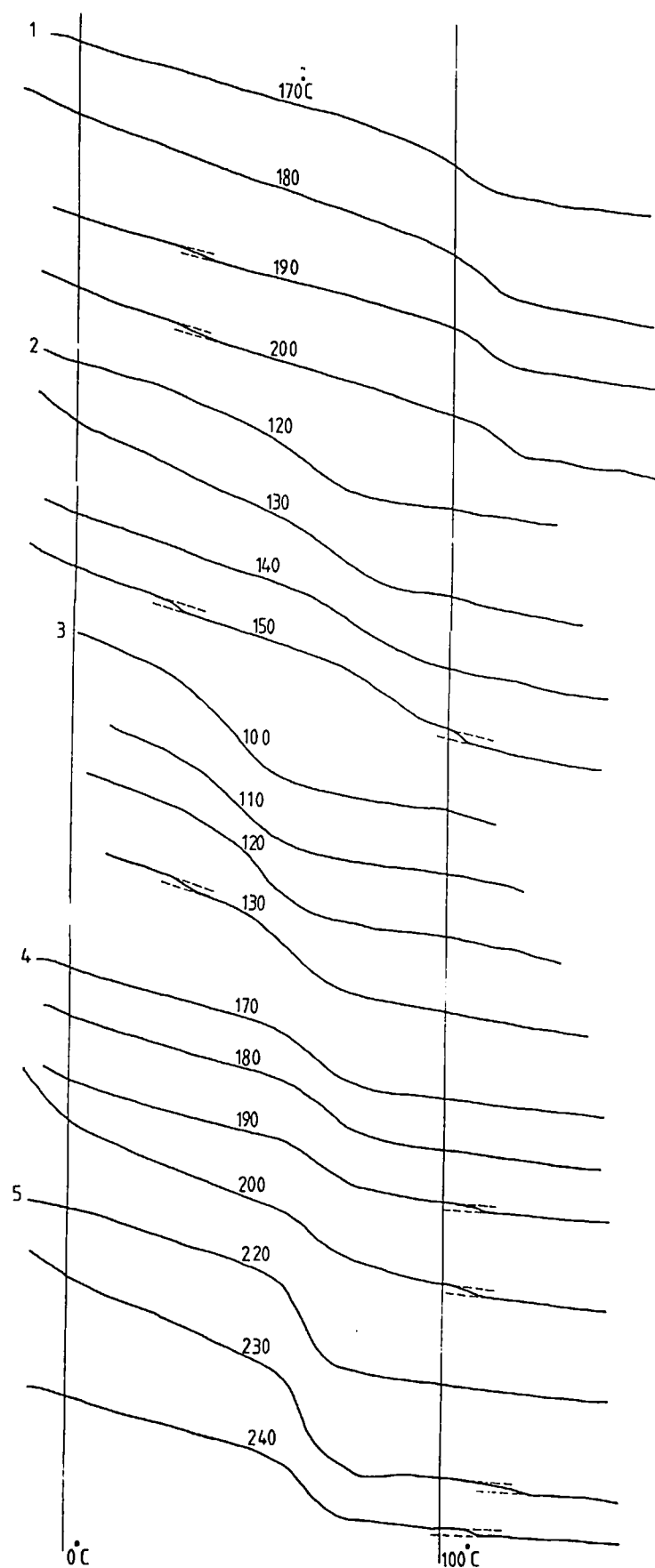


Figure 21. Phase separation observed in DTA measurements. Weight fraction of CPE in PMMA1.4/CPE16 blends: 1. 0.1003, 2. 0.2474, 3. 0.5224, 4. 0.7417 and 5. 0.8999.

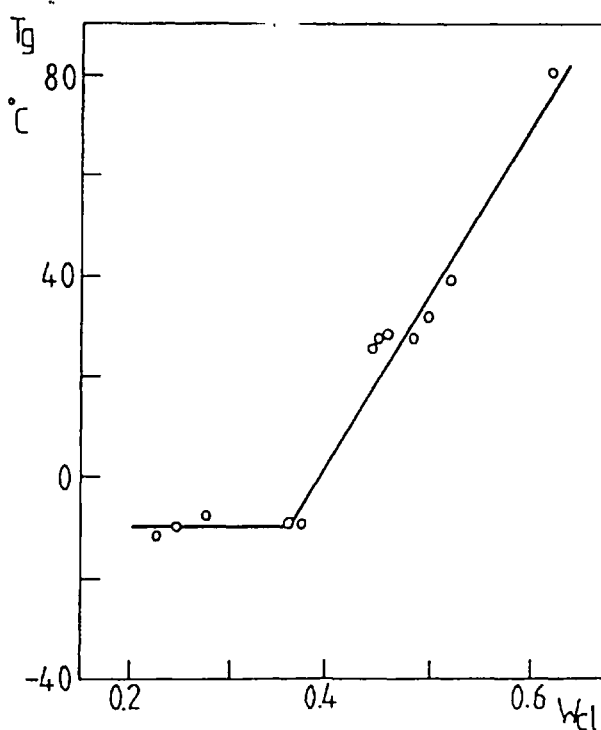


Figure 22. The glass transition temperature of CPE.  $w_{Cl}$  is the weight fraction of chlorine in CPE.

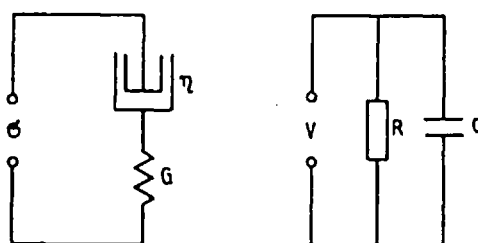


Figure 23. The mechanical and electrical Maxwell models for a viscoelastic fluid.

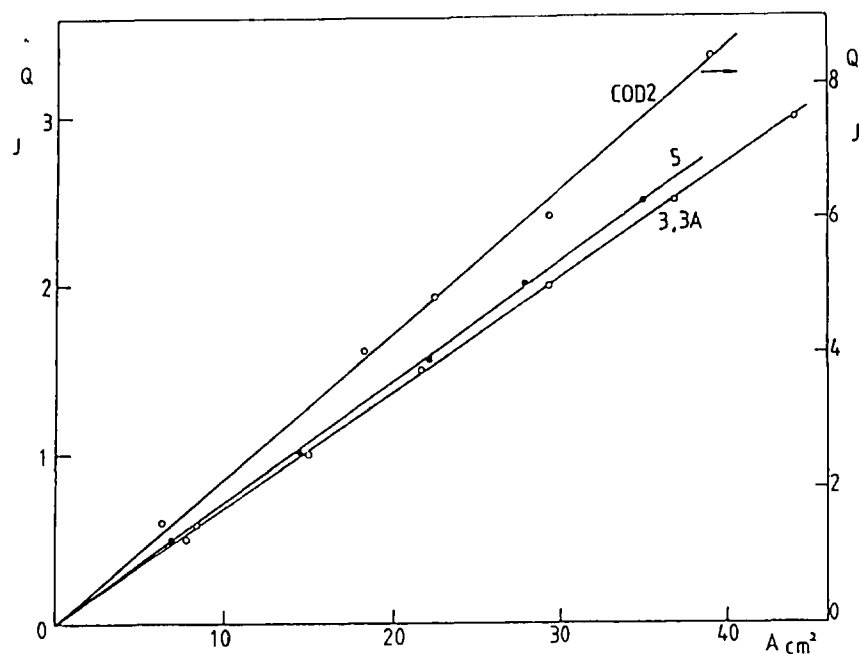


Figure 24. Calibrations in the heats of mixing measurements.

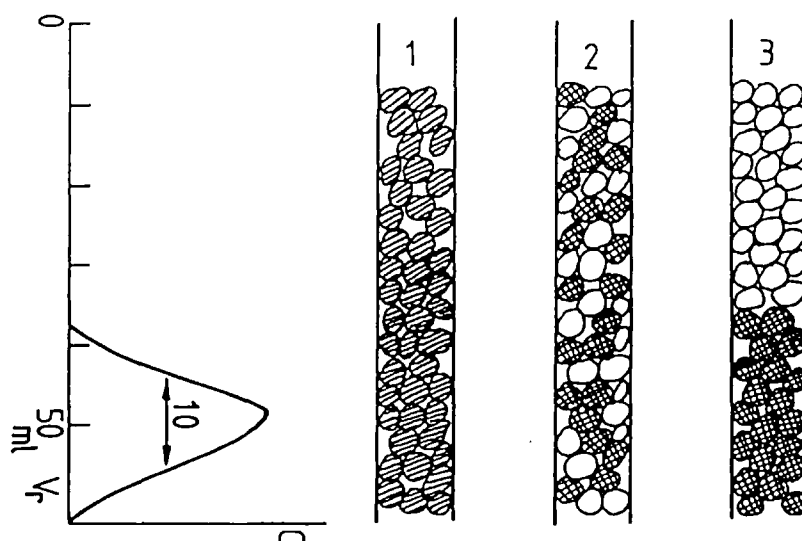


Figure 25. A presentation of the profile of concentration of the solvent probe in the column and the configurations of the columns used 1. packings coated with polyblend, 2. mixed packings and 3. packings in series.

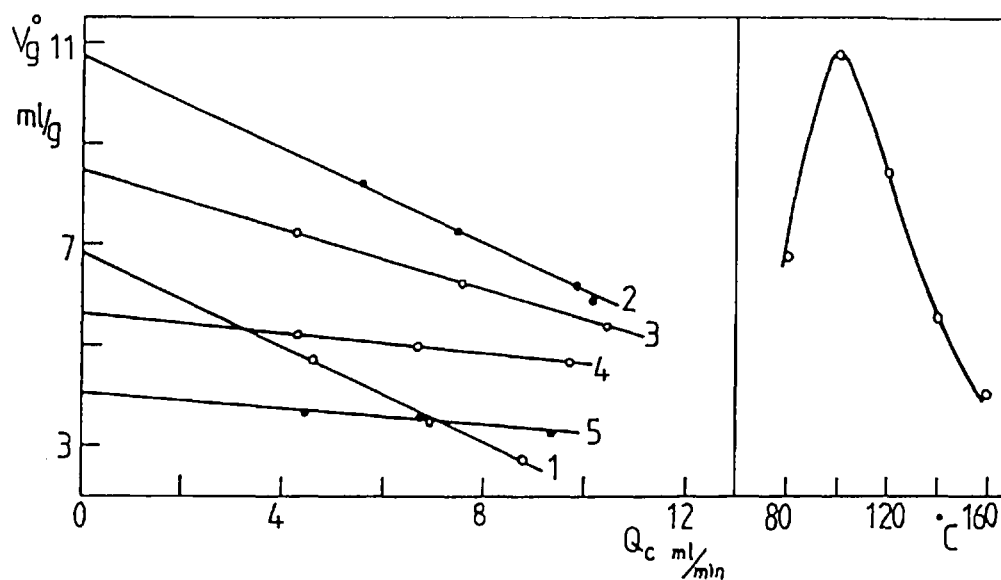


Figure 26.  $V_g^\circ$  of CPE20 as a function of flowrate of carrier gas and temperature at 1. 80°, 2. 100°, 3. 120°, 4. 140° and 5. 160°C using MEK as the probe solvent.

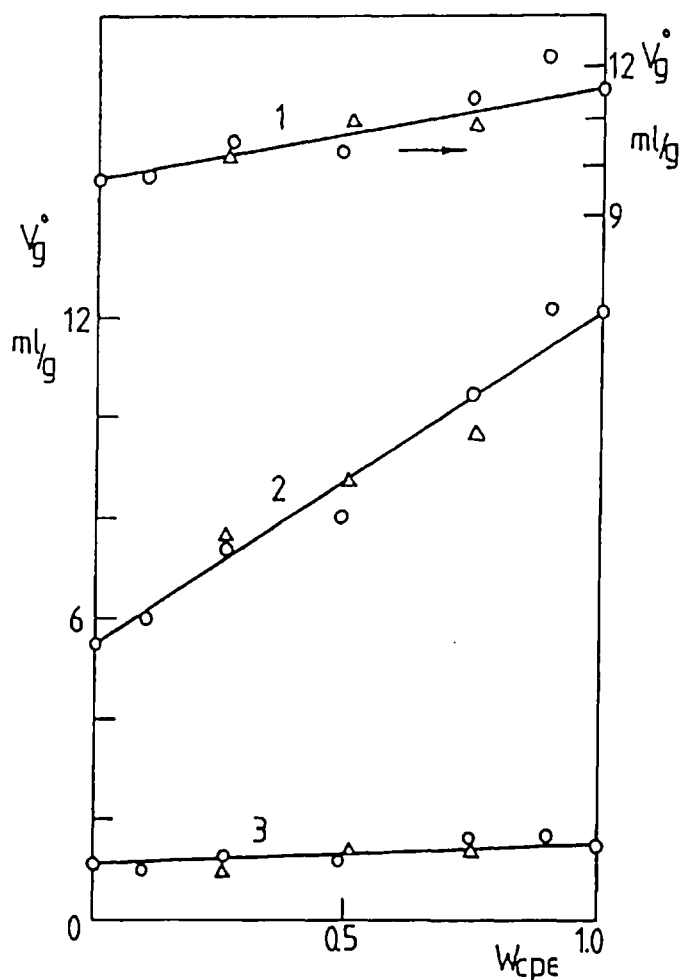


Figure 27. Specific retention volumes of the PMMA/CPE20 system.  $\Delta$  mixed packings,  $\circ$  packings coated with polyblends for three solvents: 1. MEK, 2. THF and 3. pentane at 120°C.

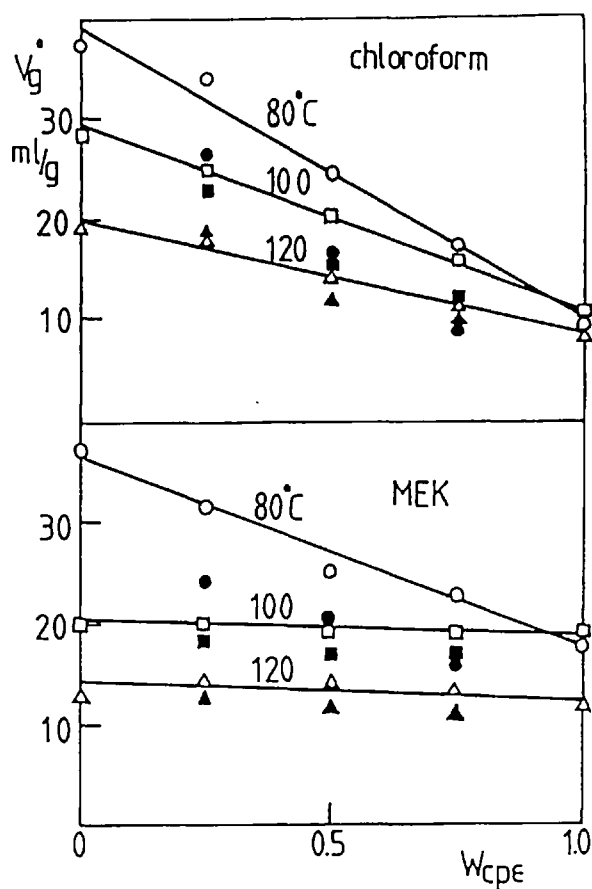


Figure 28.  
Specific retention volumes  
of the PEMA/CPE20 system  
at 80°C (○), 100°C (□) and 120°C (Δ)  
for mixed packings and  
(●, ■, ▲) for polyblends.

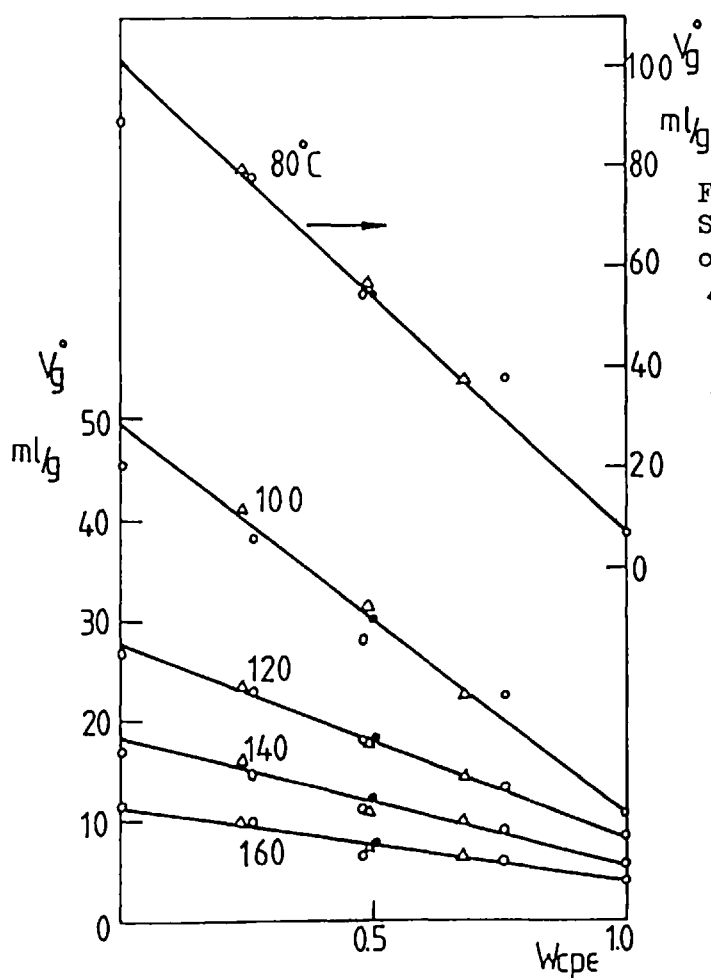


Figure 29.  
Specific retention volumes  
of the PBA/CPE20 system.  
Δ mixed packings,  
○ packings coated with  
polyblends, and  
● packings in series.

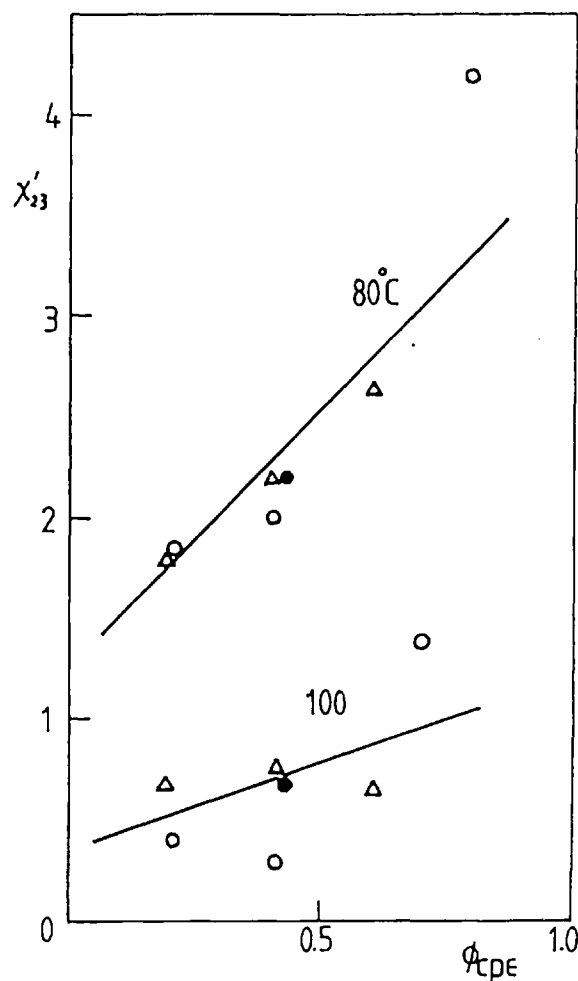


Figure 30. The apparent values of  $\chi'_{23}$ , as calculated from Eq.203 and the data in Figure 29<sup>3</sup> for the PBA/CPE20 system. The symbols are as in Figure 29.

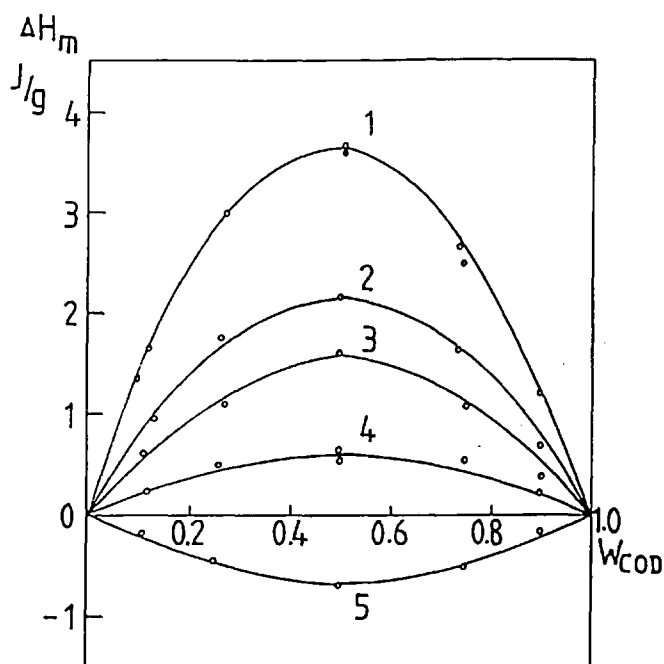


Figure 31. Heats of mixing for OMMA23 with COD plotted against weight fraction of COD. 1. COD2, 2. COD3, 3. COD3A, 4. COD4 and 5. COD5. Theoretical curves are calculated from Eq.80.

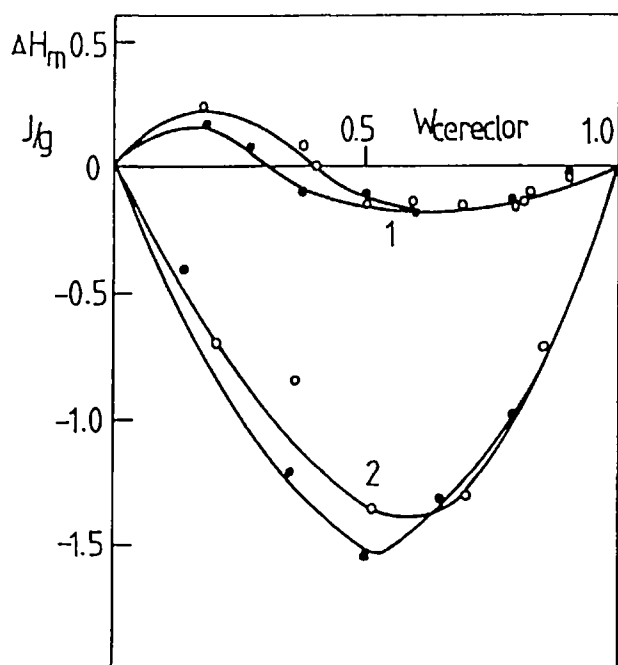


Figure 32. Heats of mixing for OMMA1 with cereclor45( 1 ) or cereclor52( 2 ) at 70°C(○) and 85°C(●).

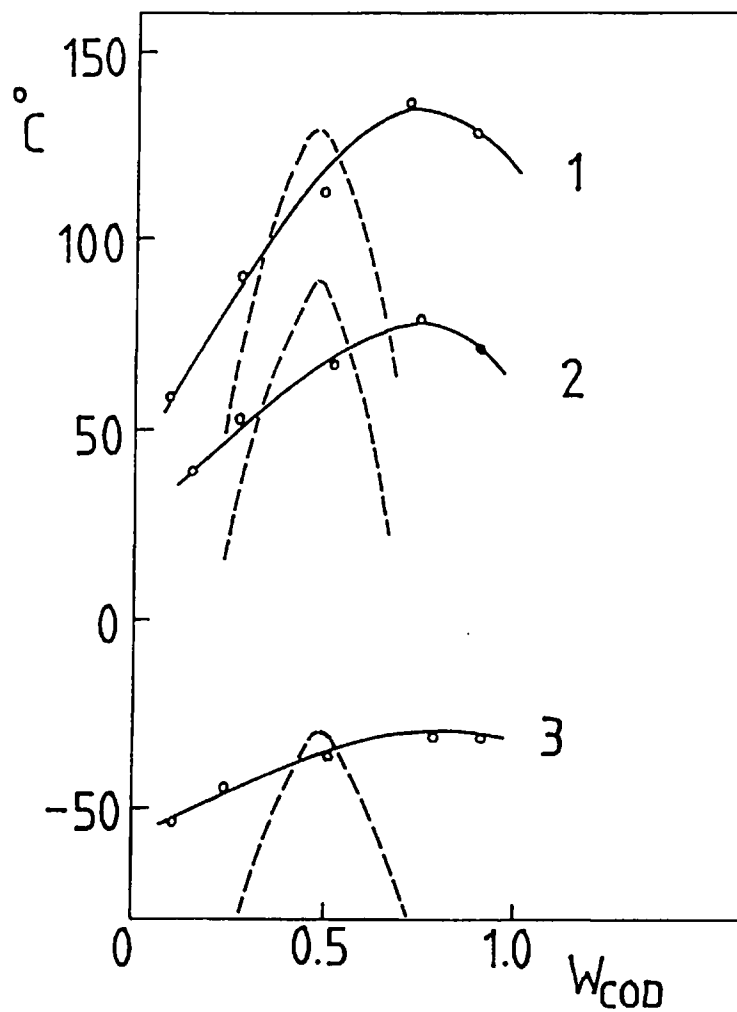


Figure 33. Phase diagrams for oligomer mixtures. 1. OMMA23/COD1, 2. OMMA23/COD2 and 3. OMMA23/COD3. The broken lines are the simulated spinodals by Eq.84.

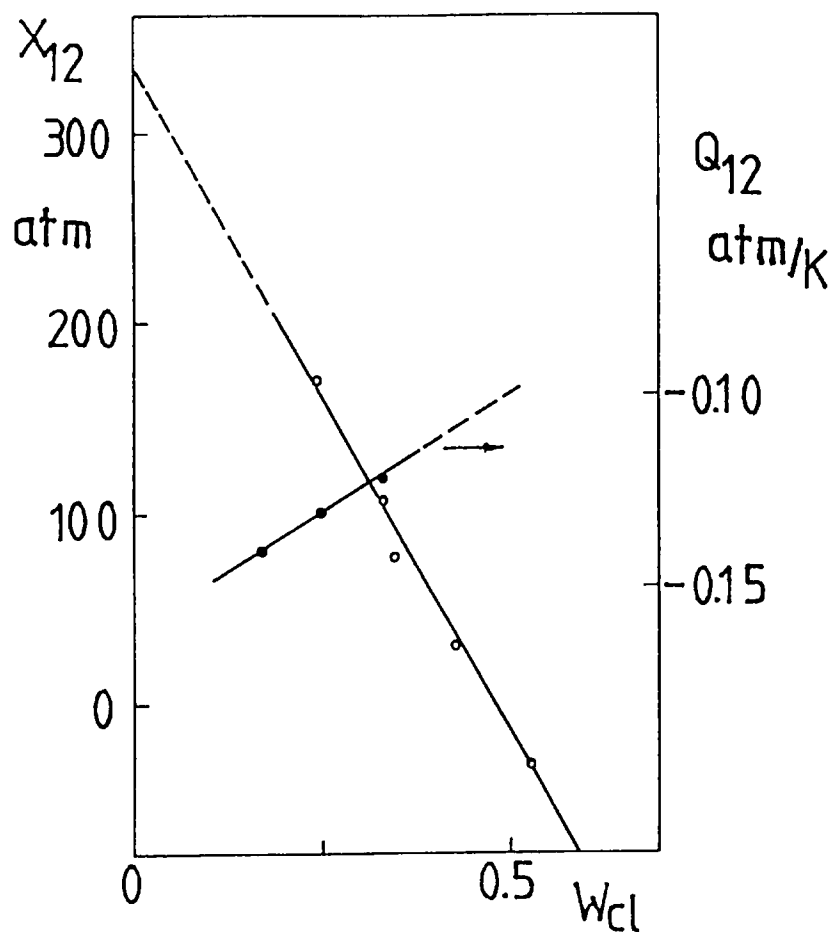


Figure 34. Values of  $X_{12}$  and  $Q_{12}$  for OMMA/COD against the weight fraction of chlorine in COD.

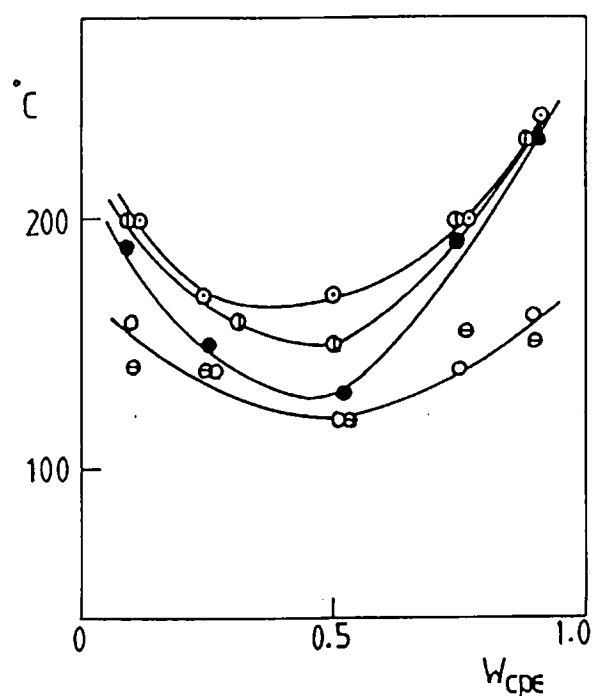


Figure 35. Experimental phase boundaries for mixtures of CPE16 with PMMA.  $\circ$  PMMA17,  $\odot$  PMMA16,  $\bullet$  PMMA1.4,  $\circ$  PMMA F6 and  $\oplus$  PMMA F5.

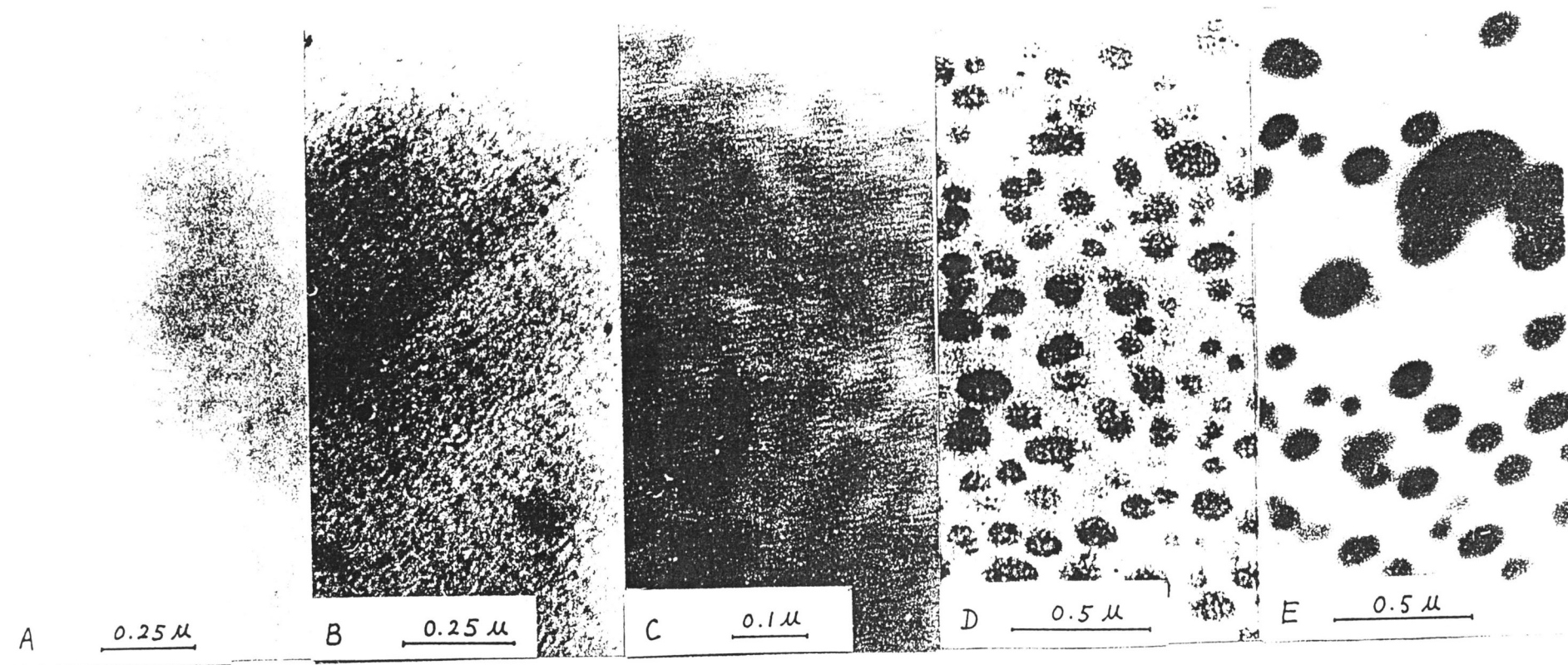


Figure 36. A TEM observation of PMMA1.4/CPE16 sample treated at different temperatures. A. room temperature, B.  $110^{\circ}\text{C}$ , C.  $130^{\circ}\text{C}$ , D.  $150^{\circ}\text{C}$  and E.  $170^{\circ}\text{C}$ . The phase separation temperature is  $140^{\circ}\text{C}$  by DTA.

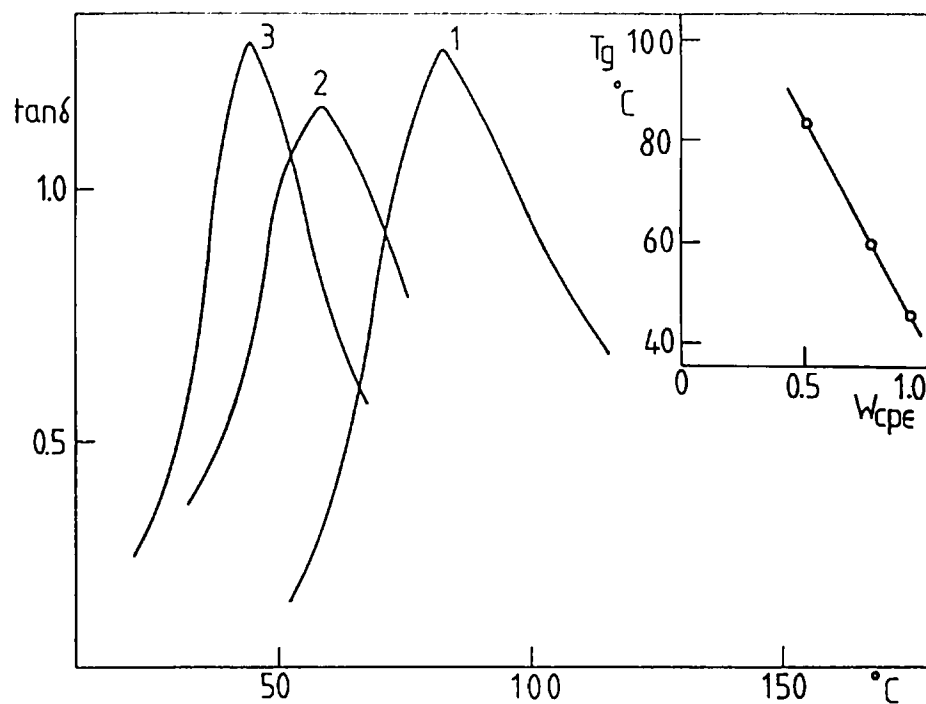


Figure 37. Dynamic mechanical results for PMMA17/CPE16 blends. Weight percent CPE: 1. 0.5026, 2. 0.7502 and 3. 0.9068.

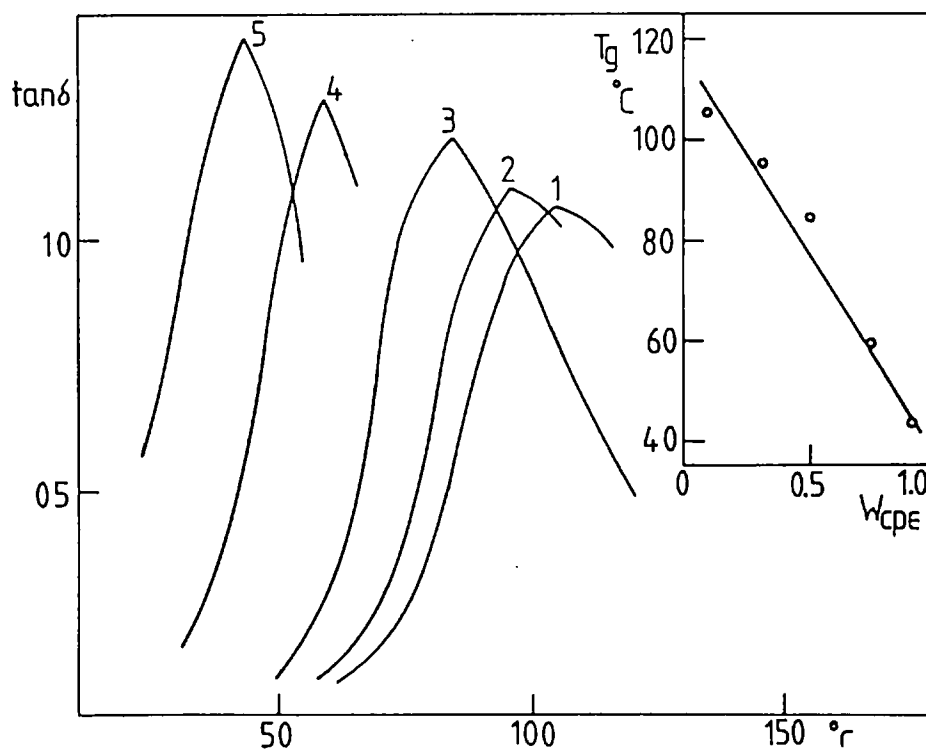


Figure 38. Dynamic mechanical results for PMMA16/CPE16 blends. Weight percent CPE: 1. 0.0910, 2. 0.3068, 3. 0.4981, 4. 0.7373 and 5. 0.9033.

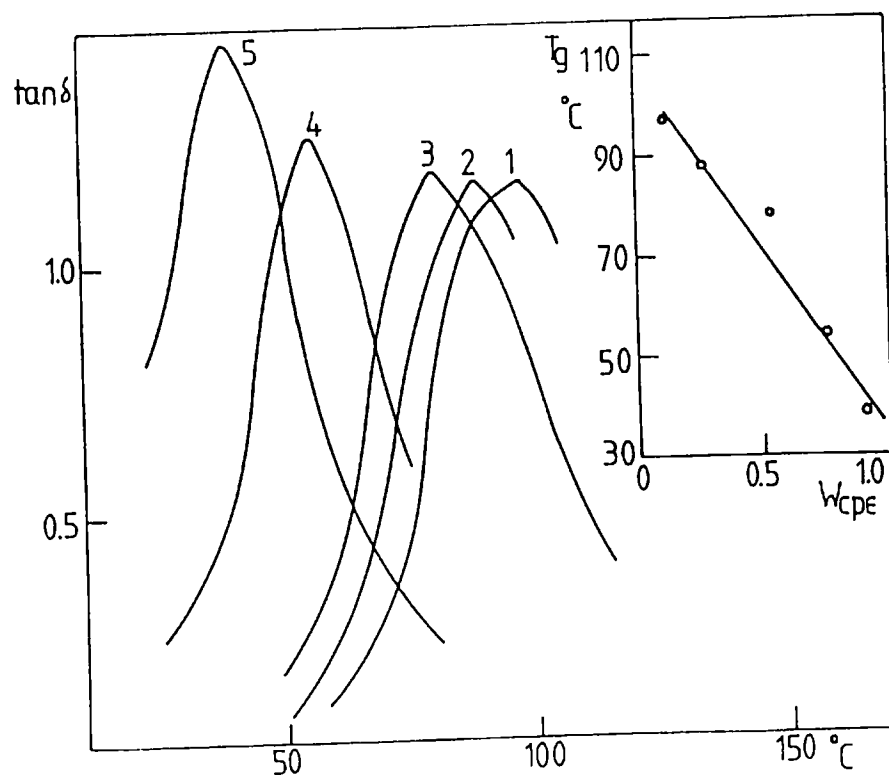


Figure 39. Dynamic mechanical results for PMMA1.4/CPE16 blends. Weight percent CPE: 1. 0.1003, 2. 0.2474, 3. 0.5224 (sample 218), 4. 0.7417 and 5. 0.8999.

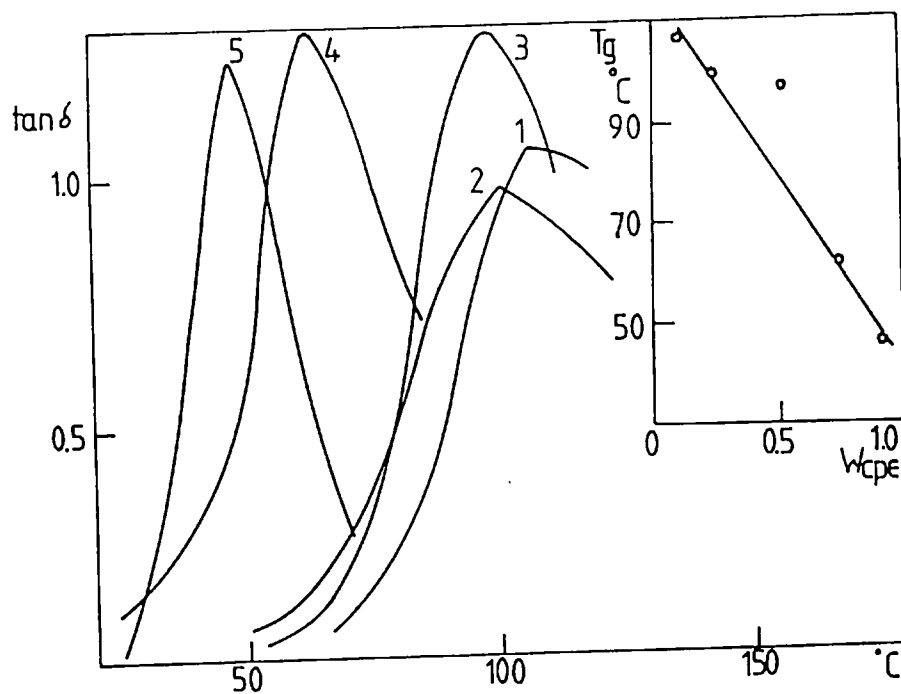


Figure 40. Dynamic mechanical results for PMMA1.4/CPE16 blends treated at  $140^{\circ}\text{C}$  for 15 minutes. Weight fraction of CPE in the samples seen in Figure 39.

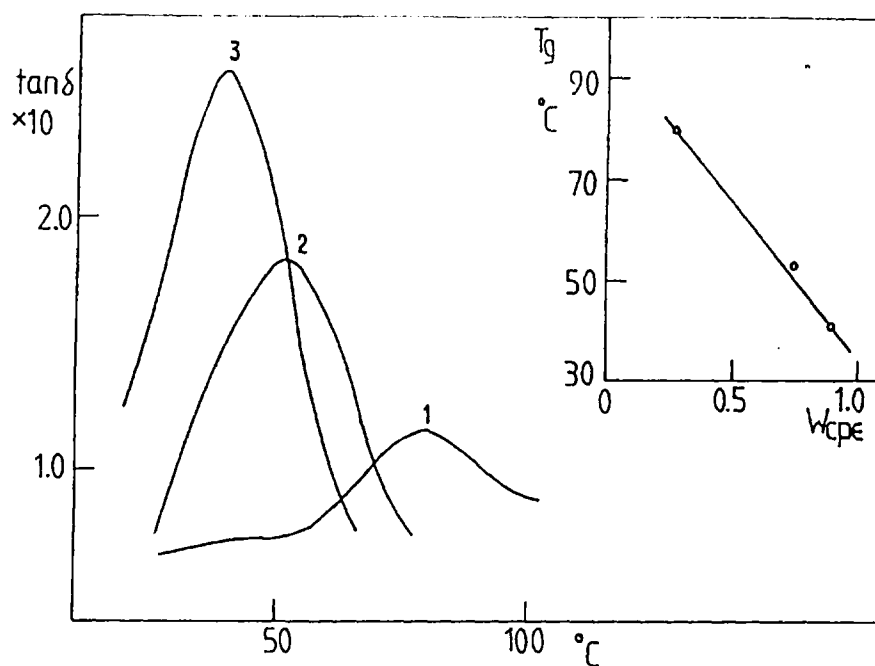


Figure 41. Dielectric results at 101 Hz for PMMA16/CPE16 blends.  
Weight percent CPE: 1. 0.2665, 2. 0.7467 and 3. 0.9040.

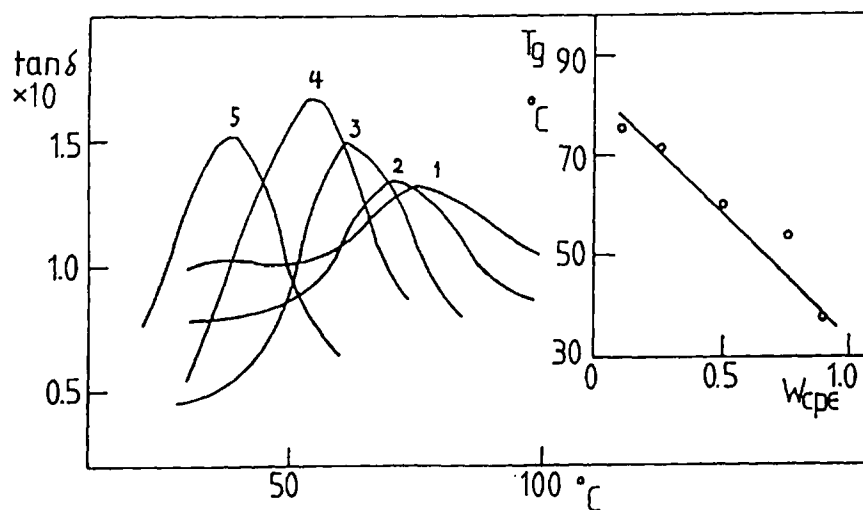


Figure 42. Dielectric results at 101 Hz for PMMA1.4/CPE16 blends.  
Weight percent CPE: 1. 0.1044, 2. 0.2506, 3. 0.5012, 4. 0.7546 and 5. 0.9004.

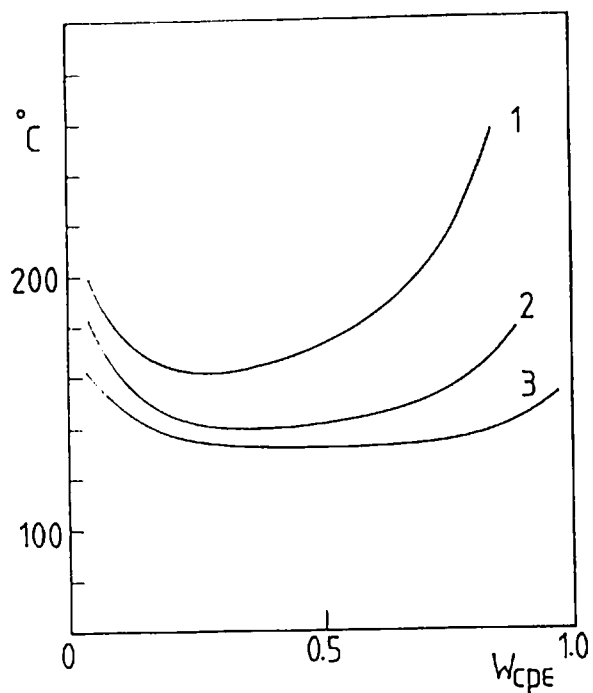


Figure 43. Simulated spinodals for mixtures of PMMA/CPE16. 1. PMMA17, 2. PMMA16 and 3. PMMA F5.

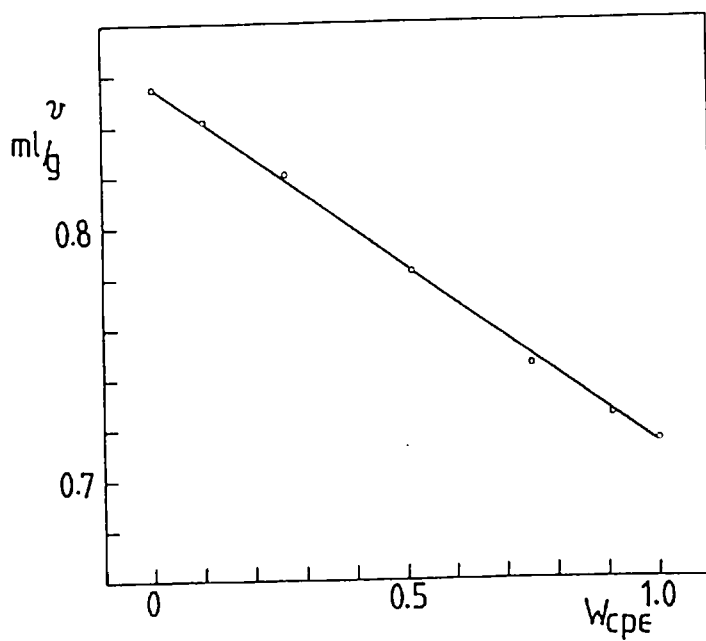


Figure 44. Specific volumes of PMMA1.4/CPE16 blends measured at  $25 \pm 0.1^\circ\text{C}$ .

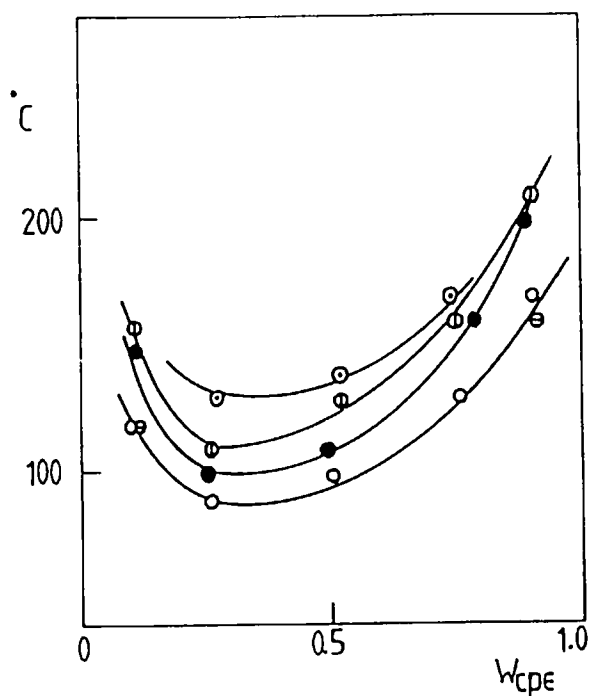


Figure 45. Experimental phase boundaries for mixtures of CPE17 with PMMA:  $\circ$  PMMA17,  $\bullet$  PMMA16,  $\bullet$  PMMA1.4,  $\odot$  PMMA F6 and  $\ominus$  PMMA F5.

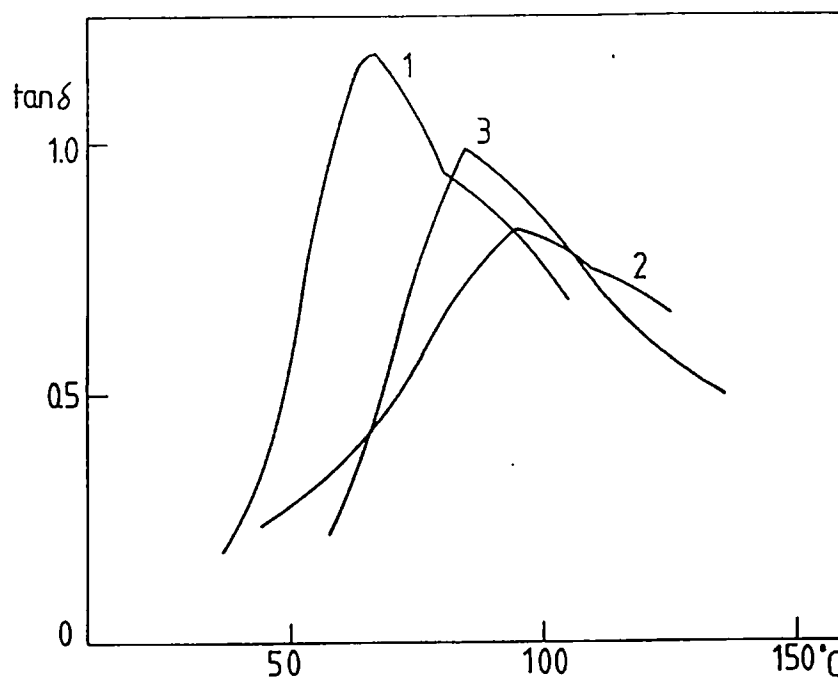


Figure 46. Dynamic mechanical results for PMMA/CPE17 blends at weight fraction 0.5. 1. PMMA17(sample243), 2. PMMA16 and 3. PMMA1.4

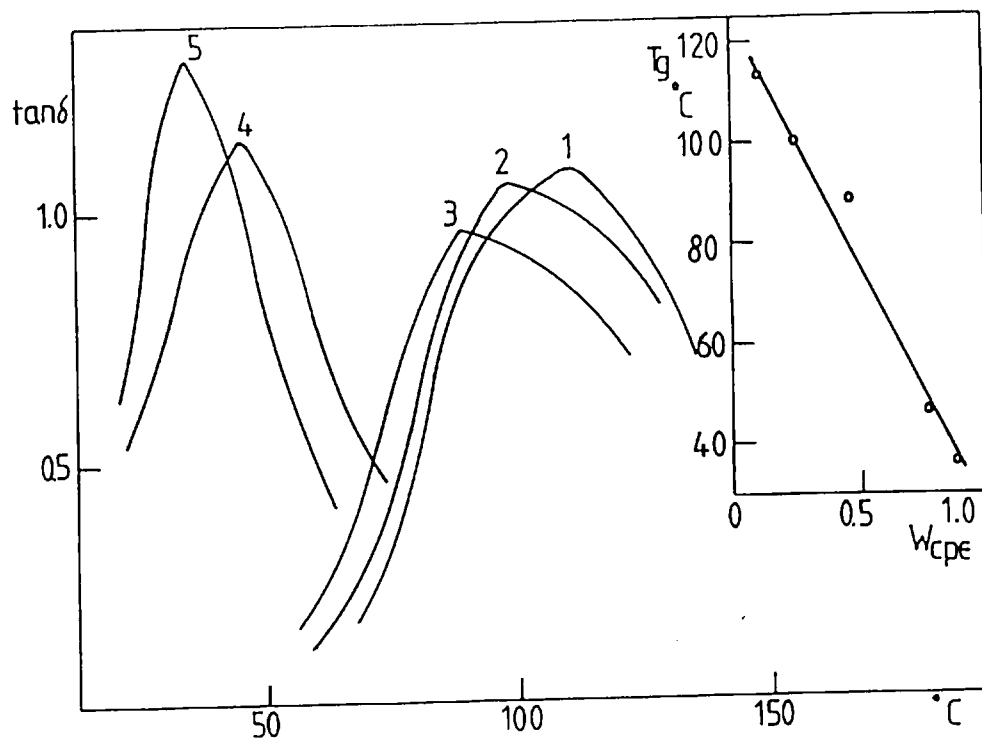


Figure 47. Dynamic mechanical results for PMMA1.4/CPE17 blends. Weight percent CPE: 1. 0.1112, 2. 0.2533, 3. 0.4828, 4. 0.7793 and 5. 0.8946.

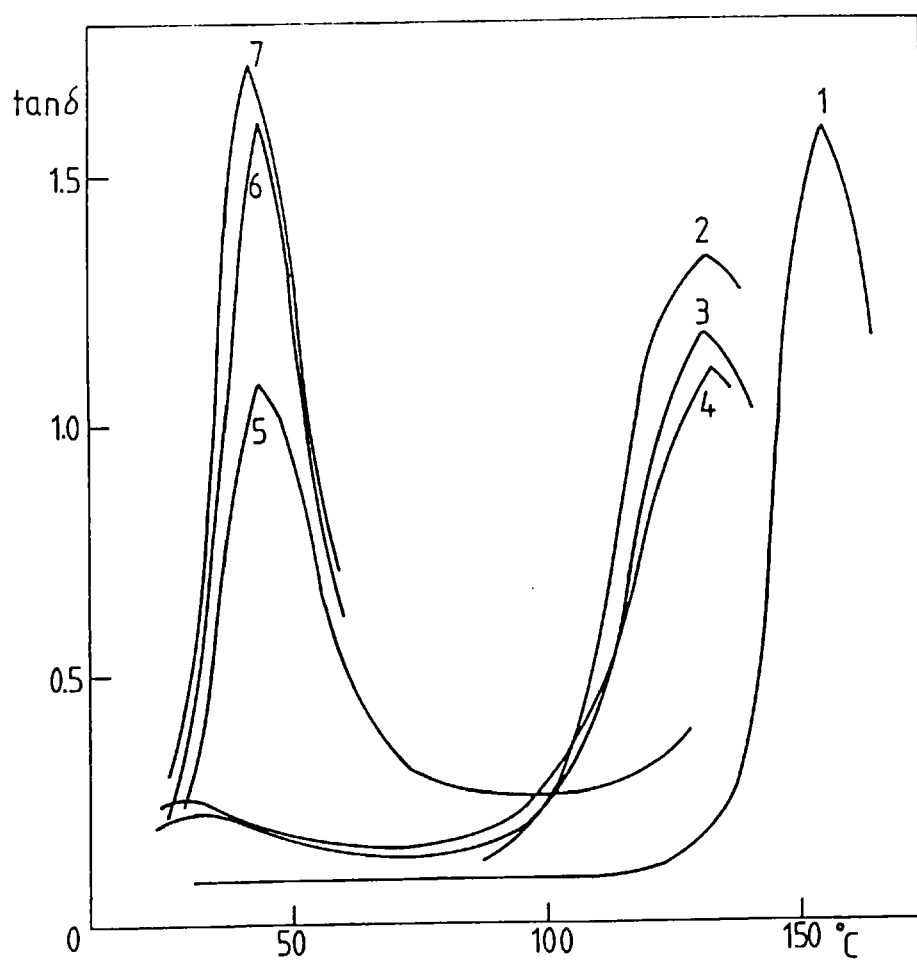


Figure 48. The same blends heated at 200°C for 15 minutes. 1. PMMA, 2-6. seen 1-5 in Figure 47, 7. CPE17.

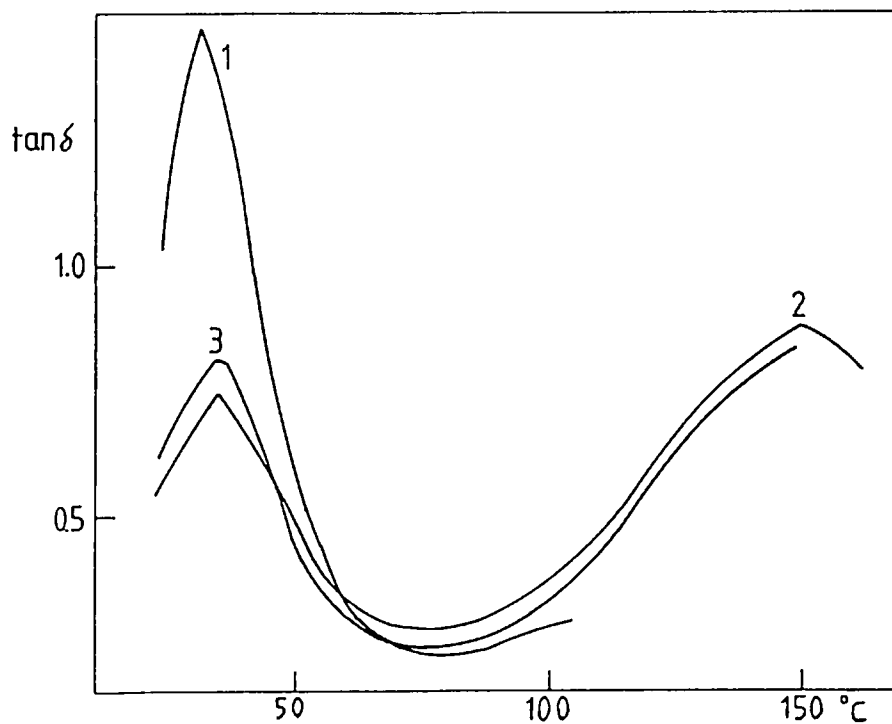


Figure 49. Dynamic mechanical results for PMMA17/CPE3 blends cast from 1. THF, weight percent CPE 0.8012, 2. chlorobenzene, 0.4788 and 3. MEK, 0.4900.

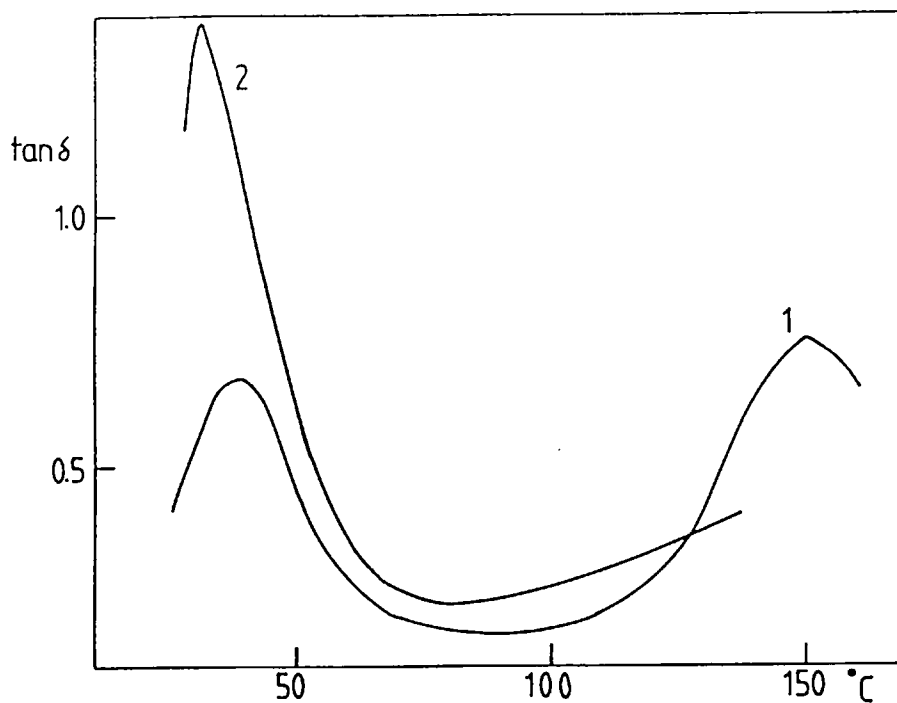


Figure 50. Dynamic mechanical results for PMMA17/CPE15 at weight percent CPE 0.7611. 1. moulded at 140°C and 2. cast from THF solution.

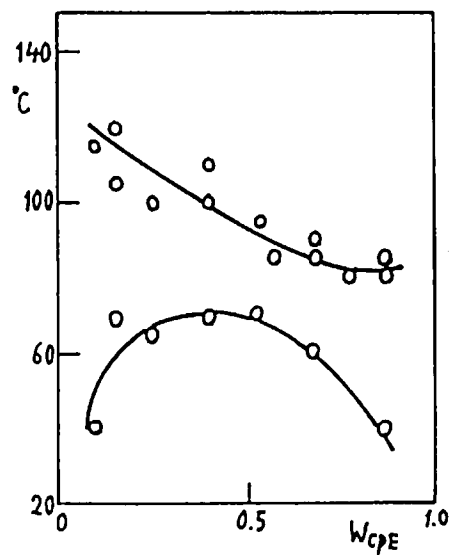


Figure 51. The transparent gap observed by light scattering turbidity for PMMA/CPE2 blends.

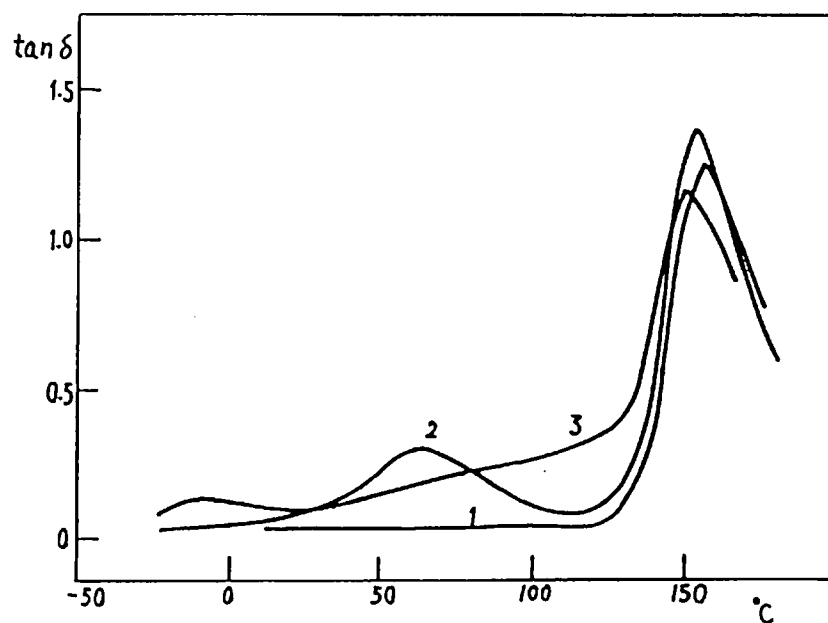


Figure 52. Dynamic mechanical results for PMMA/CPE2 blends. Weight percent CPE: 1. 0.1512, 2. 0.2504 and 3. 0.4033.

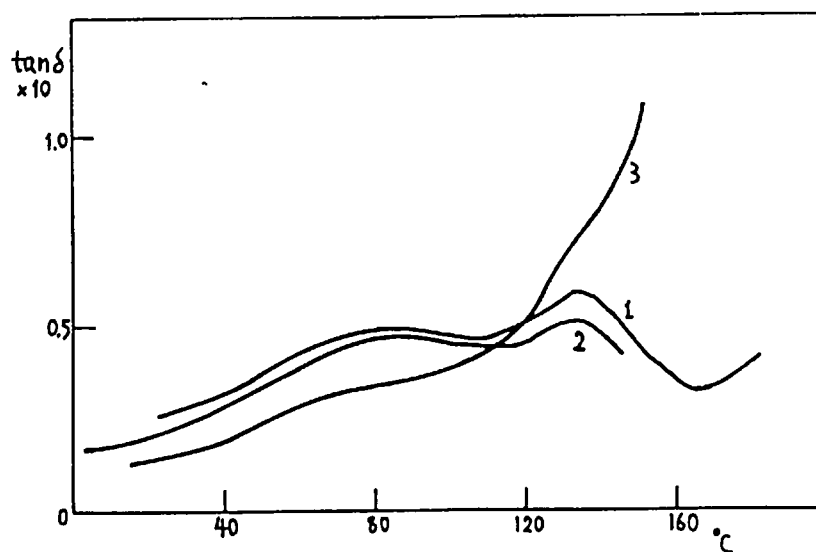


Figure 53. Dielectric results for PMMA/CPE2 blends. Weight percent CPE: 1. 0.0686, 2. 0.0995 and 3. 0.1512. 1.01 KHz.

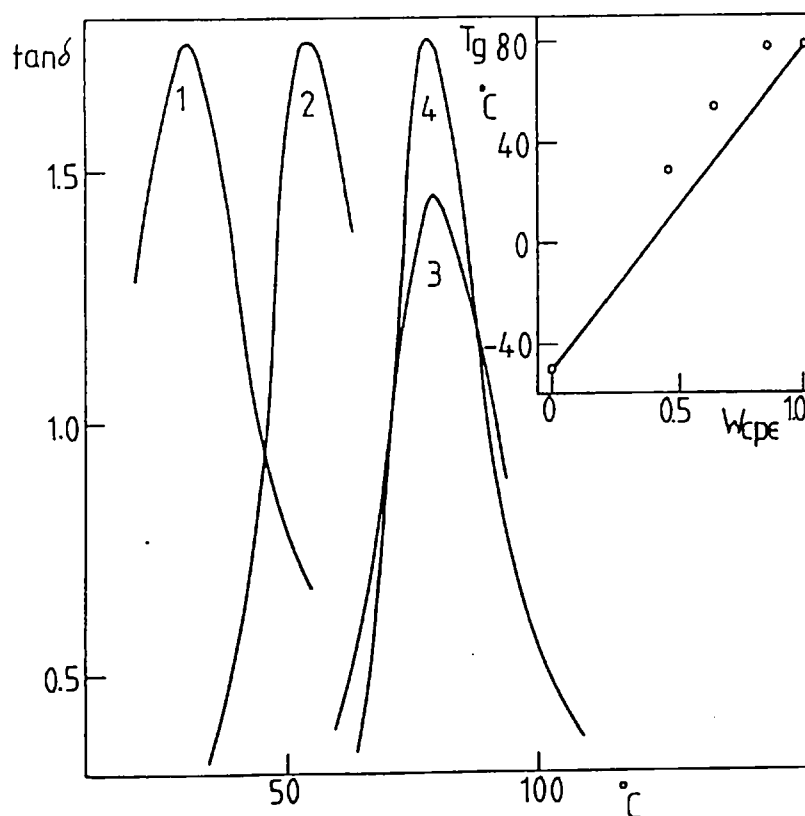


Figure 54. Dynamic mechanical results for PBA/CPE20 blends. Weight percent CPE: 1. 0.4612, 2. 0.6409, 3. 0.8473 and 4. CPE20.

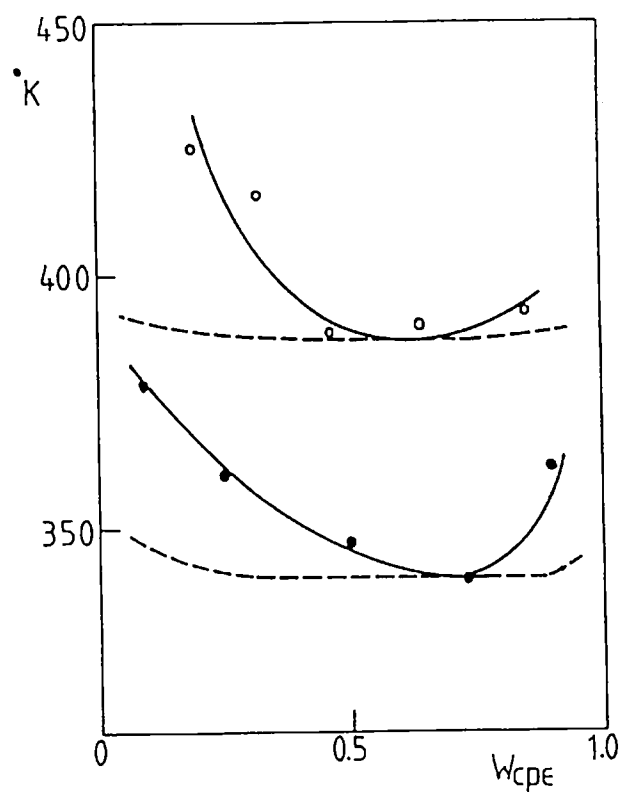


Figure 55. Phase diagrams of PBA/CPE20( $\circ$ ) and PBA/CPE17( $\bullet$ ) blends. The broken lines are the spinodals calculated from Eq.84.

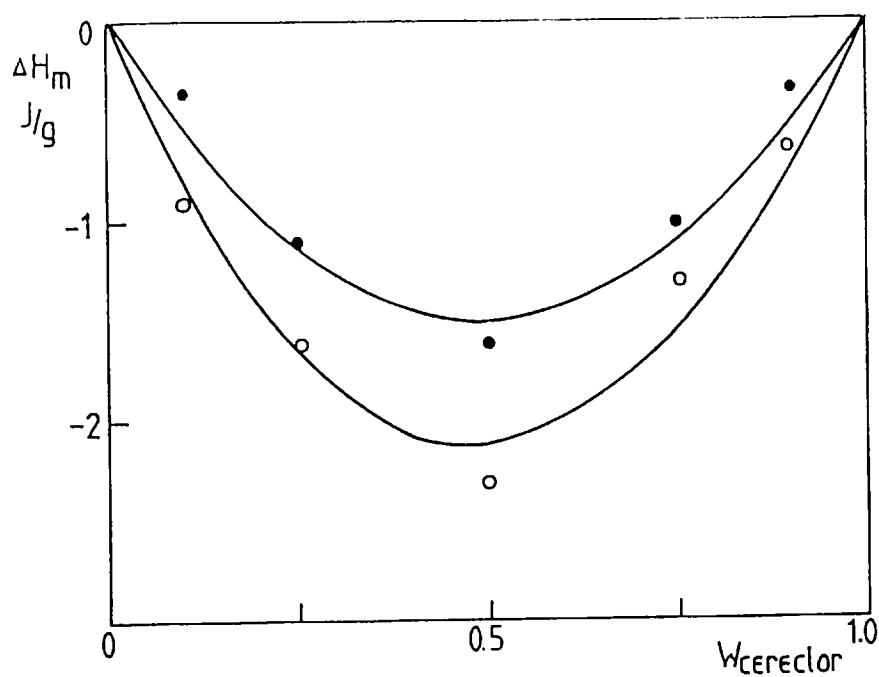


Figure 56. Heats of mixing of PBA with cereclor45( $\bullet$ ) and cereclor52( $\circ$ ) at 70°C. The theoretical curves are calculated from Eq.80.

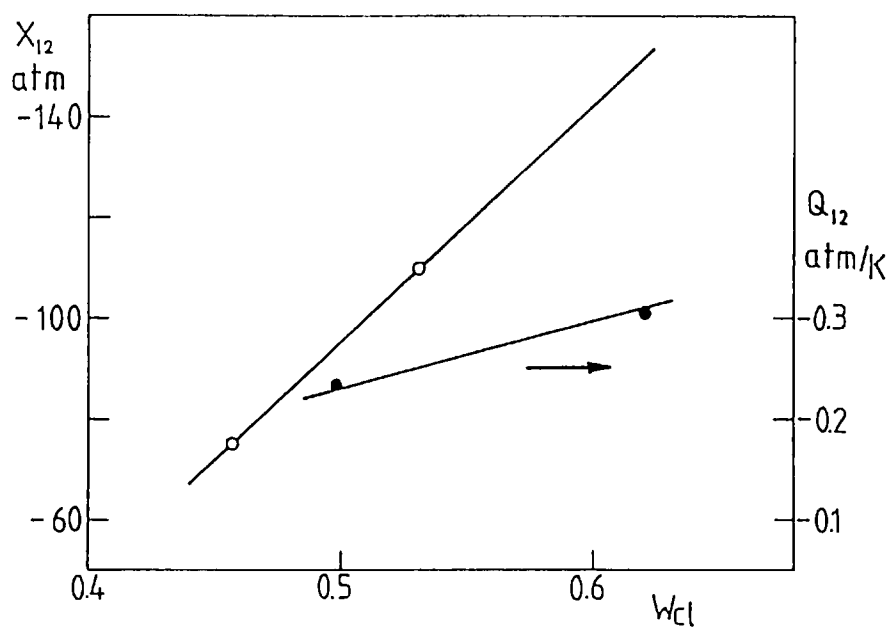


Figure 57.  $X_{12}$  and  $Q_{12}$  against weight percent chlorine in cereclor.

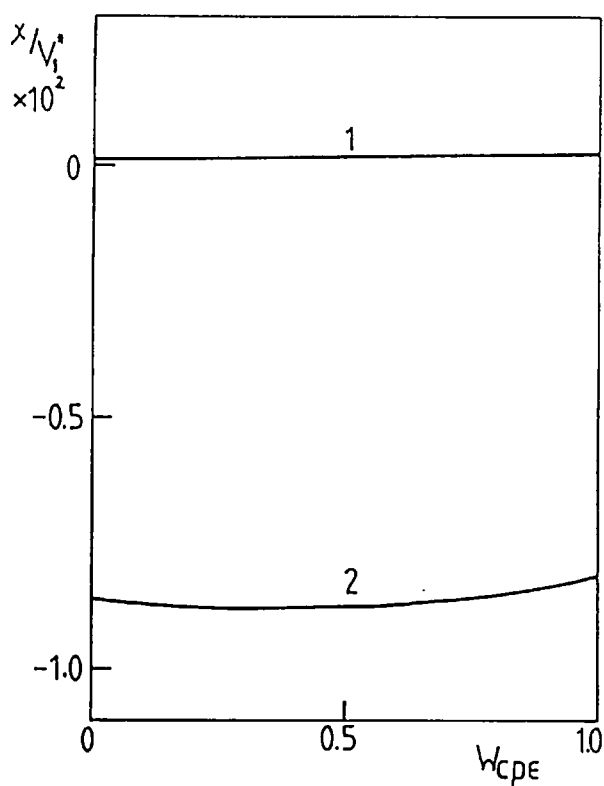


Figure 58.  $X/V_1^*$  for PBA/CPE mixtures calculated from Eq.131.  
1. CPE17 and 2.CPE20.

| 62.1 | 498 | 480 | 456 | 447 | 441 | 369 | 357 | 274 | 245 | 224 | 210 | 16.5 | Wt%     |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|---------|
| 20   | 17  | 3   | 18  | 15  | 19  | 1   | 4   | 2   | 5   | 11  | 12  | 8    | CPE     |
| -    |     |     | -   | -   | -   | +   | +   |     | +   | +   | +   | +    | 20 62.1 |
|      | -   |     | A   |     | -   | +   | +   |     | +   |     |     |      | 17 498  |
|      |     | -   |     |     | -   | +   | +   |     | +   |     | C   |      | 3 480   |
|      |     |     | -   | -   | -   | +   | +   |     |     | +   | +   | +    | 18 456  |
|      |     |     |     | -   | -   | +   | +   |     |     | +   | +   | +    | 15 447  |
|      |     |     |     |     | -   | +   | +   | +   | +   | +   | +   | +    | 19 441  |
|      |     |     |     |     |     | -   | -   | +   | +   | +   | +   |      | 1 369   |
|      |     |     |     |     |     |     | -   | -   | -   | -   | +   | D    | 4 357   |
|      |     |     |     |     |     |     |     | -   | B   | -   | -   | +    | 2 274   |
|      |     |     |     |     |     |     |     |     | -   | -   | -   | +    | 5 245   |
|      |     |     |     |     |     |     |     |     |     | -   | -   | +    | 11 224  |
|      |     |     |     |     |     |     |     |     |     |     | -   | +    | 12 210  |
|      |     |     |     |     |     |     |     |     |     |     |     | -    | 8 16.5  |

Figure 59. Compatibility among CPE samples. "-" miscible, "+" immiscible.

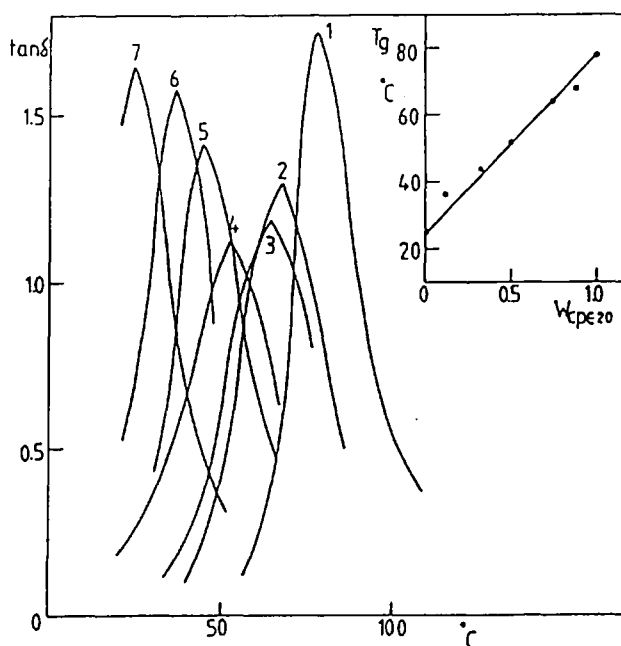


Figure 60. Dynamic mechanical results for CPE19/CPE20 blends. Weight percent CPE19: 1. 0, 2. 0.1227, 3. 0.2646, 4. 0.5025, 5. 0.7445, 6. 0.8911 and 7. 1.

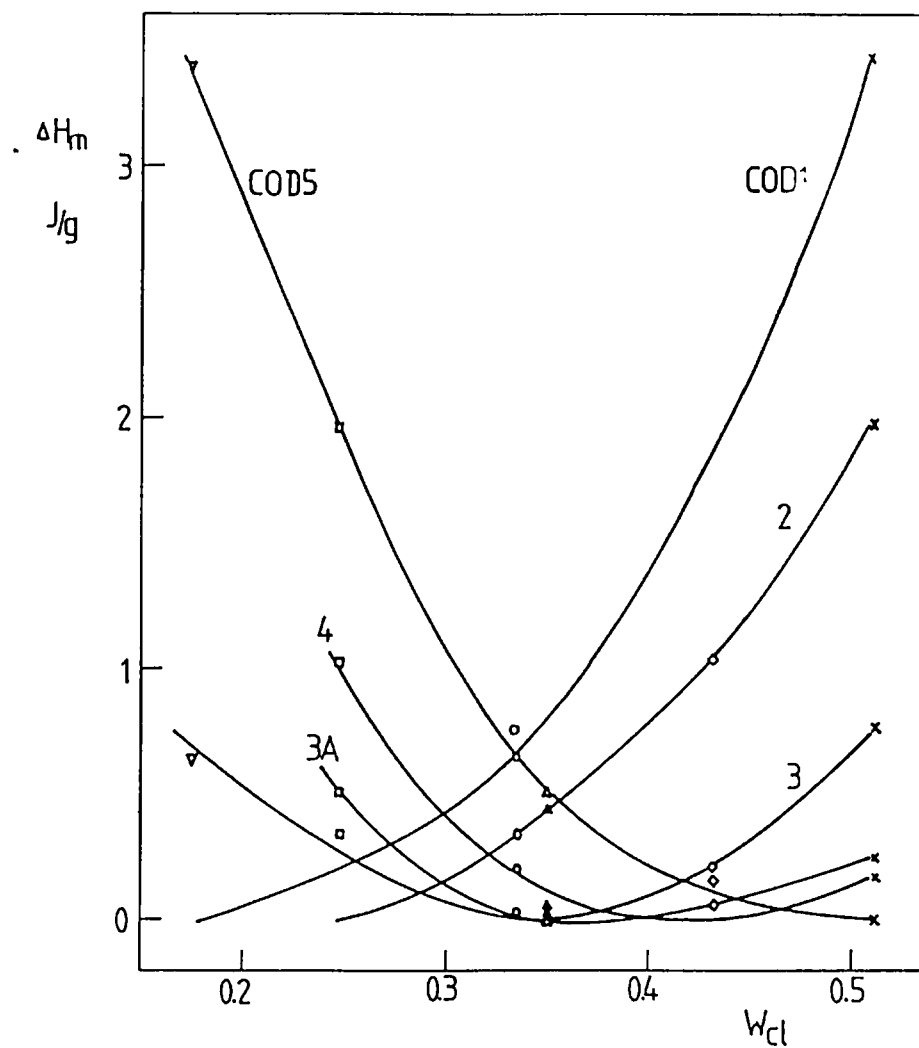


Figure 61. Heats of mixing between COD samples at weight fraction 0.5. One oligomer is denoted on the curve, the other is:  $\nabla$  COD1,  $\square$  COD2,  $\circ$  COD3,  $\Delta$  COD3A,  $\diamond$  COD4 and  $\times$  COD5.

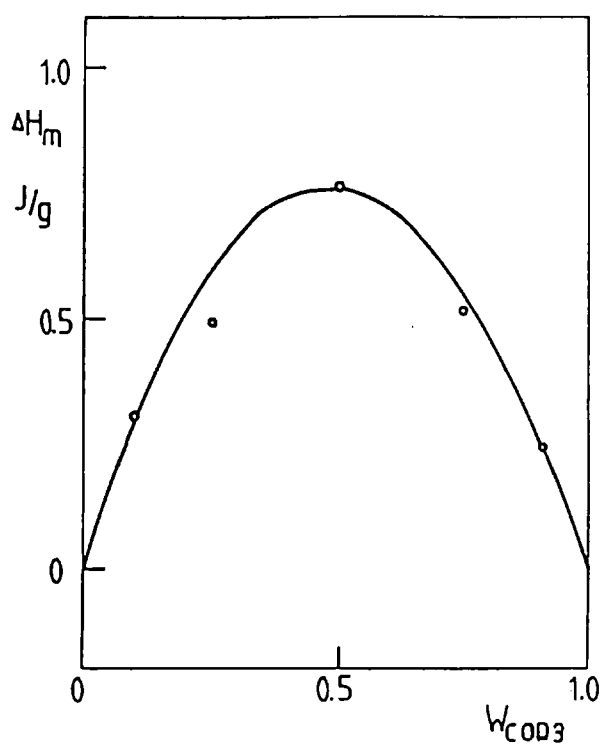


Figure 62. Heats of mixing of COD3/COD5 mixtures. The theoretical curve is calculated from Eq.80.

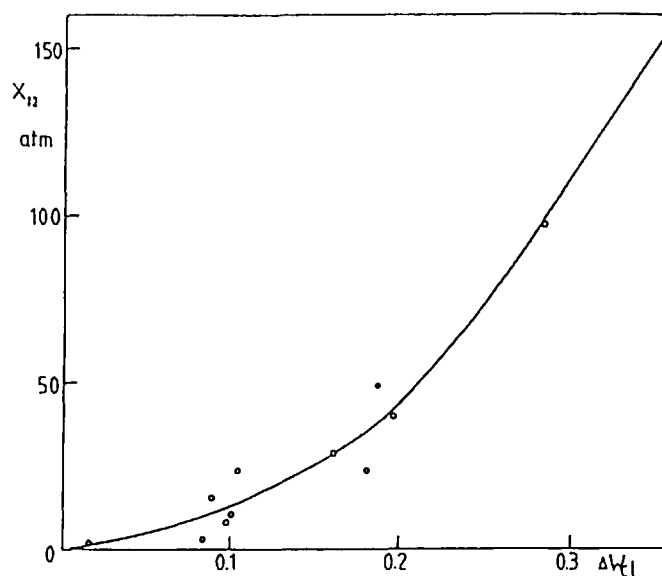


Figure 63. Interaction energy parameter  $X_{12}$  vs the difference in chlorine contents between the mixed oligomers.

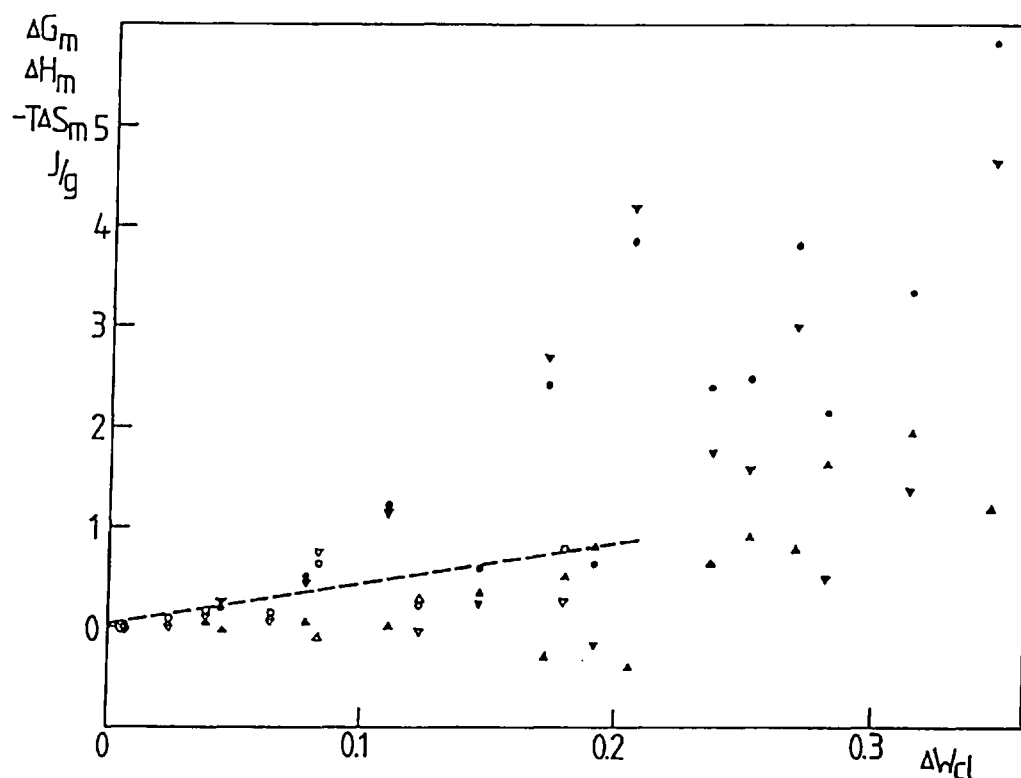


Figure 64.  $\Delta G_m$ ,  $\Delta H_m$  and  $-T\Delta S_m$  vs the difference in chlorine contents of the mixed CPE polymers.  $\circ \Delta G_m$ ,  $\Delta \Delta H_m$ ,  $\nabla -T\Delta S_m$ . Black points-immiscible, white points-miscible. From left to right: CPE/CPE 15/19, 3/18, 3/19, 12/8, 2/12, 15/1, 4/2, 3/1, 20/17, 4/12, 15/2, 20/19, 4/8, 3/2, 15/12, 20/1, 3/12, 15/8, 3/8 and 20/2.

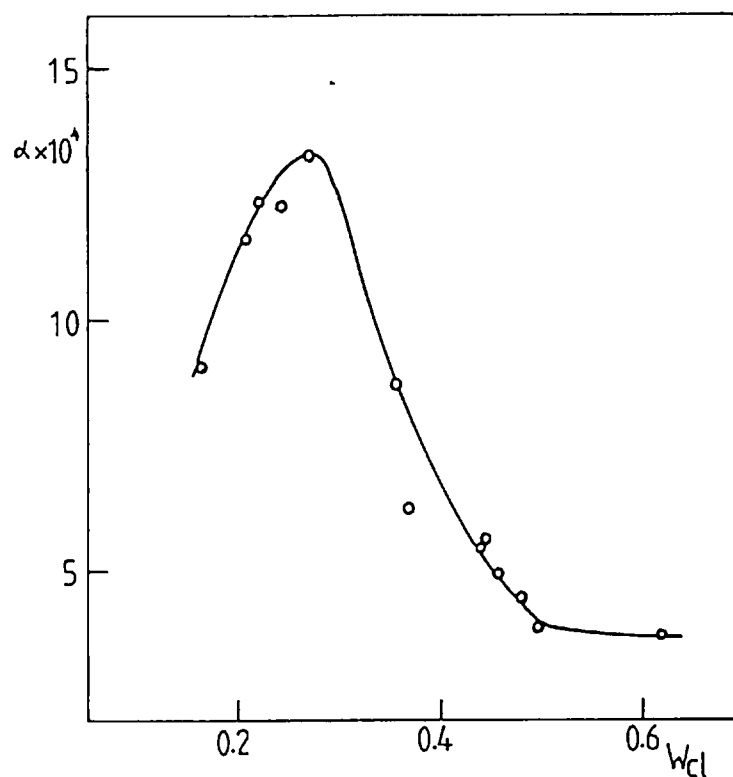


Figure 65. The thermal expansion coefficient  $\alpha$  as a function of chlorine content in CPE.

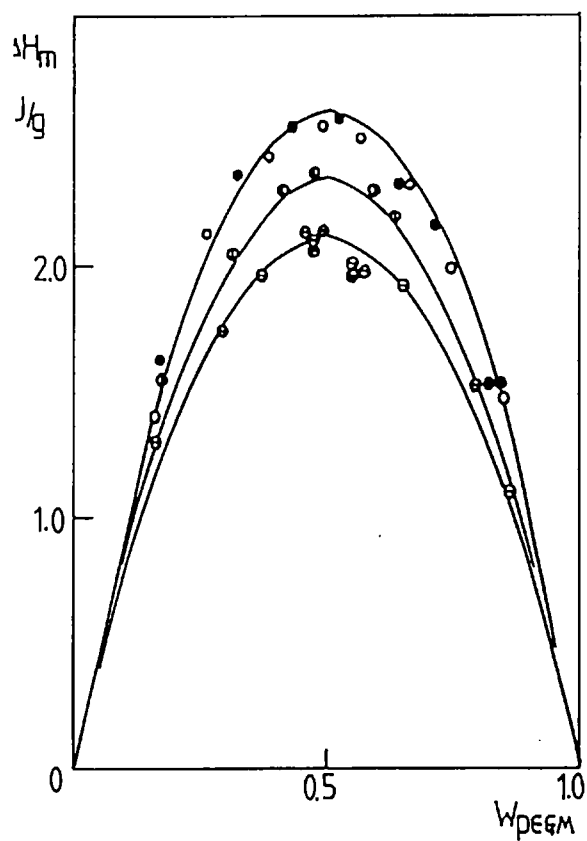


Figure 66. Heats of mixing of PEGM600 with PPGM at  $30.1^\circ\text{C}$ .  $\circ$  PPGM400,  $\bullet$  PPGM1000,  $\odot$  PPGM1500 and  $\oplus$  PPGM2000. The theoretical curves are calculated from Eq.80.

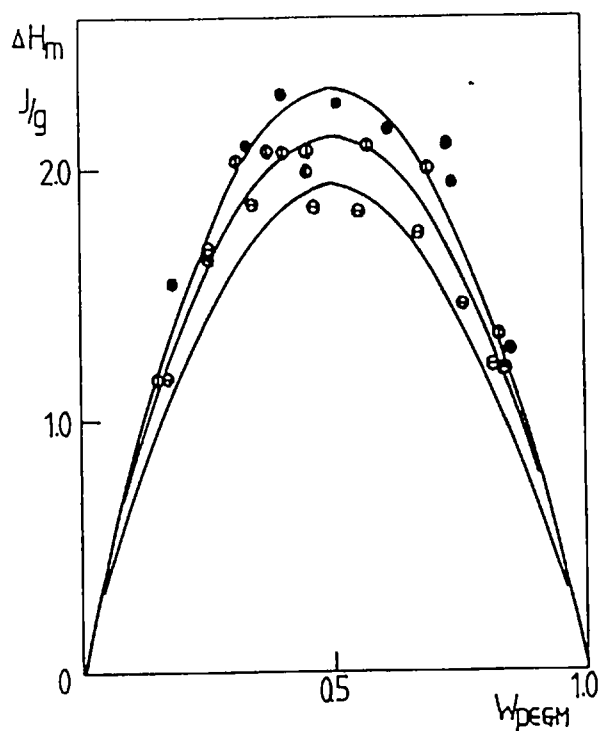


Figure 67. Heats of mixing of PEGM600 with PPGM at 50.1°C. Symbols seen in Figure 66. The theoretical curves are calculated from Eq.80.

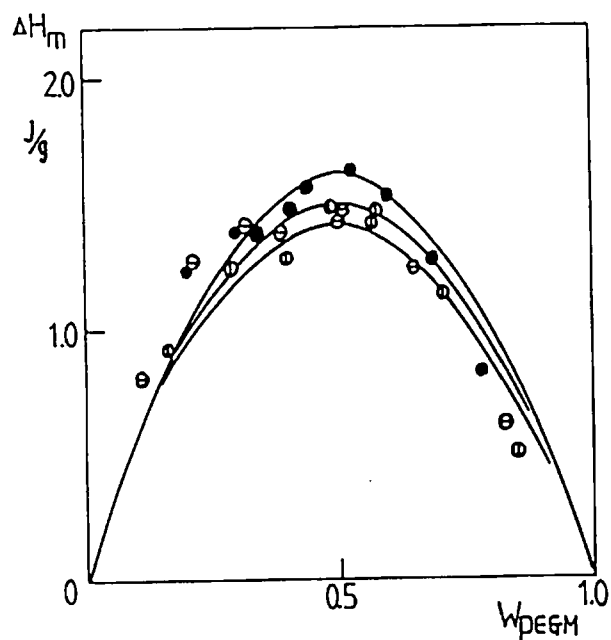


Figure 68. Heats of mixing of PEGM600 with PPGM at 70.1°C. Symbols seen in Figure 66. The theoretical curves are calculated from Eq.80.

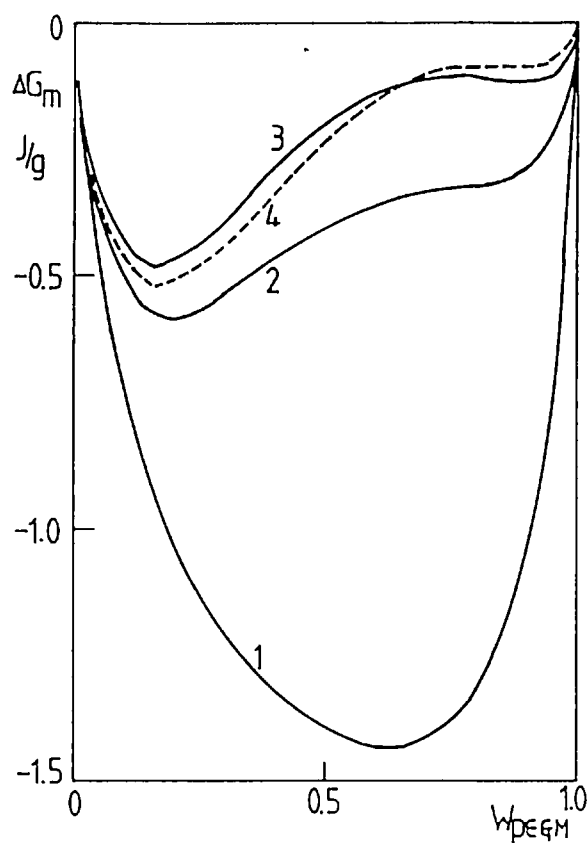


Figure 69. Free energies of mixing of PEGM600 with PPGM at 30.1°C calculated from Eq.82. 1. PPGM400, 2. PPGM1000, 3. PPGM1500 and 4. PPGM2000.

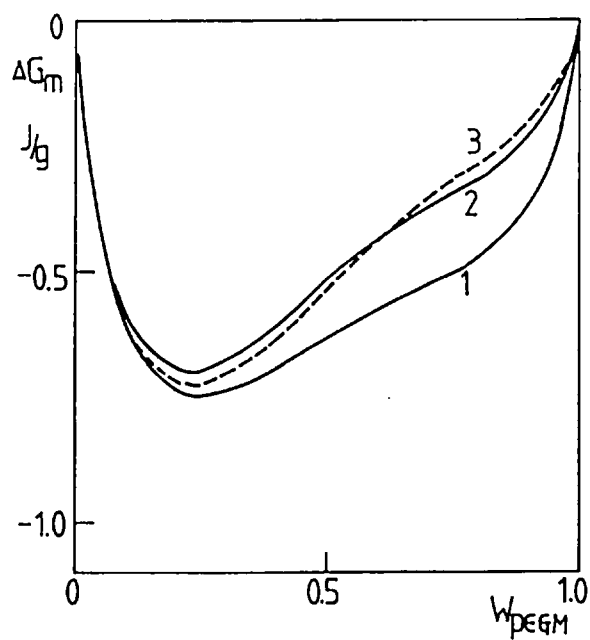


Figure 70. Free energies of mixing of PEGM600 with PPGM at 50.1°C calculated from Eq.82. 1. PPGM1000, 2. PPGM1500 and 3. PPGM2000.

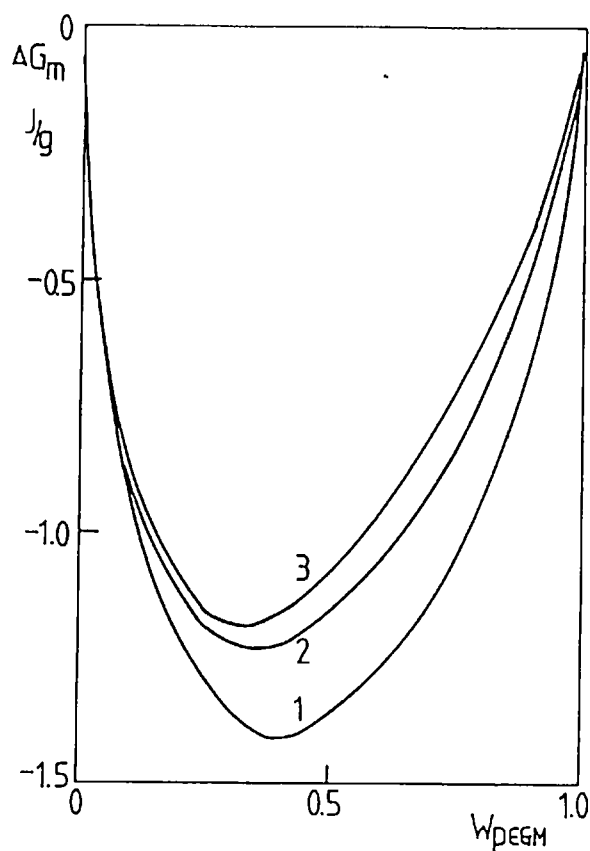


Figure 71. Free energies of mixing of PEGM600 with PPGM at 70.1°C calculated from Eq.82. 1. PPGM1000, 2. PPGM1500 and 3. PPGM2000.

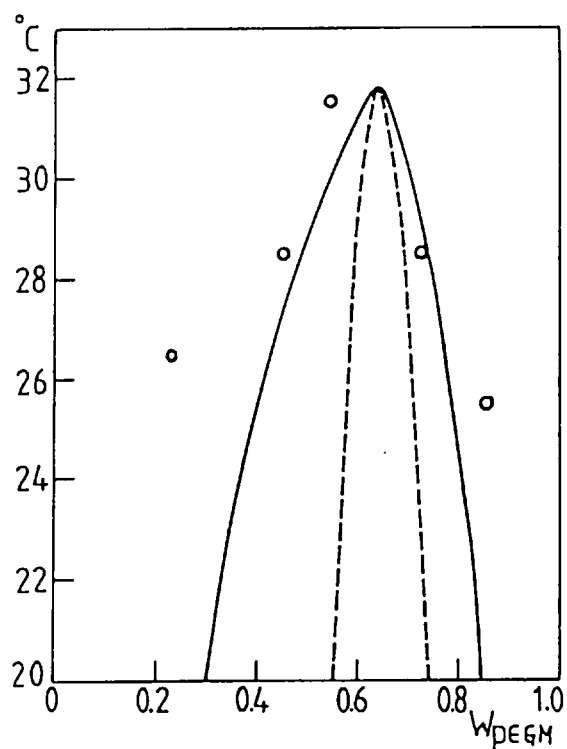


Figure 72. Phase boundary of PEGM600/PPGM2000 mixture. The binodal (—) and spinodal(---) are calculated from Eqs.11, 83 and 84.

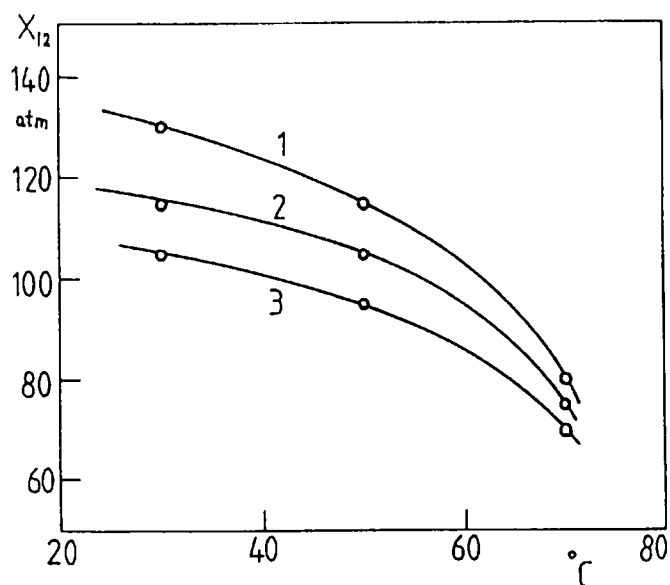


Figure 73.  $X_{12}$  as functions of molecular weight and temperature for 1. PEGM600/PPGM1000, 2. PEGM600/PPGM1500 and 3. PEGM600/PPGM2000 mixtures.

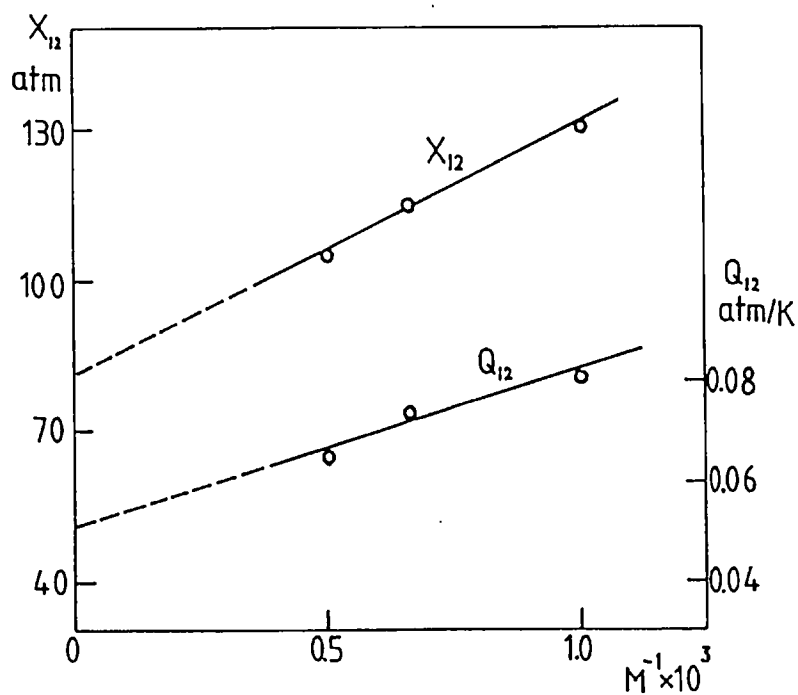


Figure 74. The molecular weight dependences of  $X_{12}$  and  $Q_{12}$  for PEGM600/PPGM system at 30.1°C.

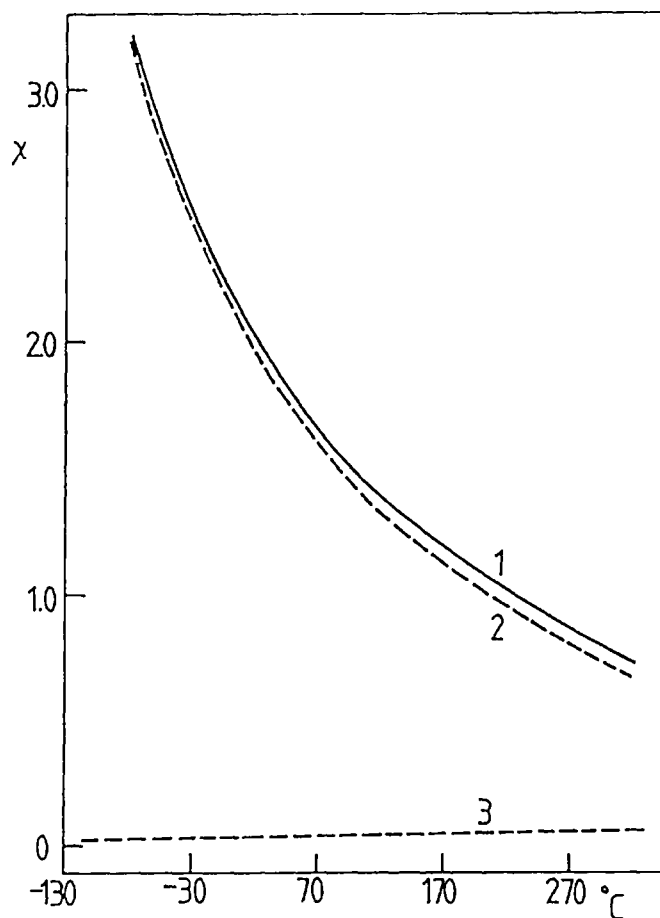


Figure 75.  $\chi$  decreases with increasing temperature for PEGM/PPGM system. 1.  $\chi$ , 2. the interaction contribution and 3. the equation of state contribution.

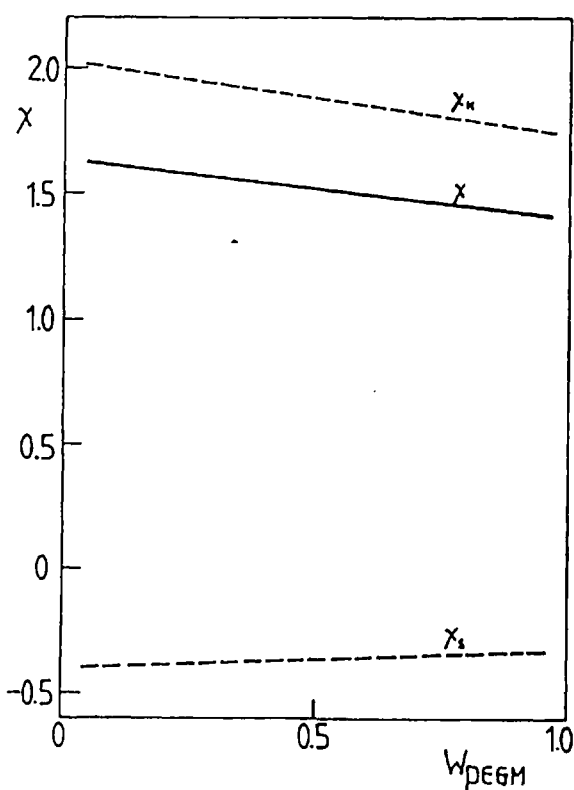


Figure 76.  $\chi$ ,  $\chi_h$ , and  $\chi_s$  for PEGM600/PPGM2000 mixture at 30.1 °C