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Phase Equilibria and Mutual Diffusion in Polymer—Polymer Systems with Chlorine-containing Components

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The experimental studies of the phase equilibria and mutual diffusion in polymer mixtures are examined. A thermodynamic analysis of the phase equilibria in the poly(vinyl chloride)-poly(methyl methacrylate) and chloropolyethylene-poly(methyl methacrylate) systems is presented within the framework of classical and new theories; the influence of the previous history of the specimens and of the chemical structure and stereoregularity of the polymer chains on the phase composition of the mixtures is demonstrated. The translational mobility of the macromolecules in the highly elastic and highly fluid states and its role in the formation of the phase structure of the mixtures and also the irreversible changes in the phase structure on thermal decomposition of chlorine-containing polymers are considered.
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I. INTRODUCTION

The interest in the problem of the compatibility of polymers is due to the need to create new polymeric materials and procedures including the blending of polymeric components. There exist nowadays extensive data whose analysis makes it possible to determine the principal trends in the research into polymer blends: the empirical search for materials with specified properties, the study of the thermodynamics of the blending of polymers, analysis of the colloidal-chemical properties of disperse systems, the study of the compatibility of various polymer pairs, and the search for new research techniques and new criteria of compatibility.

A single physicochemical approach to the analysis of polymer blends, which requires information about the equilibrium phase structure and kinetic characteristics of the systems, namely the diffusion coefficients, the decomposition constants of the components, etc., which would make it possible to predict the changes in the properties of polymer blends during their preparation, use, and storage, is particularly important. The neglect of this approach and methodological difficulties lead to the accumulation of contradictory information concerning the compatibility of polymers, which is frequently useless from the standpoint of practical employment. The difficulty of determining diffusion coefficients for polymer blends is associated with the low translational mobility of the macromolecules in a medium comprising similar molecules and the scope of the integral methods used nowadays for the determination of the compositions of the coexisting phases is extremely limited, because these methods require prolonged isothermal annealing in order to attain equilibrium throughout the bulk of the blend, which is not always attainable owing to the thermal decomposition of the components.

The present level of the development of local analytical methods with high resolution makes it possible to revise the methodology of the approach to studies of this kind, because in local contact regions the times required for the attainment of equilibrium have a significantly different scale. During the last five years, a local X-ray microanalytical method combined with scanning electron microscopy has been developed and used in the combined study of the parameters of mutual diffusion, thermal stability, and phase equilibria in polymer—polymer (P—P) systems. The pronounced "localisation" of the method ensures that the equilibrium isothermal annealing is carried out during sufficiently short periods and makes it possible to investigate any P—P systems before the onset of intense thermal decomposition and also to trace its influence on the phase structure of the blend. Such studies have been carried out in relation to systems with chlorine-containing components: poly(vinyl chloride) (PVC)—poly(methyl methacrylate) (PMMA), chloropolyethylene (CPE)—PMMA, and certain others; the phase diagrams and the diffusion constants have been obtained and the influence of the thermal decomposition of the components and the previous history of the blends on these parameters has been examined.

The aim of the present review is the analysis of the characteristic features of the phase equilibria and the mutual diffusion in polymer blends based on experimental results obtained with the aid of the local analytical methods for systems with chlorine-containing components and also the examination of the prospects which arise as a consequence of the application of these methods to the experimental solution of the problem of the compatibility of polymers.

II. THE STATE OF RESEARCH INTO PHASE EQUILIBRIA IN POLYMER—POLYMER SYSTEMS

A characteristic feature of polymer solutions is the slow attainment of equilibrium in phase separations. Even for polymer—low-molecular-weight solvent (P—S) systems, complete phase separation with formation of a single interface is not always attained;[1] this applies even more to P—P systems. Polymer blends are therefore frequently obtained

and used under conditions far from equilibrium. Nevertheless phase diagrams actually determine the structural-morphological characteristics of the structure of the materials and the trends in the variation of the properties during prolonged use. The analysis of the phase equilibrium is therefore a task of primary importance for the practical selection of the specified materials, for the determination of the conditions of their processing and storage, etc.

Until recently phase equilibria in P–P systems have been discussed solely in theoretical terms. Within the framework of the classical theories (the Hildebrand, Flory–Huggins, Tompa, and Scott theories), the miscibility is limited from above as regards molecular weight. Indeed the positive combinatorial entropy ($\Delta S_{comb} > 0$), which is related to the number of species per unit volume and which determines the entropy of mixing (ΔS_{mix}) in the Flory–Huggins–Scott lattice model, diminishes with increasing molecular weight (MW) of the components. Consequently the positive enthalpy of mixing (ΔH_{mix}), for which phase separation takes place, also diminishes with increasing MW. The incompatibility of polymeric components has been for a long time thought to be a general phenomenon precisely from these standpoints.[2,3] However, the Flory–Huggins–Scott theory is not universal; it does not take into account the concentration and temperature dependences of the interaction parameter χ_{12} and the non-combinatorial entropy contribution to ΔS_{mix} and accounts for the phase equilibrium only in those systems which are characterised by an upper critical solution temperature. This theory has received a number of improvement designed to take into account the volume changes occurring on mixing of the components and responsible for the discrepancy between the theory and the behaviour of solutions. Thus Flory divided χ_{12} into the enthalpy (χ_H) and entropy (χ_S) components. The determination of these quantities for polymer–solvent systems made it possible to explain many phenomena occurring in polymer solutions.[4] Evidently, the determination of these parameters also for P–P systems should be very important for the understanding of the thermodynamics of phase equilibria in polymer blends.

In modern theories constructed on the basis of Prigogine's general theory of corresponding states, the properties of mixtures are expressed in terms of the characteristic parameters of state of the pure components: pressure, volume, and temperature. This applies primarily to Flory's new theory, Patterson's theory, and the lattice theory of Sanchez and Lacombe. These theories take into account the influence of the structure and properties of the components on the properties of the mixture and make it possible to explain the phenomenon of both the upper and lower critical solution temperatures of polymers. Fig.1 illustrates the possible types of phase diagrams of P–P mixtures which obtain in calculations over narrow limits of variation of the parameters of the equation of state.[5]

On the basis of the new theory, Flory calculated the changes ΔH_{mix} and ΔS_{mix} on blending polyisobutylene and polymethylene in the liquid state and found that the free energy of mixing is positive ($\Delta G_{mix} > 0$) over the entire range of compositions, which indicates the incompatibility of the above polymers.[6] However, calculations of this kind involve certain difficulties owing to the large amount of labour involved in the experimental determination of the parameters of the equation of state. Only individual attempts at a general theoretical analysis of the phase equilibria of polymer mixtures on the basis of the theory have therefore been made so far. Thus McMaster[7] used modified equations of Flory's new theory to calculate the phase diagrams of P–P blends. We carried out calculations for two types of hypothetical systems. The first was selected with the maximum possible difference between the parameters of the equations of state of the components and the second was selected with identical parameters with the exception of the coefficient of thermal expansion α. The chain length, the degree of polydispersity, the pressure, and the coefficient of thermal expansion were varied alternately. For $X_{12} = Q_{12} = 0$, the phase equilibria are characterised by a lower critical solution temperature (LCST) (the values of X_{12} and Q_{12} characterise the difference between the interaction energies between identical and non-identical pairs of segments and the change in the entropy of interaction of neighbouring segments respectively). It has been shown that LCST decreases with increasing molecular weight and increases with increasing pressure; similar values of α for components 1 and 2 improve their compatibility. Whereas the presence of the LCST is characteristic in cases where $X_{12} \leqslant 0$, when $X_{12} > 0$ an upper critical solution temperature (UCST) appears together with the LCST. For high positive values of X_{12}, the diagrams assume an hour-glass form. The fulfilment of the condition $Q_{12} \neq 0$ also leads to the presence of the UCST. It is striking that the UCST has been observed over a very narrow range of values of X_{12} (from 0.005 to 0.001). The conclusion, which had a major influence on the course of further studies, namely that an equilibrium with a LCST is typical for P–P systems, was in fact reached on this basis.

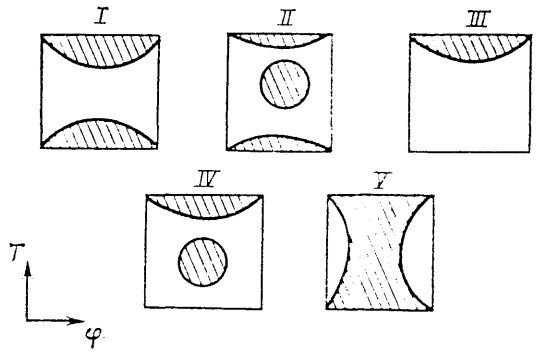


Figure 1. Schematic representation of "temperature–composition" (T–ϕ) phase diagrams predicted by the theory of the equation of state for P–P systems.[5]

However, it is noteworthy that the task is at present experimental rather than theoretical: the aim is to discover which values of the thermodynamic parameters are characteristic of P–P systems and which type of phase equilibrium is most typical for such systems. In calculations on hypothetical systems, the universality of the theory makes it possible to obtain any of the diagrams illustrated in Fig.1 subject to certain assumptions. Thus the hypothesis that $X_{12} \leqslant 0$ and $Q_{12} = 0$ (McMaster[7]) rules out the UCST version and leads to diagrams of type III (Fig.1).

The temperature dependence of X_{12} has been analysed[8] within the framework of the above theory. The following expression has been obtained:

$$\frac{\chi_{12}}{M_1 V_1^*} = \frac{P_1^*}{RT}\left[\underbrace{\frac{\bar{V}^{1/3}}{(\bar{V}^{1/3}-1)}\left(\frac{X_{12}}{P_1^*}\right)}_{A} + \underbrace{\frac{\bar{V}^{1/3}}{2\left(4/_3 - \bar{V}_1^{1/3}\right)}\cdot\tau^2}_{B}\right], \qquad (1)$$

where the quantities marked by an asterisk are characteristic parameters and those marked by a bar are reduced parameters; $\bar{V} = V/V^*$, $\bar{T} = T/T^*$, $\bar{P} = P/P^*$, $\tau = 1 - T^*/T_2^*$, and M_1 is the molecular weight of the segment. The reduced volume can be expressed in terms of the coefficient of thermal expansion:

$$\bar{V}_1^{1/3} = 1 + \frac{\alpha T}{3(1+\alpha T)}. \qquad (2)$$

Eqn.(1) shows that the χ_{12} comprise two contributions: the contribution of the term describing the interaction of a pair of segments (the first term A) and the contribution of the term describing the change in free volume on mixing the segments (the second term B). It follows from Eqns.(1) and (2) that, when $\alpha \to 0$, then $\bar{V}_1^{1/3} \to 1$ and $A \to \infty$; on the other hand, when $\alpha \to \infty$, then $\bar{V}_1^{1/3} \to 4/3$ and $B \to \infty$. The values of $\bar{V}_1^{1/3}$ quoted[8] for polymers and low-molecular-weight liquids and the results of the calculations show that the role of the free volume in the miscibility of polymers is significantly smaller than in P–S systems and smaller than the values obtained in McMaster's calculations. It has been shown that the appearance of a LCST higher than the UCST in P–P systems is theoretically impossible owing to the free volume effects, since τ should then increase to values unacceptable for the thermal stability of P–P systems.

Flory's new theory and its modifications provide criteria for the search for and the determination of compatible polymer–polymer systems. It is assumed that the conditions under which we have simultaneously $T_1^* > T_2^*$ and $P_1^* > P_2^*$ are the most favourable for the compatibility of polymers and the values of T_1^* and T_2^* themselves should not differ by more than 200 K. (Subscripts 1 and 2 correspond to the individual components.) One of the most evident criteria of Flory's new theory is the parameter X_{12}. A negative value of X_{12} implies that the polymeric components are characterised by the so-called specific interaction and the phase equilibrium has a LCST. However, it has been noted[8,9] that the case where $X_{12} < 0$ (i.e. $\Delta H_{mix} < 0$) can be abolished when $Q_{12} < 0$ ($\Delta S_{mix} < 0$), as has been shown for certain polymer–solvent systems;[4] this creates difficulties in the prediction of the types of equilibrium for P–P systems.

Thus, despite the fact that the theories mentioned are universal and provide criteria for the prediction of the compatibility of the components of the blend, they have still not been adequately analysed and so far have been interpreted in different ways. In addition, a much wider comparison between the conclusions reached in terms of different theories and experiment is necessary in order to reach a conclusion concerning the superiority of a particular theory in describing the behaviour of polymer blends and to ensure the possibility of predicting the phase equilibria by means of analytical methods.

Topological analysis based on comparison of the positions of the phase transition regions has been recently applied to P–P blends with alternating molecular weights of the components (block-copolymers).[10] This analysis provides an estimate of the general type of phase diagrams but does not determine the quantitative miscibilities of the components, which can only be obtained experimentally.

Any properties characterising the homogeneity of the system for different compositions (the intensity of the low-angle, optical, X-ray, electronic, or neutron scattering and the glass point) or the thermodynamic characteristics (free energy of mixing, enthalpy of mixing, the solubility parameter, the interaction parameter, and the specific heat) are used as experimental criteria of compatibility. As a rule, there is no agreement between the limits of compatibility found from these criteria within a single system; this is illustrated by Table 1.

A similar discrepancy can be observed also on comparing the experimental data for the compatibilities of many other pairs of polymers.[2,16] Attention has been frequently drawn to be discrepancies between the experimental results and specific causes of incompatibility have been discussed in the literature.[12,15,17] From our point of view, this situation can be accounted for by the limited nature of the criteria employed and also of the methods of their determination. Thus the compatibility data obtained by direct measurements of any parameter characterising the homogeneity of the system are limited and uncertain as regards temperature. In all probability, the information obtained refers to the temperature of the mixing of the components. The thermodynamic characteristics measured in binary systems using a third component, namely the solvent (for example, ΔG_{mix} determined by the method of Hess's cycle or χ_{12} obtained by the method of reverse gas chromatography or neutron scattering[18–20]), are also functions of the initial state of the system and cannot serve as criteria of the existence of a true equilibrium.

Table 1. The compatibility of PVC and PMMA.

Research method	Conditions of contact	$10^{-4}M_{PVC}$	$10^{-4}M_{PMMA}$	ω_1''	ω_2'	Refs.
I	Welding (433–443 K)	—	—	*	*	[11]
I	From solution in THF	8	10.7	0.02	0.06	[12, 13]
I	Ditto	23	49.3	0.01	0.05	[12, 13]
I	From melt	8	10.7	0.05	0.55	[12, 13]
I	Polymerisation of MMA in PVC	—	—	0.05	0.50	[12, 13]
II	From solution in THF	10.7	9.9	0.30	0.20	[14]
II	From melt (423–433 K)	10.7	9.9	0.20	0.20	[14]
III	From solution in DMF	5.5	8.0	—	0.60	[15]
IV	From solution in 2-butanone	5.5	8.0	**	**	[94]

Notation. Methods: I) electron microscopy; II) thermodynamic method (method based on Hess's cycle); III) determination of the glass point T_g by differential scanning calorimetry; IV) determination of the phase separation from turbidity points; ω_1'' and ω_2'—weight fractions of PVC in PMMA and of PMMA in PVC respectively determined as compatibility limits.

*Incompatible.

**Fully compatible.

An experimental criterion characterising the miscibility of the components may be the phase composition of the system determined over a wide temperature range under conditions close to equilibrium. The determination of the true phase diagrams for P–P systems is a complex task. Classical methods,[21] involving homogenisation and prolonged thermal annealing, are not always suitable for this purpose owing to the high viscosity and low thermal stability of polymers. In order to obviate these difficulties, the mixtures are prepared as a rule in an effective solvent with its subsequent removal. However, it has been shown[22] that in this case the limits of the miscibility depend on the "quality" of the solvent. They characterise the phase equilibrium in a three-component P–P–solvent system established during the formation of the mixture and corresponds to a non-equilibrium state of the binary system in the absence of a solvent. Fig.2 illustrates the variation of ω_1'' for the PVC–PMMA system obtained in "good" (dichloroethane, $\chi_{PVC} = 0.428$) and "poor" (benzene, $\chi_{PVC} = 0.77$) solvents with isothermal annealing. Evidently the equilibrium values of ω_1'' attained during annealing are higher than for the system obtained from the "poor" solvent and lower than the values found using the "good" solvent.

The accumulation of a large amount of contradictory information concerning the miscibility of polymers is probably in fact to a large extent associated with the previous history of the specimens. Unfortunately, the accumulation of contradictory information has not ceased even when the method of turbidity points, traditionally used to study P–S and polymer–oligomer (P–O) systems, was used to construct phase diagrams.[1]

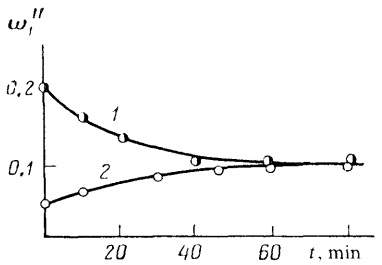


Figure 2. Variation of the limit of the compatibility of PVC and PMMA during annealing at 413 K for blends prepared from solution in DCE (curve *1*) and in benzene (curve *2*).[44]

Table 2. The phase equilibria in P_1–P_2 systems determined from turbidity points.

P_1	P_2	$10^{-4}\cdot M_1$	$10^{-4}\cdot M_2$	T_c, K	Refs.
PS	PMVE	1—20	5.1	LCST, 393-473	[23, 24]
PS	PMVE	—	—	LCST, 353; UCST, 303	[25]
PC	P-ε-CL	2.9	4.0	LCST, 533-546	[26]
PSAN (AN 28%)	PMMA	22.3	9.2	LCST, 233	[27]
PVC	PEVA (VA 63%)	—	12.5	LCST, 460-470	[28]
PVF	PMA	19.7	—	LCST, 563	[27, 29]
PVF	PEA	19.7	—	LCST, 333	[27, 29]
PVF	PMVK	19.7	—	LCST, 473	[29]
PVF	PEMA	19.7	76.2	LCST, 483	[27, 29]
PVF	PMMA	19.7	—	LCST, 623	[29]
PPO	copolymer*	3.5	14.0—73.0	LCST, 553-573	[30]
PVC	CPE	—	—	LCST, 393	[31]
CPE (27% Cl)	PMMA	10.8	12.2—72.8	UCST, 330; LCST, 353	[32]
CPE (47.8% Cl)	PMMA	12	12.2—72.8	**	[33]
CPE (36.9-51.6% Cl) Cl)	PMMA	19.8	12.2—72.8	LCST, 373-423	[33]
PE	PIB	2.9	188	LCST, 363	[34]
PMMA	ABS	10	—	LCST, 410	[34]

Notation: PC = polycarbonate, P-ε-CL = poly-ε-caprolactone, PSAN = styrene–acrylonitrile copolymer, PEVA = poly(ethylenevinyl acetate), PVF = poly(vinylidene fluoride), PMA = poly(methyl acrylate), PEA = poly(ethyl acrylate), PMVK = poly(methyl vinyl ketone), PEMA = poly(ethyl methacrylate), PPO = poly(phenylene oxide), and ABS = acrylonitrile–butadiene–styrene copolymer.

*o-Chlorostyrene-*p*-chlorostyrene copolymer.

**"Hour glass".

Analysis of the data obtained by the method of turbidity points in thin films (Table 2) shows that all the phase diagrams have a LCST and that it is as a rule in the region of temperatures traditionally considered as "non-working" temperatures for the corresponding polymer compositions. It is also noteworthy that almost always [with the exception of the polystyrene–poly(methyl vinyl ether) (PS–PMVE) system] no thermodynamic analysis of the phase diagrams and their comparison with known theoretical and experimental data can be found in the literature. For example, the polyisobutylene–polyethylene system (PIB–PE) has a LCST above the liquidus curve according to Tyukova et al.,[34] while according to Flory et al.[6] the system is fully incompatible over the entire range of compositions at temperatures above the melting point T_m. Furthermore, the character of the phase equilibria and the range of critical solution temperatures T_c frequently conflict with the available experimental facts.

As an example, we may quote the PS–PMVE system, since it has been studied most thoroughly: the variation of the LCST with the molecular weight has been demonstrated,[35] a study has been made of the mechanism of the phase separation, and the diffusion coefficient has been found.[24] The values of χ_{12} have been measured at two temperatures; the values obtained suggest a U-shape relation between χ_{12} and T. On this basis, it has been suggested[24] that two critical solution temperatures, namely LCST and UCST, exist in the system. Later two critical solution temperatures T_c were found experimentally for this system:[25] the UCST at 303 K and the LCST at 353 K [sic.]. The intensity of the scattering of a laser beam on passing through the PS–PMVE–benzene system has been measured for constant compositions of the mixture and a variable content of the solvent with subsequent extrapolation to zero content of the solvent.

However, it is noteworthy that extrapolation of the miscibilities of a P–P–S system to the values for the P–P system is impossible not only owing to the error associated with the low concentration limits of the dissolution of high-molecular-weight components in low-molecular-weight solvents but also because of fundamental considerations, since such extrapolation presupposes an additive relation between the miscibilities of the binary and ternary systems, which conflicts with the theories of polymer solutions. Furthermore, additional limitations as regards temperature (apart from the glass points T_g and decomposition temperatures T_{decomp} of the polymers), associated with the crystallisation temperature T_{cryst} and boiling point T_b of the solvent, apply to this method. The identity of the LCST and the T_b of benzene is striking in this connection.[25]

We may note that other investigators[36] showed by the method involving the determination of the velocity of sound and by electron microscopy that the PS–PMVE system, also obtained from solution in toluene, is microheterogeneous when the PMVE content is between 5 and 70% in the range from the normal temperature to 413 K. Evidently these results conflict with the full compatibility of the components, which should obtain in the temperature range investigated in conformity with the phase diagram obtained in previous studies.[23-25] Thus, the final elucidation of the phase equilibrium in this system requires allowance for all the known experimental data.

Such discrepancies throw doubt on the validity of the application of the method of turbidity points particularly when the authors failed to observe reversible turbidity (in the PSAN–PMMA system)[27] or when T_c is very close to T_{decomp} of the components.[29,31-33] The authors of a review[17] draw attention to the necessity to take into account the influence of various chemical processes between the components of mixtures on their compatibility. However, the same investigators failed to attempt in their own study[27] a serious analysis of the system investigated precisely from these standpoints assuming that the weight loss up to 22% in the PVF–PEMA system which they observed does not affect the character of the phase equilibria.

Mixtures with chlorine-containing components, such as PVC and CPE, capable of undergoing dehydrochlorination even at $T = T_g$,[90] which significantly alters the chemical structure and hence also their miscibility with other polymers, merit especial attention from this standpoint. Thus, according to some data,[31] the PVC–CPE (42% Cl) mixtures

are characterised by an equilibrium with a LCST at 393 K, while according to other data[37] these mixtures are compatible to only a limited extent at temperatures below 393 K and the degree of chlorination of CPE must not be less than 48%. For a 30% chlorine content in CPE, the polymer is incompatible with PVC, PMMA, and certain other polymers even on mixing in a common solvent.[38] A phase diagram having both a UCST and a LCST has been published[32] for the CPE (27% Cl)–PMMA system, while an "hour glass" diagram has been obtained for the CPE (47.8% Cl)–PMMA system. In another study[33] the same workers obtained a phase diagram with a LCST for the CPE (49.8% Cl)–PMMA system (Table 2). Such a wide variety of types of phase equilibria within the limits of virtually a single system cannot be explained from a purely thermodynamic point of view if one disregards the chemical reactions occurring during the annealing of the system and also other kinetic factors which include mass-exchange processes and the thermal stability of the polymers. All these factors make the problem of the simultaneous study of phase equilibria and the translational mobility and thermal stability of the components one of the most urgent and general in the study of the compatibility of P–P systems.

Definite advances have been achieved in this field with the aid of a qualitatively different approach to the methodology of the study of P–P systems, namely in the investigation of the local contact regions of polymer components using highly resolving diffusion methods. The principle of these methods is based on the study of the distribution of the concentrations ω in the direction of the diffusion flux x in a local region after diffusional annealing of the specimens in contact over a period t. Such methods include, for example, the method of scanning infrared spectroscopy with a spatial resolution of 100 μm,[39] an interference micromethod with a resolution of ~10 μm,[40] and the electron probe (X-ray spectroscopic) microanalysis whose spatial resolution is ~1 μm.[40–42] There exists a definite correspondence between the form of the concentration profiles and the phase diagrams (Fig.3), which makes it possible to obtain, simultaneously with the diffusion constants, quantitative information about the compositions of the coexisting phases over a wide temperature range.[43] The application of the method of X-ray microanalysis, based on the recording of the characteristic X-ray emission of the element analysed, makes it possible to follow quantitatively, apart from the determination of the above information, the variation of the chemical structure of the components of the systems investigated directly on the basis of the change of the intensity of the analytical line after isothermal annealing.[44]

Various oligomeric and polymer–oligomer systems have now been investigated with the aid of the interference micromethod. Phase diagrams and mutual diffusion coefficients for mixtures have been obtained: elastomers–oligoester acrylates and oligomethylenes,[45,46] PVC–oligoester acrylates,[47] elastomers–epoxy-ologiomers, etc.[48] The influence of the end group, the chain length, and the nature of the components on the phase equilibria and mutual diffusion in mixtures has been studied. The advantages of the local methods, whereby one can determine equilibria which are not established throughout the bulk of the specimen but only at the contact boundary, are particularly evident and it is necessary to investigate more complex P–P systems or rapid processes. Thus in the study of epoxide–rubber hardening systems[49] only the application of the interference micromethod made it possible to follow the evolution of the phase states determined by the varying degree of departure of the system from the critical solution temperatures during the continuous variation of the chemical nature of the epoxide component during the hardening process, to identify the diffusion-controlled stages in the formation of heterogeneous polymer compositions, and to determine the process conditions ensuring a specific regulation of the physicomechanical properties of the material.

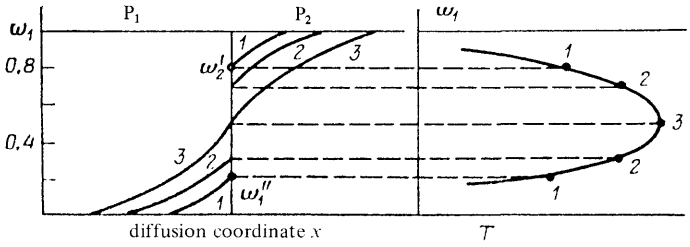


Figure 3. Schematic illustration of the transition from diffusion profiles in terms of ω–x plots to the ω–T phase diagram for the P_1–P_2 system. The numerals opposite the curves (*1* → *3*) correspond to an increase in the annealing temperature (case with a UCST).[43]

The X-ray microanalytical method, whose spatial resolution makes it possible to retain the time scale of the diffusional annealing in the region of minutes, is used in the study of blends of polymers with high molecular weights. This method, the apparatus for which is combined with that for scanning electron microscopy, has been developed in greatest detail and has been used in the study of mutual diffusion and phase equilibria in polymer mixtures with chlorine- and fluorine-containing components, such as PVC–PMMA, PVF–PMMA, CPE–PMMA, PVC–P-ε-CL, etc.[22,44,50–53] The mutual diffusion coefficients and phase diagrams have been obtained for the PVC–PMMA system and the influence of the molecular weight, the chemical stability, and the structure of one of the components as well as the previous history of the system on the phase composition of the mixture has been investigated.[22,44,50,54–56] These experimental data provide the necessary and sufficient information for the consideration of the processes occurring in the system from the instant of the formation of the real mixtures up to the establishment in the latter of the phase structure corresponding in terms of composition to the equilibrium phase diagram, which can be responsible for the discrepancies between the existing experimental results mentioned above. Certain characteristic features of the phase equilibria and of the diffusion and other properties characterising P–P mixtures will be considered below on the basis of the system indicated.

III. PHASE EQUILIBRIA IN THE POLY(VINYL CHLORIDE)–POLY(METHYL METHACRYLATE) SYSTEM

The phase diagrams for mixtures of PVC and PMMA with different molecular weights have been obtained in the temperature range 400–470 K (Fig.4a).[56] The low-temperature branches of the binodals cannot be obtained by this and other methods owing to the loss of translational mobility by the macromolecules in the region of the T_g, while the high-temperature branches (at $T \gtrsim 470$ K) cannot be obtained owing to the intense thermal decomposition of PVC. Fig.4 shows that the regions of the homogeneous mixing expand with increase of temperature, which is characteristic of systems with a UCST; this effect is greater the lower the molecular weight of PMMA.

The critical concentrations (Table 3) of mixtures of PVC and PMMA, corresponding to the mixing of components at the critical points, are close to 0.5 over the entire range of experimental molecular weight ratios M_{PMMA}/M_{PVC}, from 0.45 to 5.12, in contrast to a solution of PVC in the PMMA monomer whose phase diagram is appreciably asymmetric (Fig. 4*b*) and the critical composition corresponds to a comparatively low PVC concentration ($\phi_c = 0.12$). The experimental values of ϕ_c in the PVC–PMMA system, found from the point of intersection of the rectilinear diameter and the composition axes, are compared in Table 3 with the values calculated on the basis of the Flory–Huggins–Scott theory from the equation $\phi_c = n_2^{1/2}/(n_1^{1/2} + n_2^{1/2})$, where n_1 and n_2 are the degrees of polymerisation of the components. Only a qualitative agreement is observed between the experimental and calculated quantities, particularly for molecular weight ratios differing appreciably from unity.

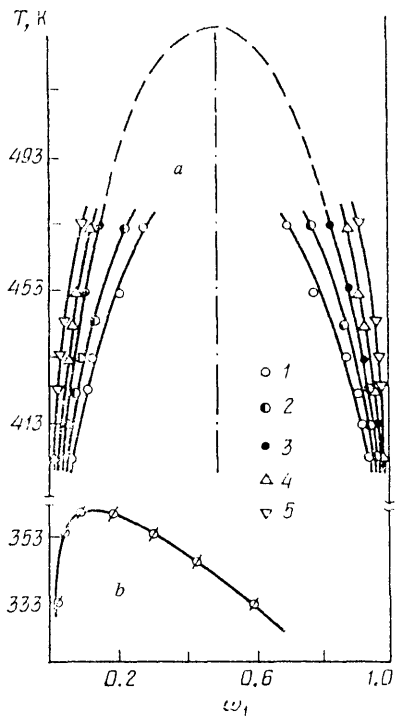


Figure 4. Phase diagrams for the PVC–PMMA (*a*) and PVC–MMA (*b*) systems; $M_{PVC} = 1.4 \times 10^5$; $10^{-5}M_{PMMA}$: 1) 0.64; 2) 1.12; 3) 1.87; 4) 3.02; 5) 7.26.[56]

Table 3. The critical parameters of the PVC–PMMA system.[56–58]

M_{PMMA}/M_{PVC}	φ_c (expt)	φ_c (calc.)	UCST, K
0.45	0.49	0.34	538
0.80	0.50	0.45	522
1.33	0.50	0.51	533
2.15	0.51	0.58	545
5.18	0.51	0.64	556

The influence of the molecular weight on the magnitude and position of T_c has been studied also in the PS–PMVE system.[35] However, it is difficult to reach a conclusion concerning the form of the binodal on the basis of these data, because the temperature range in which they were obtained did not exceed 20 K with the exception of one instance where it amounted to 70 K and it was evident that the binodals are disposed symmetrically; this corresponded to the ratio $M_1/M_2 \approx 1$.

On plotting $\omega_1'(\omega_1'')$–M or $\omega_1'(\omega_1'')$–$1/M$ phase diagrams for isothermal conditions, it is possible to find quantitative relations between the molecular weight and the phase composition of the solution.[45,57] Linear relations have been observed for the PVC–PMMA system: $\omega_1' = \omega_{1,\infty}' + K'M^{-1}$ and $\omega_1'' = \omega_{1,\infty}'' - K''M^{-1}$ (here K' and K'' are empirical constants and $\omega_{1,\infty}'$ and $\omega_{1,\infty}''$ are the solubilities of the components when $M_{PMMA} \to \infty$). Approximate estimates obtained by extrapolating the ω_1'–$1/M$ straight lines to regions of high and low molecular weights showed that an increase of temperature from 433 to 473 K is accompanied by a change of $\omega_{1,\infty}$ from 0.01 to 0.06 in terms of weight fractions of PVC; under these conditions, $(M_{PMMA})_c = 16\,000$ at 433 K, 26 000 at 453 K, and 35 000 at 473 K. Such analysis yields preliminary quantitative information about the miscibility when the molecular weight of one of the components is varied, which is important for the practical employment of the blend.

Theoretical analysis of the experimental binodals is of special interest for the understanding of the processes occurring on blending polymers. Such analysis for the PVC–PMMA system has been carried out within the framework of the classical Flory–Huggins–Scott theory, the improved Flory theory, and the new Flory–Patterson theory.[58] The interaction parameters χ_{12} (Table 4) were calculated from the equation of the binodal based on the Flory–Huggins–Scott theory:

$$\ln \varphi_1' + \left(1 - \frac{n_1}{n_2}\right)\varphi_2' + n_1\chi_{12}(\varphi_2')^2 = \ln \varphi_1'' + \left(1 - \frac{n_1}{n_2}\right)\varphi_2'' + n_1\chi_{12}(\varphi_2'')^2.$$

Table 4. The parameters χ_{12} and $(\chi_{12})_c$ for the PVC–PMMA system as a function of M_{PMMA}.[56,58]

$10^{-5}M_{PMMA}$	$10^3\chi_{12}$				$10^3(\chi_{12})_c$
	413 K	433 K	453 K	473 K	
0.640	2.430	2.280	2.125	2.080	1.640
1.120	1.877	1.714	1.557	1.435	1.130
1.870	1.777	1.520	1.359	1.196	0.824
3.020	1.658	1.381	1.216	1.063	0.645
7.269	1.660	1.274	1.130	0.951	0.434

Account was taken of the experimental values of ϕ_1 and ϕ_2 in the experimental temperature and molecular weight ranges; the $(\chi_{12})_c$ were obtained from the equation

$$(\chi_{12})_c = \frac{1}{2}\left(\frac{1}{n_1^{1/2}} + \frac{1}{n_2^{1/2}}\right)^2 .$$

It is striking that the χ_{12} have low positive values which vary consistently as T and the molecular weight are altered. The relations between the χ_{12} and $1/T$ are linear in the experimental temperature range. Here χ_{12} is almost equal to χ_{21}, which indicates the absence of a concentration dependence of this parameter and is reasonable for the observed symmetry of the binodals. The dependence of χ_{12} on $1/T$

has been used[46,47] for the thermodynamic analysis of P–O blends: the determination of the consolute temperatures, the enthalpy and entropy components of χ_{12}, etc. The linearity of this relation observed for the PVC–PMMA system and the deviation of the constant from the zero value permitted an analogous analysis for the P–P system. The UCST (Table 3), the high-temperature branches of the binodal (see the dashed line in Fig.4*a*), χ_H, and χ_S were determined (Table 5).

Table 5. The values of χ_H and χ_S for the PVC–PMMA system.[56,58]

$10^{-5}M_{PMMA}$	$10^3\chi_H$				10 χ_S	$10^3(\chi_H)_c^*$
	413 K	433 K	453 K	473 K		
0.640	3.25	3.20	3.05	3.00	−1.92	2.56
1.120	3.54	3.41	3.22	3.00	−1.67	2.80
1.872	3.82	3.57	3.39	3.24	−2.05	2.80
4.020	3.90	3.62	3.45	3.40	−2.24	2.89
7.269	4.11	3.72	3.58	3.40	−2.45	2.88

*$(\chi_H)_c = \chi_c - \chi_S$.

Such formal analysis permits the estimation of the contribution of each parameter to the miscibility of the polymers. It follows from Table 5 that χ_H is a decreasing function of temperature, which is the reason for the observed decrease of χ_{12} with increase of T. As the molecular weight rises, χ_H also increases and to a lesser extent at higher temperatures T. At the critical point the quantity $(\chi_H)_c$ is almost constant and independent of the molecular weight except for the system having the lowest molecular weight. Evidently this is associated with the independence of the miscibility parameters δ of the molecular weight in the experimental range of values of M_{PMMA} from 1.12×10^4 to 7.26×10^5. On the other hand, χ_S has negative values, which increase in absolute magnitude with increase of M_{PMMA}.

Comparison of the thermodynamic parameters in Tables 3–5 shows that negative values of χ_S should have a definite significance for P–P systems characterised by a UCST, because they correspond to a positive value of the non-combinatorial entropy ($\Delta S_{non\text{-}comb} > 0$) and make an additional contribution to the free energy of mixing. Their increase with increasing molecular weight probably partly compensates the characteristic decrease of ΔS_{comb} associated with the decreased number of molecules per unit volume. The competition between these two processes apparently explains also the attainment of a plateau on the relation between T_c and the molecular weight as the Θ temperature is approached. The Θ temperature for the PVC–PMMA system, found from the linear plot of $1/T_c$ against $1/M^{1/2}$, is 588 K; it is striking that it lies appreciably above T_{decomp} for the polymers.

Thus it is evident that a high negative value of χ_{12}, ensured by a high non-combinatorial contribution to the entropy of mixing, can obtain in P–P systems with a UCST only at temperatures greatly exceeding those corresponding to their chemical stability. In this connection it is essential to mention the results of Ielenic's study.[20] A negative interaction parameter ($\chi_{12} = -0.0044$) has been obtained for blends of high-molecular-weight PVC and PMMA by the method of neutron scattering. Since the PVC–PMMA system is only partly compatible (Table 1, Fig.4*a*) and is heterogeneous over a wide range of compositions,[13,59] the view, expressed above, that the thermodynamic quantities determined for the specimens using a third component characterise the equilibrium in the P–P–solvent three-component system and cannot serve as criteria of the compatibility of the P–P binary system at a normal temperature is evidently valid. The same order of magnitude (in terms of the absolute value) of the quantity χ_{12} obtained by the neutron scattering method[20] and the values quoted in Table 4 [56,58] suggest that a conformational state of the macromolecules identical with that which should obtain at a temperature above the Θ temperature and corresponding to a non-equilibrium conformation at the experimental temperature is realised on formation of the P–P system in the presence of a solvent.

Thus theoretical analysis of the experimental phase diagram showed that the phase equilibrium in the PVC–PMMA system, characterised by a UCST, depends significantly on the molecular weight of one of the components and that this dependence is qualitatively described satisfactorily within the framework of the Flory–Huggins–Scott theory and the improved Flory theory. However, this agreement obtains only for the ratios $M_1/M_2 \geq 1$ and $M_1 > 10^5$. It has been shown that the deviation of the parameters of the PVC–PMMA system for $M_{PMMA} = 6.4 \times 10^4$ from the theory (see Tables 3 and 5) is associated with the influence of the free volume effect, which is not manifested for higher values of M_1.

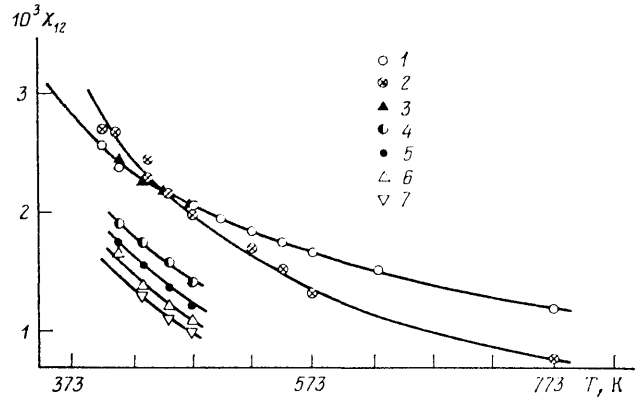


Figure 5. Temperature variation of χ_{12} (1) and the interaction term (2) calculated by Eqn.(1); 3)–7) the values of χ_{12} derived from external binodals as a function of M_{PMMA}.[58] The minima on curves *3*–*7* correspond to curves *1*–*5* in Fig.4.

The influence of these effects has been traced in the analysis of the temperature variations of χ_{12} calculated by Eqn.(1). The contribution of the free volume term B in Eqn. (1) to the overall quantity χ_{12} can be seen from Fig.5, in which the dependence of χ_{12}/Mv_1^* on T (curve *1*), the temperature variation of the interaction term in Eqn.(1) (curve *2*), and the dependence of χ_{12} on T (curves *3*–*7*) are compared. It is seen that curves *4*–*7* are parallel to curve *2*, while curve *3*, corresponding to the system with $M_{PMMA} = 6.4 \times 10^4$, is parallel to curve *1*. Consequently the miscibility of PVC and PMMA for $M_{PMMA} > 6.4 \times 10^4$ is determined solely by the interaction of the components, while under conditions where $M \leq 6.4 \times 10^4$ the difference between the free volumes exerts an appreciable influence. Evidently the latter influence will increase with decrease of M_{PMMA} and with increase of the difference between M_{PVC} and M_{PMMA}. However, calculations showed[58] that the appearance of a

LCST above the UCST in this system (U-shaped dependence of χ_{12} on T) requires necessarily the complete conversion of one of the polymers into the monomer, which would ensure an increase of τ by an order of magnitude and the predominance of the contribution by the second term of Eqn.(1) to the overall quantity $\chi_{12}/M_1 v_1^*$. Analogous calculations have been carried out for the PS–PMMA system and it has been shown that the UCST lies above the decomposition temperatures of the polymers.[60]

Although analysis of this kind is qualitative and in no way replaces the experimental study of compatibility, its employment makes it possible to account for certain features of the phase equilibria in specific systems.

Many attempts have been made recently[15,61–64] to determine the compatibility of polymers (including PVC) with stereoregular components. Fig.6[58] presents sections of the binodal for the PVC–*iso*-PMMA system; it is seen that PVC and stereoregular PMMA (as well as α-PMMA) are partly compatible and phase equilibrium is characterised by the presence of a UCST; secondary processes (associated with crystallisation or other structural transformations) are superimposed on the amorphous equilibrium and complicate its character and the form of the binodal above the melting point of *iso*-PMMA. At temperatures below the melting point, *iso*-PMMA is less compatible with PVC than *a*-PMMA, while above it the solubility of *iso*-PMMA in PVC increases appreciably. The overall tendency in the phase equilibrium and the PVC–*iso*-PMMA system, determined by sections of the binodal,[58] does not conflict overall with the data of other workers, demonstrating a particular degree of limited compatibility of the system in the range $T < T_m$ (melting point), T_{fl} (fluidity temperature) of the polymers.[15,62,64]

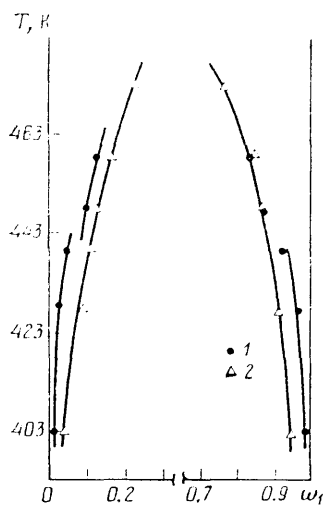


Figure 6. Temperature variation of the compositions of the coexisting phases in the PVC–*iso*-PMMA (1) and PVC–*a*-PMMA (2) systems with identical molecular weights.[58]

IV. MUTUAL DIFFUSION OF POLY(VINYL CHLORIDE) AND POLY(METHYL METHACRYLATE)

The study of the diffusion coefficients and of the characteristics of their variation is a necessary component in the investigation of P–P mixtures, because, together with phase diagrams, they constitute the theoretical basis for the determination of the conditions for the processing of blends, the formation of the phase structure of the material, and the estimation of its thermodynamic and kinetic stabilities.

The mutual diffusion coefficients D_v for PVC and PMMA, determined in the temperature range between T_g and T_{decomp} by X-ray microanalysis, vary in the range from 10^{-14} to 10^{-17} m^2 s^{-1}.[54] Table 6 presents the values of D_v measured at 453 K and the activation energies for diffusion E_D, calculated from the temperature relations $D_v(T)$. The energies E_D for blends with *a*-PMMA are independent of the molecular weight of the diffusing species and the diffusion medium and amount on average to 113 kJ mol^{-1} for the diffusion of PVC in PMMA (D_{12}) and to 134 kJ mol^{-1} for the diffusion of PMMA in PVC (D_{21}). These values are close to the activation energies for viscous flow E_η of the components and demonstrate the segmental character of the movement of macromolecules in polymer blends.

Table 6. Diffusion coefficients and activation energies for diffusion in the PVC–PMMA system.[54]

Diffusing species (M)	Diffusion medium	$10^{15}D_v$, m^{2}s^{-1} (453 K)	E_D, kJ mol^{-1}
PMMA (64 000)	PVC C-70 (140 000)	3.90	137
PMMA (112 000)	ditto	1.40	131
PMMA (187 200)	»	0.50	136
PMMA (302 400)	»	0.21	136
PMMA (726 900)	»	0.09	134
iso-PMMA (100 000)	»	0.43	—
PVC C-70 (140 000)	PMMA (64 000)	2.50	115
Ditto	PMMA (112 000)	1.50	112
»	PMMA (187 200)	1.20	112
»	PMMA (302 400)	1.10	115
»	PMMA (726 900)	1.00	115
»	*iso*-PMMA (100 000)	0.35	—

The diffusion parameters presented in Table 6 are fairly unique not only because they have determined for the first time for the PVC–PMMA system but also because nowadays the diffusion parameters of macromolecules in a medium consisting of similar macromolecules are known only for a small number of systems. Thus the self-diffusion and mutual diffusion coefficients have been determined by the radioactive label and spin-echo relaxation methods for polymers and systems: PS, styrene–n-butyl acrylate copolymer (in Bueche's work), PS_1–PS_2,[65] natural rubber (NR), synthetic isoprene rubber (SIR)–NR system,[66] polydimethylsiloxane (PDMS),[67,68] and certain others.[69–72] Certain systems in the elastic and fused states have been investigated by local methods, particularly by the interference micromethod: PIB–synthetic buta-1,4-diene rubber (SBR), PE–atactic polypropylene (*a*-PP), PE–SIR, etc.[73,74]

Analysis of the available data showed that the values of D determined by various workers at temperature above T_{fl} and T_m are 10^{-12}–10^{-14} m^2 s^{-1}, while in the highly elastic state they are lower by 3–5 orders of magnitude (10^{-15}–10^{-19} m^2 s^{-1}). The values of D_{12} and D_{21} obtained for the first time with the aid of local X-ray microanalysis agree well with the values of D determined by the traditional methods. Fig.7 illustrates the temperature variation of the coefficients D_{12} and D_{21} for the PVC–PMMA system and those of D^* and D_{12}^* for other systems in terms of the reduced variables lg D and $T-T_g$.

It is seen that the values of D for various polymers with similar molecular weights fit on a single straight line to within 40%. It is reasonable that the values of D_{12}^* for the diffusion of SIR in vulcanised natural rubber, D_{12}^* for the methylvinylpyridine synthetic rubber (SMVPR), containing a polar component in the side chain, as well as D_V for the PVC–*iso*-PMMA system are exceptions. Evidently the mechanism of the diffusion process in the PVC–PMMA system is analogous to the mechanism of the diffusion of other linear amorphous polymers: PS, NR, poly(butyl acrylate) (PBA), etc. The values of D for a further series of polymers, such as polyacrylates, polymethacrylates, a-PP, and amorphous rubbers, will probably fit on the straight lines in Fig. 7. Deviations are to be expected for systems with specific properties (polar, crystallisable, and structured systems).

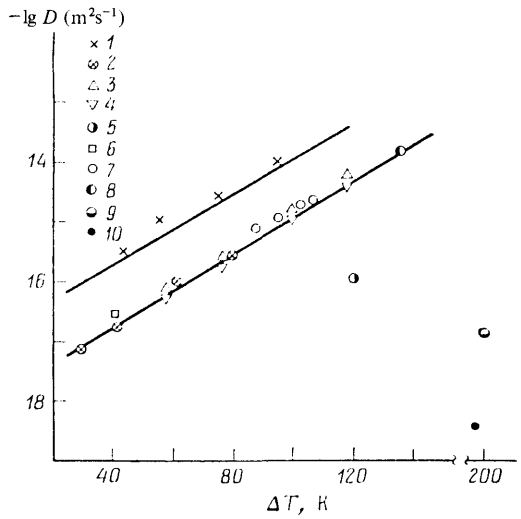


Figure 7. Dependence of the diffusion coefficient D on the difference between the experimental temperature and T_g: 1) D_{21} for PVC–PMMA ($M = 6.4 \times 10^4$); 2) D_{21} for PVC–PMMA ($M = 7.26 \times 10^5$); 3) D_{12} for PVC–PMMA ($M = 6.4 \times 10^4$); 4) D_{12} for PVC–PMMA ($M = 7.26 \times 10^5$); 5) D_{21} for PVC–*iso*-PMMA ($M = 10^5$); 6) D^* = SBR;[69] 7) D^* for PBA; 8) D_{12}^* for PS; 9) D_{12}^* for SIR–NR_{vulc};[66] 10) D_{12}^* for SMVPR.[70]

The studies of the dependence of D on the molecular weight of the diffusing species and the diffusion medium have acquired much importance for the understanding of the mechanism of the translational movement of macromolecules in P–P systems. The influence of the molecular weight of the diffusing species for a constant molecular weight of the medium on the diffusion of PMMA in PVC (D_{21}) and the influence of the varying molecular weight of the diffusion medium for a constant molecular weight of the diffusing species on the diffusion of PVC in PMMA (D_{12}) are illustrated in Fig. 8. It is seen that, with increase of the molecular weight of the diffusing species, the absolute values of D diminish. In the experimental molecular weight range and for all the experimental temperatures, the following relation holds:

$$D = AM^{-b}, \qquad (3)$$

where A and b are empirical coefficients. The coefficient b is a function of temperature and decreases with increase of temperature from 1.57 at 413 K to 1.40 at 473 K.[54]

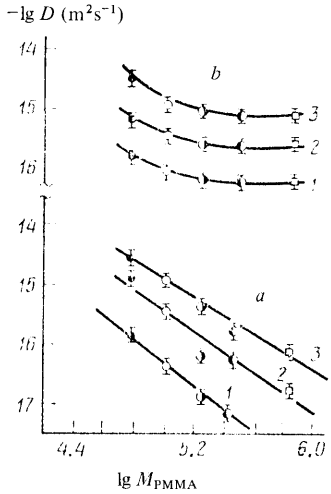


Figure 8. Dependence on the diffusion coefficients D_{21} (a) and D_{12} (b) on M_{PMMA} at different temperatures (K): 1) 413; 2) 433; 3) 453.[54]

A change in the molecular weight of the diffusion medium for a constant molecular weight of the diffusing species leads to the dependence of $\lg D$ on $\lg M$ characteristic for binary systems; the plot has the form of a concave curve described by the expression $\lg D_{12} = \lg D_{12}^{\infty} + n/M_2$, where $n = 3.5 \times 10^4$ is a constant and D_{12}^{∞} is the diffusion coefficient at $M \to \infty$. It is striking that D_{12}^{∞} is attained for the ratio $M_{diff.species}/M_{medium} = 1$ and is not related to M_c (the molecular weight between the entanglement nodes).[54]

The available theories of macromolecular movement are based on the concept of a randomly intertwined structure of the amorphous polymer with a characteristic value of M_c. Bueche's theory considers the energy lost in friction betwen sections of the chain in the course of the translational movement of the molecule and takes into account the entanglements which retard the movement, because one molecule carries behind it others intertwined with it. The theory predicts a dependence of D on M raised to the power 3.4. The "reptation" models of de Gennes[75,76] and Edwards,[77,78] which also take into account the entanglement nodes but deal with the movement of macromolecules which, in essence, bypass these nodes during movement in a closed "tube", significantly differ from Bueche's model. According to De Gennes and Edwards,[75–78] the power exponent b in Eqn. (3) should be 2.

We may note that the values of b determined for the PVC–PMMA system are significantly lower than those predicted theoretically, although the molecular weights of the components of the diffusion pair exceed the molecular weight corresponding to the formation of an entanglement network [M_c(PMMA) = 3×10^4] and are not constant, as predicted by the theory.

The fact that the entanglement network does not influence the diffusion of the macromolecules was noted in an earlier study[66] of D_{12}^* in the SIR–NR system; it was later noted by Tanner[67] and was subsequently formulated in a general

form[79] in the analysis of the experimental data. However, the controversy on this question still continues.[72,76,80,81] It is therefore of interest to analyse the available experimental data for the $D = f(M)$ relations. The studies of the self-diffusion of normal paraffins and PE oligomers yielded $b = 1.7$. According to Bresler et al.,[66] D_{12}^* is proportional to the molecular weight raised to the power of −1.3. The self-diffusion of PEO and PDMS has been investigated[67,68] over a wide range of molecular weights and the power exponent b proved to be 1.7. When the partial self-diffusion coefficients were investigated, it was found that $b = 1$. Kumagai et al.[65] investigated D^* and D_{12}^* for PS; they obtained $b = 1$ for $D_{12}^*(M)$ and $b = 2$ (2.7) for $D^*(M)$. It was also possible to calculate b from Skewis's data[69] (D_{SBR}^*) and the data of Nikiforova et al.[74] ($D_{vPP-SIR}$); $b = 1.65$ and 1.2–1.4 in the former and latter cases respectively.

Thus the experimental values of b can be divided into two groups—those determined from the self-diffusion coefficients D^* and those found from the partial self-diffusion and mutual diffusion coefficients D_{12}^* and D_v (Table 7). Since the values of D_v in infinitely dilute solutions characterise the translational mobility of the polymer in another polymer, it follows that D_v and D_{12}^* have a similar physical significance. For the first group, the parameters b vary from 1.7 to 2, which agrees fairly well with the values predicted theoretically.[76] However, for the second group, b has values ranging from 1 to ~1.6. Evidently the modern theory does not as yet yield a description of the translational movement of macromolecules in P–P systems characterised by the coefficients D_v and D_{12}^* and corresponding to the experimental results. Isolated attempts have only been made to account for such experimental observations by a mixed mechanism of the macromolecular movement.[81]

Table 7. The parameter b in Eqn.(3) for different P–P systems.[45,54,66–71,74].

System	D	b	System	D	b
SIR-NR	D_{12}^*	1.31	PE*	D^*	1.7
PS-PS	D_{12}^*	1.0	PS	D^*	2 (2.7)
PDMS-PDMS	D_{12}^*	1.0	PDMS	D^*	1.7
PP-SIR	D_v	1.2–1.4	SBR	D^*	1.65
PE-SIR	D_v	1.2			
PVC-PMMA	D_v	1.4–1.57			

*Oligomers.

Thus the experimental studies of blends of PVC and PMMA and analysis of data for other systems have shown that the thermal translational mobility of macromolecules in P–P systems is determined, in the case of amorphous linear components, by diffusion coefficients in the range ~10^{-15}–10^{-19} $m^2 s^{-1}$ at temperatures above T_g and in the range 10^{-12}–10^{-14} $m^2 s^{-1}$ above T_{fl} (or T_m in the case of crystallisable polymers); this mobility depends on the molecular weight of the diffusing species in accordance with Eqn.(3) and $b < 2$ and is independent of the molecular weight of the medium when $M_{diff.sp.}/M_{medium} \leq 1$. Attention should be drawn to the fact that the translational mobility of the macromolecules in the P–P system is on the whole low on the macroscopic time scale and yet is fairly high on the microscale, particularly at temperatures above T_g, i.e. at the processing temperature and at the real temperatures at which many P–P systems are actually used. This must be taken into account in considering certain features of the formation of the phase structures of polymer blends.

V. THE PHASE STRUCTURE OF HETEROGENEOUS BLENDS OF POLY(VINYL CHLORIDE) AND POLY(METHYL METHACRYLATE)

Blends based on PVC and PMMA, formed from the melt and the solution and in other ways, are heterogeneous systems with a large area of the interface in the range from room temperature to the decomposition temperatures of the components.[12,13,59,82] This agrees well with the limited miscibility of the polymers, which follows from the phase diagrams (Fig. 4*a*). However, the results of indirect measurements of the comptability of PVC and PMMA (Table 1) indicate discrepancies between the absolute compositions of the coexiting phases obtained by different workers.

In this connection it must be emphasised that the low translational mobility of the macromolecules and the high viscosity of P–P systems, which prevent their separation into phases during the finite period of the experiment and which lead to the formation of kinetically stable metastable disperse structures,[83] at the same time are responsible also for the capacity of P–P systems for supercooling. The latter factor should result in the variation of the composition of the coexisting phases as a function of temperature, time, the quality and concentration of the solvent, and other specific processing conditions. The specific features of the translational mobility on the macroscale and the microscale are such that the range of variation of the composition can extend over a large temperature and concentration range: according to the data in Table 1 and the paper of Walsh and McKeown,[84] the composition varies within the limits from incompatibility to complete miscibility. The question arises whether most of the information available today on the compatibility of various P–P systems,[16] including the PVC–PMMA system (Table 1), does not in fact refer to real materials obtained under specific processing conditions and not to equilibrium P–P systems. Examination of this question appears to be extremely important for the understanding of the entire problem of phase equilibria in polymer–polymer systems—from the critical assessment of the methods for the determination of phase diagrams and the type of phase equilibria in P–P systems to the stability of composite materials.

The influence of the conditions in the preparation of blends of PVC and PMMA on the limits of their miscibility has been investigated[13,59] by electron microscopy (Table 1). It has been shown that the character of the disperse structure and also the limits of its manifestation depend on the concentration and rate of evaporation of the solvent; the influence of the quality of the solvent on the miscibility is illustrated in Fig. 2.[22]

The present level of development of analytical electron microscopy combined with methods for the calculation of the dimensions of the disperse phases and X-ray microanalysis for the identification of the phase composition, on the one hand, and also the familiar theories of mass transfer in disperse systems, on the other, make it possible nowadays to proceed tc the analysis of the disperse phase structure of P–P blends from the standpoint of the kinetics of the attainment of phase equilibria.

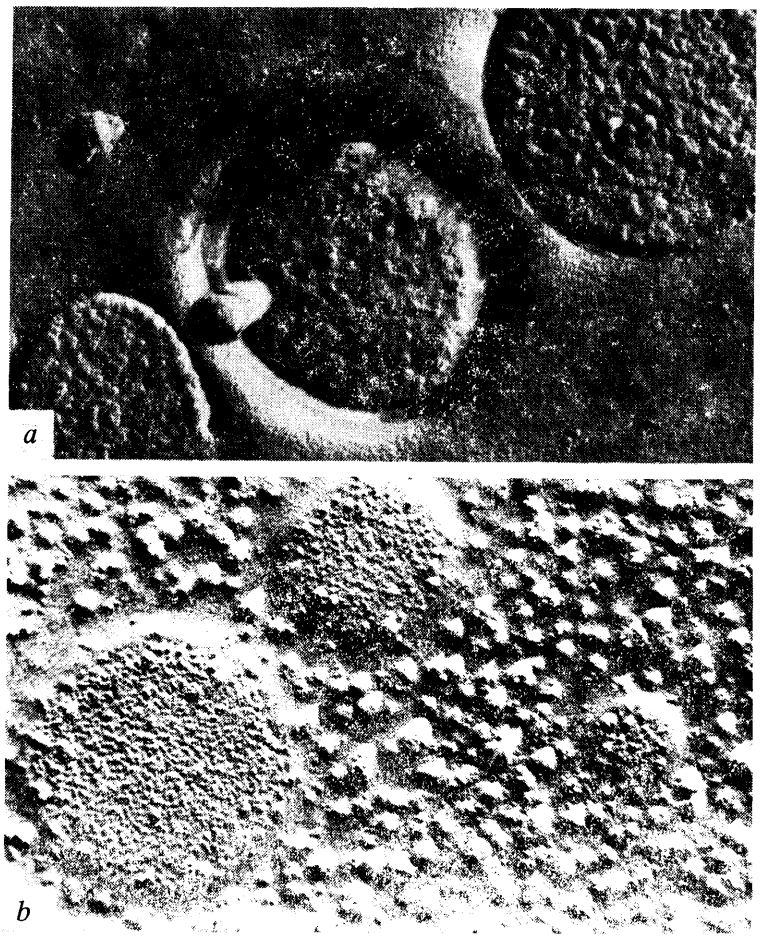


Figure 9. Photomicrographs of the PVC–PMMA system (1 : 3) obtained from solution in cyclohexanone: *a*) before annealing; *b*) after annealing for 30 min at 433 K.[82]

Thus a special study has been made[82] of the influence of the conditions of preparation and thermal annealing on the phase structure of PVC–PMMA blends in comparison with the phase diagrams obtained by Chalykh and Sapozhnikova.[56] The blends prepared from solutions in cyclohexane or THF are initially in a state far from phase equilibrium. X-Ray microanalysis has shown that the compositions of the dispersion medium (PMMA) and the disperse phase (PVC) are supersaturated relative to the corresponding solubility curve on the diagram in Fig. 4*a*. The higher the rate of evaporation of the solvent and the lower the film formation temperature, the greater the deviations from the phase diagram. Thermal annealing of such specimens at a temperature higher by 30 to 40 K than T_g for the components leads to additional phase separation (Fig. 9). The composition of the disperse phases then tends to that of the coexisting phases which follows from the phase diagram at the given temperature. It is striking that an increase of the duration of annealing does not alter the composition of the coexisting phases but does affect the character of the distribution of species with respect to size. A decrease of the concentration of the finely disperse phase and an increase of the size and number of large particles in the PVC–PMMA system take place in conformity with the redistribution of the substance in the direction from the surfaces of the small particles towards the large particles observed for low-molecular-weight systems. The kinetics of this process are described by the Lifshits–Slezov theory, according to which the change in the number of species during prolonged annealing is defined by the equation

$$\partial N/\partial t = (2\sigma D c_p V_m/r^*)\,(RT\partial/\partial r[(r-r^*)N(r,\ t)/r^2]), \qquad (4)$$

where σ is the interfacial tension, D the diffusion coefficient, c_p the solubility at $r \to \infty$, V_m the molar volume, r the radius of the particle, and r^* the equilibrium radius of species in the dispersion medium.

The solution of this differential equation for the Gaussian distribution of particles with respect to dimensions is given by the equation

$$N(0)/N(t) = 1 + t/\tau \qquad (5)$$

where

$$\tau = 9RT/8D\sigma V_m^2 c_p r^3(0)\,. \qquad (6)$$

The applicability of the Lifshits–Slezov theory to P–P systems has also been demonstrated to another study[85] in relation to the polybutadiene ($M = 1.5 \times 10^4$)–poly(propylene oxide) ($M = 1.5 \times 10^3$) system. On the basis of electron microscopic

observations on the kinetics of the transformation of the disperse phase structure and on the basis of Eqns.(4)–(6), the phase diagram has been obtained for this system, characterised by a UCST.

Thus it is evident that, by following the kinetics of the changes in the phase structures of polymer blends, it is possible to determine the miscibility of the components; and, conversely, knowing the miscibility and diffusion parameters, it is possible to predict with the aid of Eqn.(4)–(6) the changes which will occur in the disperse system during use.

Fig.10 presents the phase diagram for the PVC–PMMA system and illustrates the position of the spinodal calculated on the basis of the Flory–Huggins–Scott theory from the equation

$$(\chi_{12})_{sp} = \frac{1}{2}\left[\frac{1}{n_1(\varphi_1)_{sp}} + \frac{1}{n_2(\varphi_2)_{sp}}\right].$$

Lines corresponding (according to different authors' data) to the limits of the miscibility in the system, obtained at normal temperatures but using a solvent, are drawn on the diagram parallel to the ordinate axis. Comparison of the positions of these straight lines relative to the binodal and the spinodal in different temperature ranges demonstrates the changes which should occur in the specimens during thermal annealing and also the causes of the quantitative discrepancies between the results of different workers.

It can be seen that, with the aid of solvents, disperse systems corresponding to a metastable state are formed (shaded region between the binodal and the spinodal) over a wide temperature range. This is naturally the reason why the annealing of such systems at temperature above T_g alters the compositions of the coexisting phases in the direction determined by their positions relative to the binodal. Thus the system obtained from a solution in cyclohexanone (straight line 4 in Fig.10) was initially supersaturated relative to the equilibrium compositions of the coexisting phases, which was demonstrated by X-ray microanalysis and electron microscopy. Annealing of such a system at 433–443 K leads to a thermally induced phase separation (Fig.9) and to a decrease of the miscibility limits ω_1'' and ω_2'), while at 473 K it leads to their increase and the dissipation of the particles of the disperse phase.[82] The displacement of ω_1'' and ω_2' along the composition line during annealing is indicated in Fig.10 by arrows.

An analogous displacement of the composition points on the phase diagram has been observed during the annealing of a system prepared from solutions in THF, DCE, and benzene or from the melt after rapid cooling.[22,50,56,82] It is noteworthy that the observed nucleation decomposition and growth of the particles of the disperse phase confirm that the system formed initially was located in the metastable region of the phase diagram.

Thus the phase diagram determines the general trend in the variation of the disperse phase structure of the blend during thermal annealing. Thermally induced phase separation is not then always a sign of a LCST; it can be also a consequence of kinetic processes involving the establishment in the system of the equilibrium compositions of the coexisting phases. It is striking that in this case irreversible changes take place in the phase structure of the polymeric material obtained initially.

At the present time the kinetics of the phase separation of P–P systems via both spinodal and nucleation mechanism have been investigated very little indeed. It follows from a review[86] or another communication[87] that the efforts of investigators have been directed towards the search for and elucidation of the conditions for the spinodal or nucleation mechanisms of the decomposition of P–P systems. However, the question arising from the study of the kinetics of the attainment of phase equilibria in the experimental determination of binodal and spinodal curves remains open. The large number of unexplained contradictory data on the compatibility of polymers, so frequently discussed in the literature[15,16,59,94] (and other communications), is probably in fact associated with this factor.

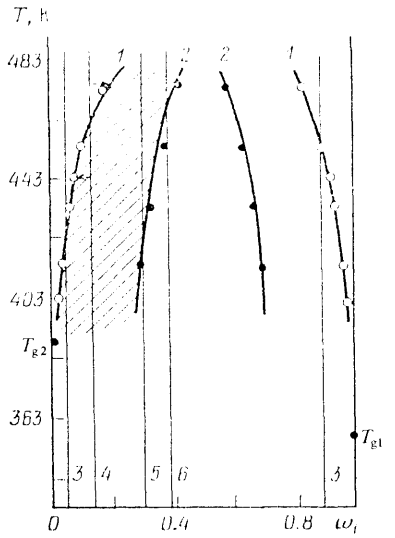


Figure 10. Phase diagram for the PVC–PMMA system: 1) sections of the binodal; 2) sections of the spinodal. The vertical lines correspond to the limits of compatibility of the system obtained using a solvent according to different data: 3) Razinskaya et al.;[13] 4) Matveev et al.;[82] 5) Tager et al.;[14] 6) Shrer et al.[15]

VI. THE INFLUENCE OF IRREVERSIBLE THERMAL DEGRADATION PROCESSES INVOLVING THE CHLORINE-CONTAINING COMPONENTS ON THE MISCIBILITY IN POLYMER BLENDS

The kinetic thermal decomposition processes influencing irreversibly the compatibility of polymers have been examined for at least two reasons. The first is associated with the stability of the phase structure of the blends during their preparation and use and the second with the very problem of the construction of phase diagrams, because the low thermal stability combined with the high viscosity of the polymers actually creates the problem of the attainment of equilibrium under the conditions of isothermal annealing without appreciable chemical transformations. This applies particularly to blends whose composition includes chlorine-containing components (PVC, CPE, etc.), which are capable of intense dehydrochlorination even at $T > T_g$. Numerous data, to a large extent contradictory (see Section II), have now been obtained on the compatibility of polymers with participation of PVC and CPE,[31–33,37,38], but special studies of the influence of their thermal decomposition on compatibility with other polymers have not been made. The application of local X-ray microanalysis made it possible to obtain simultaneously information about the phase diagrams, the diffusion constants, and the thermal stability parameters of chlorine-containing components, which made it possible to demonstrate

quantitatively the influence of thermal decomposition on the character of the phase diagrams of the PVC–PMMA and CPE–PMMA systems.[44,48]

The kinetic curves for the thermal decomposition of PVC at early stages are presented in Fig. 11*a*. The range of times investigated was chosen in accordance with those necessary to obtain equilibrium values of ω_1'' and ω_2'. These data on the kinetics of the decomposition of PVC, obtained with the aid of X-ray microanalysis, are consistent with the familiar data of different workers.[89–91]

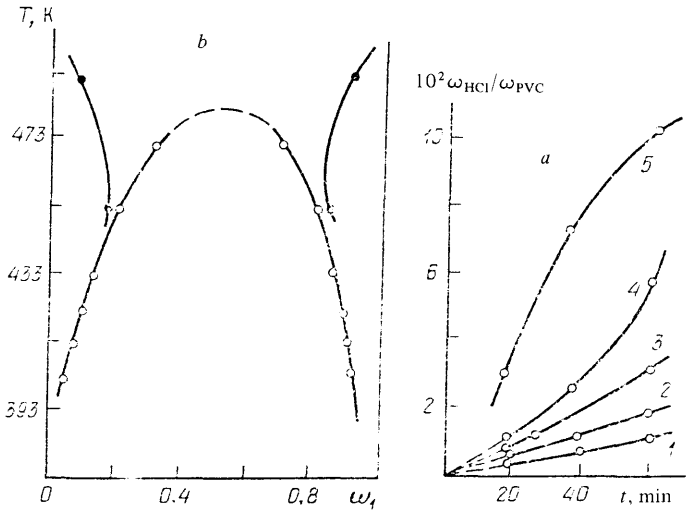


Figure 11. *a*) Kinetic curves for the dehydrochlorination of PVC at different temperatures [*T* (K): 1) 433; 2) 443; 3) 453; 4) 473; 5) 493]; *b*) variation of the phase structure of the PVC–PMMA system after annealing under the conditions of intense thermal decomposition (filled circles).[88]

Fig. 11 shows that annealing at 423–433 K for 60 min and at 443–453 K for 30 min leads to a loss of chlorine equivalent to a weight fraction of only 0.01. Such a change in the chemical structure does not influence the overall form of the binodal characteristic of systems with a UCST. In this case, when the temperature or duration of the annealing exceed the temperature of the chemical decomposition or the induction period of the decomposition reaction (for example, the system has been annealed at 493 K for 20 min or at 453 K for 60 min), the miscibility of the polymers diminishes. The values of ω_1'' and ω_2' obtained under these conditions impart to the phase diagram the "hour glass" character (Fig. 11*b*). However, such a change in the temperature variation of ω_1'' and ω_2' should be explained by the decrease of the miscibility of the components on formation of unsaturated conjugated bonds and partial structure formation in PVC [89] and not by the thermodynamic characteristics, as has been done in a number of studies[32,33,92,94] on blends with chlorine-containing components. Vigorous thermodynamic decomposition processes occurring for certain values of *T* and *t*, limited the possibility of obtaining the complete binodal for the PVC–PMMA system in two investigations.[42,56]

Whereas the PVC dehydrochlorination processes have been studied in fair detail and the variation of the compositions of the coexisting phases illustrated in Fig. 11*b* may prove to be self-evident, in the case of other chlorine-containing polymers, in particular CPE, the relation between the phase equilibrium and the thermal decomposition is significantly more complex.

The miscibility curves for the CPE (62% Cl)–PMMA system and the kinetic CPE thermal degradation curves are illustrated in Fig. 12.[44,88] The phase diagram is complex and resembles the type of diagrams with a "latent maximum", familiar in metallography, which is characteristic of systems undergoing chemical transformations during thermal annealing.

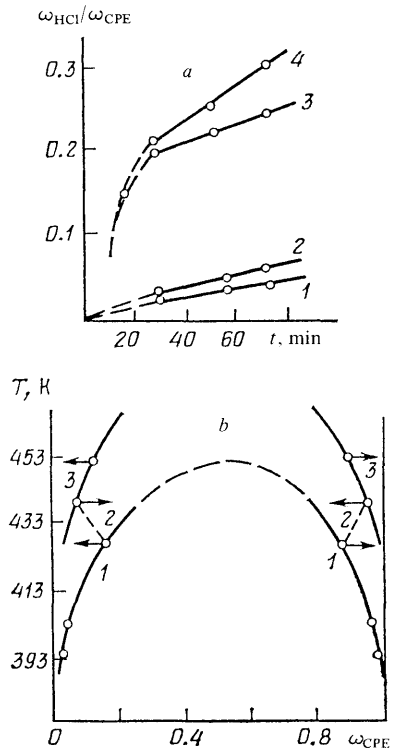


Figure 12. *a*) Kinetic curves for the dehydrochlorination of CPE at different temperatures [*T* (K): 1) 403; 2) 428; 3) 439; 4) 458]; *b*) "composition–temperature" curves for the CPE–PMMA system (for explanation, see text).[95]

We shall consider the dehydrochlorination process occurring during the annealing of the system. It follows from the kinetic curves (Fig. 12*a*) that up to 428 K dehydrochlorination proceeds at a constant rate up to an annealing time of 80 min and the loss of HCl from the CPE specimen amounts to a weight fraction not exceeding 0.03. At 439 K a sharp increase of the rate of elimination of HCl is observed already for short thermal exposures and the loss of HCl is in this case equivalent to a weight fraction of 0.23. An increase of temperature to 453 K hardly alters the degree of dehydrochlorination compared with 439 K. Thus initially a sharp increase of the rate of evolution of HCl is observed (at temperatures above 428 K) and this is followed by retardation, probably owing to the decreased overall chlorine content in the specimens and the appearance of CPE having a higher stability.[93]

We shall now examine Fig.12*b* and compare it with Fig.12*a*. Sections *1* on the "composition–temperature" curve indicate an increase of the miscibility of CPE and PMMA with increase of temperature to 428 K. The chlorine content in CPE is in this case 61%. The jump along sections *2* at 439 K corresponds to a change in the chlorine content in CPE up to 39% (sections *2* are designated in Fig.12*b* by dashed lines because the process is reversible). An increase of temperature to 453 K for an annealing time of 25 min does not alter the chlorine content in the specimen and the values of ω_1'' and ω_2' increase (section *3*). It is seen from the above comparison that this system represents a combination of two systems: CPE (61% Cl)–PMMA and CPE (39% Cl)–PMMA. Like the PVC–PMMA system, the two systems are characterised by phase diagrams with a UCST, but the CPE containing 39% Cl is less compatible with PMMA than the CPE containing 61% Cl. This fact can be satisfactorily accounted for by the extremum in the variation of $(\delta_1-\delta_2)^2$, where δ_1 and δ_2 are the miscibility parameters of PMMA and the CPE decomposition products respectively, with the chlorine content in CPE (Fig.13).

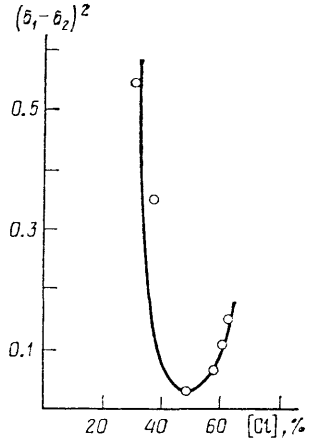


Figure 13. Dependence of $(\delta_1-\delta_2)^2$ on the chlorine content in CPE for the CPE–PMMA system; the values of δ were calculated from the additive contributions by different atomic groups.[95]

Thus it has been shown that the stability of chlorine-containing polymers and their decomposition kinetics have a decisive influence on their compatibility with other polymers and on the character of the phase diagrams for the blends. The extremum in the variation of the miscibility with the chlorine content in the specimen suggests that both trends in the variation of the miscibility operate—both towards its decrease and towards its increase as a function of the thermal decomposition conditions. Thus the slower decomposition of CPE, which depends on the initial PE, the conditions and degree of chlorination, etc., shifts the positions of ω_1'' and ω_2' along section *2* in Fig.13 towards higher values, while longer annealing (for $t > 25$ min), which leads to structure formation in CPE, entails a decrease of ω_1'' and ω_2'. The possible movements of the composition points are indicated by arrows in Fig.13. The combination of the characteristic features of the kinetics of the thermal decomposition of CPE with the complex dependence of the miscibility on the chlorine content in the polymer have in fact enabled the authors[32,33] to obtain a wide variety of types of "phase equilibria" within the limits of the single CPE–PMMA system; diagrams I, III, and V (Fig.1). The results of Chalykh and co-workers[44,88] have shown that the complete description of systems containing unstable components requires a more complex model taking into account the time variation of not only the temperature and composition but also of the chemical structure of the system.

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Thus the review has considered many specific phenomena and properties characteristic of P–P systems and determined mainly by the non-equilibrium nature of their phase structure. The non-equilibrium structure, associated with the low translational mobility and thermal stability of the polymers, arises under the real conditions for the formation of the blends and is manifested by a deviation of the compositions of the disperse phase and the dispersion medium from the equilibrium compositions of the coexisting phases. It reflects the previous history of the blends and influences the mode of variation of the properties during further use. This is observed in experimental studies of the miscibility of polymers and constitutes the basis of numerous contradictions in results obtained by different workers. The data on the translational mobilities of the components of polymer blends examined in this review show that, the attainment of real advances in the study of the equilibrium states in condensed P–P systems requires the abandonment of the traditional integrated methods in favour of local methods employed at a microlevel. In this connection it appears useful to develop and apply the methods of analytical electron microscopy in the study of P–P systems. Highly resolving analytical methods make it possible to carry out a combined study of the phase equilibria, translational mobilities, and thermal decomposition processes, which is essential both from the standpoint of the reliability of the phase diagrams and for their practical employment.

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