Miscible polymer blends: 1. Thermodynamics of the blend melts poly(methyl methacrylate)–poly(ethylene oxide) and poly(methyl methacrylate)–poly(vinylidene fluoride)

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The composition, temperature and pressure dependences of thermodynamic characteristics have been studied for the melts of blends of poly(methyl methacrylate) (PMMA) with poly(ethylene oxide) (PEO) and poly(vinylidene fluoride) (PVDF). The experimental data have been treated in terms of the Sanchez–Lacombe equation of state, and the parameter χ_{12} has been calculated. In addition, the SAXS patterns of these blends have been examined above the melting temperature (T_m) for PEO and PVDF.

(Keywords: poly(methyl methacrylate); poly(ethylene oxide); poly(vinylidene fluoride); miscibility; interaction parameter; *PVT* property; homogeneity)

INTRODUCTION

In the study of materials, considerable effort is currently being expended to obtain new high performance polymeric materials. One of the approaches is to use blends based on thermodynamically miscible polymers forming solutions at the segment level.

Current theory makes it possible to assess the thermodynamic miscibility of polymers mainly from the concentration dependences of the glass transition and melting temperatures[1]. However, these dependences are generally distorted by non-thermodynamic (morphological, non-equilibrium) effects, which is the main disadvantage of this approach. Studying correlations between the thermodynamic characteristics of the melts and the interaction parameter χ_{12}, which describes quantitatively the miscibility level of the components of the blend, seems to be a better method. In addition, the phenomenon of thermodynamic miscibility is generally considered in isolation from its cause, namely, specific interactions between the blend components[2,3]. Most of the literature is confined merely to stating such interactions without examining their effects on the thermodynamic 'macro'- and 'micro'-characteristics of melts and the solid state of the binary blends[4,5]. But, in solving practical problems, one needs to know the behaviour of the thermodynamic characteristics of binary blends as a function of the nature and level of the specific interactions between the blend components.

In the studies reported here we examined the equilibrium *PVT* properties of melts of the linear flexible-chain polymers poly(ethylene oxide) (PEO), poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA), as well as those of PEO-, PVDF- and PMMA-based blends over wide ranges of temperatures and pressures. The microstructure of the blend melts was also studied.

EXPERIMENTAL

We examined the following polymers: PEO with $M_n = 2\times10^3$ (PEO-2, Fluka AG) and $M_n = 125\times10^3$ (PEO-125, Union Carbide), i.e. with molecular weights lower and higher, respectively, than the critical weight for PEO[6]; PVDF with $M_n = 550\times10^3$, $M_z/M_w = 2.92$; and a home-produced atactic PMMA with $M_n = 500\times10^3$, $M_z/M_w = 1.59$. The molecular weights of the samples were determined viscosimetrically. The starting polymers were cleansed of impurities by reprecipitation: PEO-2 from acetone into isooctane; PEO-125 also from acetone into isooctane; PMMA from acetone into hexane; and PVDF from *N*,*N*-di(methyl acetamide) into distilled water. To prepare the blends, dilute (1 mass.%) solutions of the starting polymers were mixed in a certain proportion and stirred for a few hours. During the subsequent continuous stirring the solvent was thickened by evaporation.

The equilibrium *PVT* properties of the melts PEO/PMMA and PVDF/PMMA were studied with the aid of a modified high pressure dilatometer[7,8]. A primary treatment of the data was performed in terms of Tait's equation[9]:

$$V = V_0[1 - 0.0894\ln(1 + P/B)] \qquad (1)$$

where V and V_0 are the specific volumes of the melt at the pressure P and at normal pressure, respectively, and B is the 'material' elasticity constant of the melt. The value of V_0 was chosen to minimize the deviation of B from its mean value, the error amounting to $5\times10^{-4}\,\mathrm{cm^3\,g^{-1}}$.

Subsequent analysis of the *PVT* properties was made

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in terms of the Sanchez–Lacombe equation of state[10]:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1-\tilde{\rho}) + \tilde{\rho}] = 0 \qquad (2)$$

where $\tilde{\rho} = \rho/\rho^*$, $\tilde{T} = T/T^*$ and $\tilde{P} = P/P^*$; ρ^*, T^* and P^* are characteristic parameters which, as follows from previous work[11], may be determined analytically.

X-ray diffraction studies over the range 0.1–5° were made on the PEO/PMMA samples at 393 K and on PVDF/PMMA at 453 K, with the use of the MUD-1 device[12]. CuK_α anode emission with $\lambda = 1.54$ Å was used along with a nickel filter. The experimental values of the scattering intensity were normalized to the intensity of the original beam, with the adsorption and variation of the optical path taken into account. The scattering curve was recalculated from 'slit' collimation to 'point' collimation, according to a standard computer program.

RESULTS AND DISCUSSION

Figure 1 shows a logarithmic plot of the temperature dependences (ln B) of the polymers and blends studied at normal pressure. For pure PMMA, after a linear section between 423 and 393 K, the ln B curve exhibits a sharp bend and increases between 373 and 293 K, which is typical of polymer transition into a glassy state. Linearity of ln B dependence is observed for the blend PEO-2 with PMMA mass content $w = 0.8$ over the range 423–373 K and for all the other PEO/PMMA blends over 423–343 K (*Figure 1a*). The blends PEO-125/PMMA have ln B values between those for PEO-2 and PMMA, and the temperature dependences are also linear. It is remarkable that for the blends PEO-2/PMMA and PEO-125/PMMA with $w = 0.1$ and $w = 0.2$ the values of ln B at 343 K practically coincide.

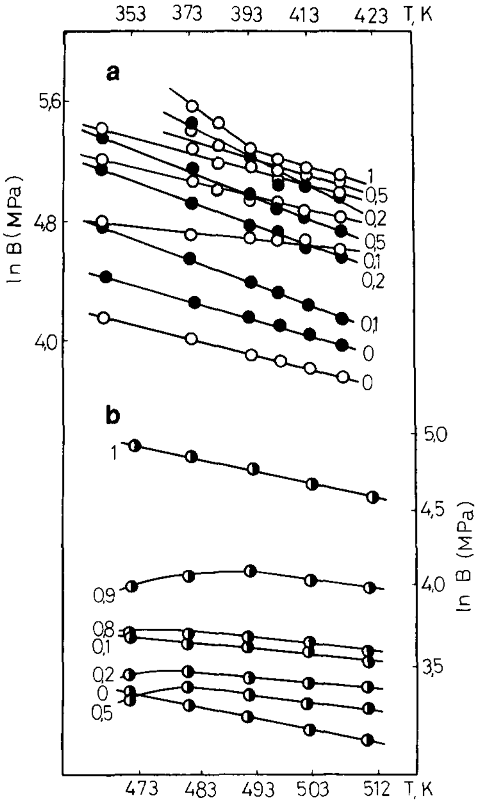

Figure 1 Temperature dependence of ln B for (a) PEO/PMMA and (b) PVDF/PMMA: ○, blends with PEO-2; ●, blends with PEO-125 ($P = 0.1$ MPa). Mass contents of PMMA are shown near the curves

The data obtained imply that, in the temperature ranges under consideration, the binary melt blends may be homogeneous at the level of macromolecular coils. The point is that the separation into two amorphous phases accompanied by transition through the region of unstable states and high compressibility would inevitably manifest itself in an anomalous decrease of the parameter B.

Figure 1b shows the temperature dependences of ln B for pure PVDF and PMMA in the temperature range 473–513 K, as well as those for the corresponding blends. For PVDF and PMMA a linear dependence ln $B(T)$ is observed. For the binary blends (except for that with $w = 0.1$) the dependence deviates from linearity towards the lower values (i.e. the higher values of β, where $\beta = -(1/V)(\partial V/\partial P)_T$ is the isothermal compressibility of the melt) as temperature increases. This may be considered an indirect indication of an increase in the heterogeneity of the blends PVDF/PMMA with decreasing temperature. For the composition $w = 0.1$, the $\ln(B) = f(T)$ dependence is linear over the entire temperature range under consideration, which, in principle, points to a higher homogeneity of this melt than of the other blends.

Figure 2 presents the composition dependences of specific volume, bulk thermal expansion coefficient $\alpha = (1/V)(\partial V/\partial T)_P$ and isothermal compressibility β for the systems PEO/PMMA and PVDF/PMMA at normal pressure. For PEO/PMMA, V_0 manifests negative deviations from additivity (in other words, negative values of the excess miscibility volume, $\Delta V_{\mathrm{misc}} < 0$). We believe that the detected melt 'densification' effect implies that between the PEO and PMMA macromolecules specific interactions occur with energy exceeding the energy level of intermolecular interactions within each component of the blend. For the system PEO-125/PMMA, the absolute values of $\Delta V_{\mathrm{misc}} < 0$ are smaller than for PEO-2/PMMA; in the region of $w \geqslant 0.5$, V_0 practically coincides with the additive values. The suggestion of the presence of specific interactions within the melt is also confirmed by lower experimental values (than the additive values) of the bulk thermal expansion coefficient α and the thermal compressibility coefficient β for all the blends studied. Note that after the initial rapid drop in the region $w \leqslant 0.2$, α and β do not change with further increase of w, but retain values close to those of α and β for the starting PMMA. As one would expect, increasing the molecular weight of PEO leads to a decrease in the coefficients α and β and, hence, in their excess values.

Figure 2b shows the negative deviations from additivity for the values of specific volume and isothermal compressibility coefficient are observed in the system PVDF/PMMA as well, at $w \leqslant 0.25$, while for other compositions, these parameters exhibit positive deviations from additivity. The bulk thermal expansion coefficient has negative deviations over the entire range of compositions, the drop at $w \leqslant 0.25$, just like that in the system PEO/PMMA, being followed by a region of approximately constant values of α equal to those of the starting PMMA.

Figure 3 demonstrates that the characteristic parameters T^*, V^*_{sp} and P^* of the equation of state (2) also exhibit non-additive variations with composition. Each of the 'excess' parameters T^*, V^*_{sp} and P^* (the difference between the calculated and additive values) is a measure of its deviation from the value predicted by the lattice theory of liquids. Hence, the 'excess' parameters may characterize indirectly the level of interaction between

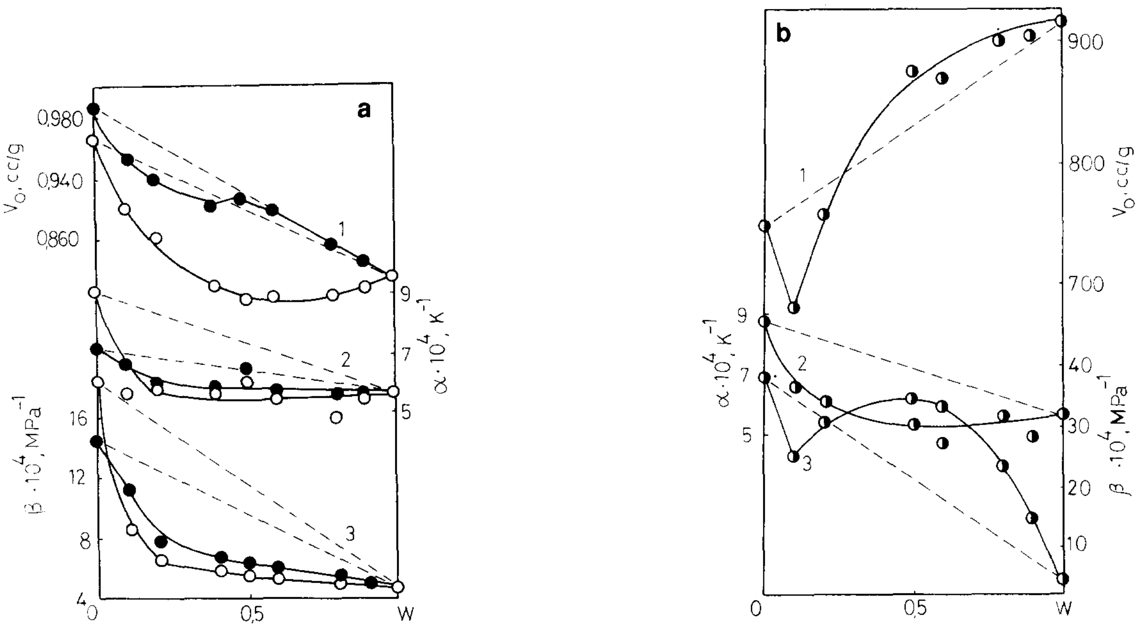

Figure 2 Composition dependences of specific volume V_0 (1), coefficient of bulk thermal expansitivity α (2) and isothermal compressibility β (3) of the blends studied for (a) PEO/PMMA ($P=0.1$ MPa, $T=393$ K) and (b) PVDF/PMMA ($P=0.1$ MPa, $T=493$ K): blends with PEO-2; ●, blends with PEO-125; ---, additive behaviour of parameters

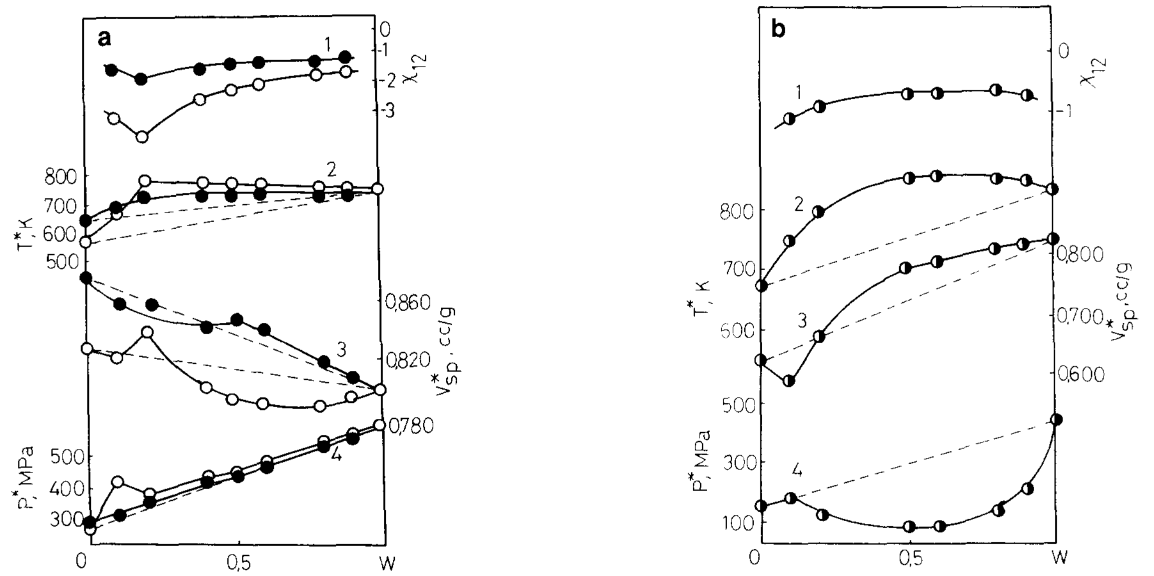

Figure 3 Composition dependences of the thermodynamic interaction parameter of the Sanchez–Lacombe equation of state χ_{12} (1), and its characteristic parameters, temperature T^* (2), specific volume V^*_{sp} (3) and pressure P^* (4) for (a) PEO/PMMA ($P=0.1$ MPa, $T=393$ K) and (b) PVDF/PMMA ($P=0.1$ MPa, $T=493$ K): ○, blends with PEO-2; ●, blends with PEO-125; ---, additive behaviour of parameters

the components of the system. For PEO-2/PMMA, the contact interaction energy T^* and the cohesion energy density P^* show positive deviations from additivity and an extremum at $w=0.2$ and $w=0.1$, respectively. For the system PEO-125/PMMA, the variations of T^* and P^* with composition are more monotonous: for PVDF/PMMA (*Figure 3b*) only T^* has positive deviations from additivity, while V^*_{sp} behaves similarly to V_0, and the cohesion energy density over the range $0.1 \leqslant w < 1.0$ is lower than the additive values.

According to Reference 10, one may calculate the thermodynamic interaction parameter χ_{12} as a measure of the deviation of the contact interaction energy from its additive values:

$$\chi_{12}=[\phi T^*_1+(1-\phi)T^*_2-T^*]/\phi(1-\phi)T \qquad (3)$$

where $\phi=(w/\rho^*_1)/[w/\rho^*_1+(1-w)/\rho^*_2]$, $\rho^*=1/V^*_{sp}$. As seen from *Figure 3a*, for PEO/PMMA, the parameter χ_{12} appears to be negative and have a minimum at $w=0.2$. The absolute value of χ_{12} exceeds the values derived from Nishi's analysis of the melting temperature depression for the crystalline phase[12]. An increase in the molecular weight of PEO leads to an increase in χ_{12}. The fact that the position of the minimum of the curve $\chi_{12}(w)$, for PEO/PMMA with varying PEO molecular weights, seems to be independent of composition evidently means that the set of blends we have treated in the range of compositions under study was not quite representative.

For PVDF/PMMA, χ_{12} calculated from equation (3) also turns out to be negative and, for $0.2 < w < 0.8$, weakly dependent on composition (*Figure 3b*). For a higher content of one of the components (in the regions of $w > 0.8$

and $w<0.2$) the parameter χ_{12} tends to decrease.

To our thinking, the behaviour of the composition dependences of thermodynamic characteristics and the parameters of the equation of state (2), as established for PEO/PMMA, implies that specific interactions between active fragments of the macromolecular PEO and PMMA are being gradually levelled off, the stronger ones at $w \leqslant 0.2$, the weaker ones at $0.2<w<1.0$. So, this behaviour cannot be accounted for by the effect of the PMMA coils overlapping in the melt of PEO.

As we have reported in our infrared spectroscopy studies[11], with PMMA present in PEO-2 melts, the band of hydrogen bonding between the hydroxyl endgroups and ether oxygen in the PEO-2 chain (3510 cm^{-1}) widens and becomes bimodal. The dissociation energy of the hydrogen bonding calculated with the aid of Drago's empiric relation[13] is 15.06 kJ mol^{-1} of pure PEO-2. This is indicative of two types of hydrogen bonding, rather than variation of the crystallinity of solid polymer samples. It is easy to show that, for PEO-2/PMMA, a complete levelling of such interactions is achieved at $w=0.1$ (under conditions of strict monodispersity of PEO-2), or at $0.1<w<0.2$ (assuming that the low molecular fractions of PEO-2 are present, even as a relatively low proportion). The insignificant hydroxyl group content in the high molecular PEO-125 is, evidently, responsible for low (compared with the system PEO-2/PMMA) values of the excess thermodynamic functions of the melt.

In some reports[14–16], specific interactions of either the hydrogen bonding type[16] or dipole–dipole type[14,15] have been suggested between the components of the system PVDF/PMMA. In PVDF macromolecules, the active fragments may be represented by the fluor atoms favourably distributed in space, while in PMMA, as well as in PEO/PMMA, carbonyl groups may be active.

Specific hydrogen-bonding type interactions between the components of PEO/PMMA should lead, in principle, to a lower critical solution temperature (LCST) for the given pair of polymers[17]. Unfortunately, for many polymer pairs, the CST is beyond the temperature and pressure ranges attainable experimentally: it is either below the transition temperature, where it cannot be determined because of infinitely large relaxation times, or above the temperature at which the polymers still keep their chemical identity. Sanchez[10] suggested a method for determining the CST position by analysis of the temperature dependence $\frac{1}{2}\psi^2\tilde{T}P^*\beta$ in the frame of the equation of state of the lattice liquid. Applying the analysis to PEO/PMMA, we have shown earlier[11] that this system has the LCST located far beyond the experimental range of temperatures and pressures.

We think that the CST position may also be found from analysis of the temperature and pressure dependences of the interaction parameter χ_{12}, as described below.

From the available set of experimental data on V, α, $\beta(w, T, P)$, one may determine, from equation (3), the values of $\chi_{12}(w, T, P)$ in the desired range of temperatures and pressures. Since for both the individual polymers and their blends there exists, at any temperature and pressure, a dependence $T^*(T, P)$, the parameter χ_{12} need not be normalized with respect to the temperature and pressure variation of T^*. Moreover, we suggest that the parameter χ_{12} should be calculated not at an abstract pressure $P=0$, as is generally done in theory, but at a realistic pressure $P=0.1$ MPa. At $P=0$, the P-containing terms of the expressions used for calculating the characteristic parameters of the state equation[12] (e.g. P. β) become zero, which leads to $\chi_{12} \neq f(T, P)$. At $P=0.1$ MPa, however, a temperature dependence of χ_{12} can be analysed that reflects variations V, α and β; the parameter χ_{12} can thus be calculated for any pressure $P \geqslant 0.1$ MPa.

Figure 4 presents the temperature and pressure dependences of the parameter χ_{12} derived with the use of the method described above. For the system PEO-2/PMMA (*Figure 4a*), the parameter χ_{12} increases slightly with increasing temperature, which corresponds to a high LCST. (In other words, in the temperature range 393–423 K, the specific interactions that lead to the miscibility of the polymers in the system PEO/PMMA are still strong.) The derivatives $(\mathrm{d}\chi_{12}/\mathrm{d}T)_p>0$ determined at $w=0.9$ and $w=0.2$ have magnitudes of the order of $(1 \div 5) \times 10^{-3}\,\mathrm{K}^{-1}$.

Figure 4a also shows the pressure dependence of the parameter χ_{12} for the blends with $w=0.9$ and $w=0.2$ at 393 K. For $w=0.9$, $(\mathrm{d}\chi_{12}/\mathrm{dP})_T<0$ in the pressure range 0–75.5 MPa and then changes sign. For $w=0.2$, $(\mathrm{d}\chi_{12}/\mathrm{d}P)_T>0$ over the entire range of pressures. Note that the initial decrease in $\chi_{12}(P)$ and its subsequent increase are typical of all the PEO/PMMA blends studied

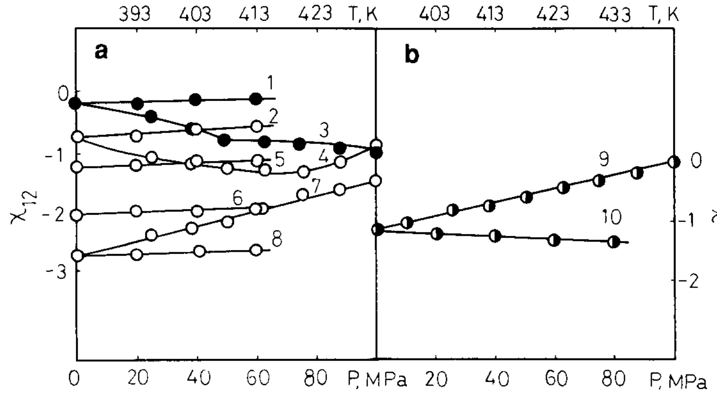

Figure 4 Temperature and pressure dependences of the thermodynamic interaction parameter of the Sanchez–Lacombe equation of state χ_{12} for (a) PEO/PMMA and (b) PVDF/PMMA: ○, blends with PEO-2; ●, blends with PEO-125. 1, 2, $w=0.9$, $P=0.1$ MPa; 3, 4, $w=0.9$, $T=393$ K; 5, $w=0.9$, $P=50.3$ MPa; 6, $w=0.2$, $P=50.3$ MPa; 7, $w=0.2$, $T=393$ K; 8, $w=0.2$, $P=0.1$ MPa; 9, $w=0.1$, $T=473$ K; 10, $w=0.1$, $P=0.1$ MPa

(an exception is PEO-2/PMMA with $w=0.2$). This behaviour of $\chi_{12}(P)$ may be due to the change of the 'sign' of the thermal pressure coefficient $\gamma=\alpha/\beta$, as has been reported by McMaster[18] and Lacombe[19].

The blend with $w=0.2$ which exhibits $(d\chi_{12}/dP)_T>0$ corresponds to the highest levelling of specific interactions and to consolidation of the melt at normal pressure, so that a further increase in pressure leads to destruction of the interaction network, i.e. an increase in the parameter $\chi_{12}(P)$.

For the blends PEO-125/PMMA, $(d\chi_{12}/dP)_T<0$ over the whole range of compositions, which may be explained by a lower level of specific interactions leading to lower (compared with the blends PEO-2/PMMA) values of the excess specific volume. The values of $(d\chi_{12}/dP)_T$ for the blends with $w=0.9$ and $w=0.2$, in the pressure range 0–75.5 MPa, are -7.6×10^{-3} and 12.2×10^{-3}, respectively.

The temperature and pressure dependences of the parameter χ_{12} for the system PVDF/PMMA with $w=0.1$ are shown in *Figure 4b*. Both the dependences are linear: $(d\chi_{12}/dT)_p=-4.5\times10^{-3}\,K^{-1}$; $(d\chi_{12}/dP)_T=1.12\times10^{-2}\,MPa^{-1}$. This behaviour of $\chi_{12}(T,P)$ points to the existence of an upper critical solution temperature (UCST) for the given polymer pair, the strong dependence $\chi_{12}(P)$ indicating a relative proximity (from below) of the UCST to the temperature range under consideration[20]. It is remarkable that the same conclusion for PVDF/PMMA has been derived by Suzuki *et al.* based on dynamic mechanical analysis and Fourier transform infrared spectrography data[21].

Phenomenological analysis of the thermodynamic characteristics of blends made in terms of the available equations of state would provide information about their molecular parameters. As to direct observations of the microstructure, these may be only possible with the help of light, X-ray and neutron scattering methods. These methods enable one to ascertain the structural features of the blends, the magnitude of fluctuations of density, concentration and orientation, and the free volume of the system.

Density fluctuations are determined by Ruland[22] as

$$Fl=\frac{N^2}{\bar{N}}=\lim_{s\to0}\frac{I(s)}{Nf^2(s)}=\lim_{s\to0}\frac{I_{\mathrm{el\,un}}(s)}{\rho_e}=\rho_e kT\beta \qquad (4)$$

where N is the number of monomers, $f(s)$ is the atomic (monomeric) structure factor, $s=4\pi\sin\theta/\lambda$ and ρ_e is the electron density. It appeared that, for the polymer studied, the values of the thermal density fluctuations for the infinitely fluctuating volume, as determined by extrapolating the linear section of the scattering curve in the coordinates $\lg I-2\theta^2$, are: $Fl=2.740$ for PEO-2, $Fl=2.050$ for PEO-125 and $Fl=0.658$ for PMMA (393 K); for the system PVDF/PMMA (493 K) $Fl=5.490$ for PVDF and $Fl=1.018$ for PMMA. Note that the differences in the Fl values for PEO, PVDF and PMMA reflect those in the values of the isothermal compressibility, β, of the polymers.

Table 1 shows the scattering intensity I_0 for the polymers and blends studied, which has been determined by the procedure described in Reference 22. As seen from the table, the blends are characterized by a higher scattering intensity than the individual polymers. The liquid systems which are homogeneous at the macroscopic level are known to make an additional contribution to the thermal density fluctuation value in the form of composition (concentration) fluctuations. It has been concluded[23] that, for the melt PEO-2/PMMA, the behaviour of $I_0(w)$ cannot be explained only by density fluctuations, but implies the existence of composition fluctuations as well. Evidently, the same explanation is valid for the behaviour of $I_0(w)$ in other systems considered here: PEO-125/PMMA and PVDF/PMMA. Moreover, the existence of such significant composition fluctuations (see *Table 1*) should not be associated with any geometry of the domain structure type. Concentration fluctuations are known to develop in low molecular systems which are not liable to separation (e.g. low molecular alcohol solutions in high molecular solutions, alcohol solutions in benzene[24]). Such fluctuations may be due to the difference in both the forces of intermolecular interaction (see *Figure 3*) and the size and topological features of the monomeric units of the polymers studied. At the same time, the systems treated here may also be considered microheterogeneous (weakly segregated) at a segment level[20,25].

CONCLUSIONS

Analysis of the experimental studies of the systems PEO/PMMA and PVDF/PMMA leads to the following conclusions.

The miscibility of the components of the blend melt is due to specific interactions between the components. The miscibility results in homogeneity of the melt at a macroscopic level of the order of the coil size and in negative deviations from additivity for the specific volume, bulk thermal expansion and isothermal compressibility coefficients over the entire range of compositions of PEO/PMMA and, at $w=0.25$, of PVDF/PMMA. An increase in the molecular weight of one of the components leads to a decrease in the negative excess thermodynamic parameters of the melt and, hence, to deterioration of the miscibility of the components.

Analysis in terms of the Sanchez–Lacombe equation of state, applied systematically to the melts over a wide range of temperatures and pressures, has shown that the 'excess' characteristic parameters reflect actual physical alterations which occur in the blends under effects of temperature and pressure. From analysis of the dependences $\chi_{12}(T)$ and $\chi_{12}(P)$, one may derive conclusions on the position of the CST for the polymer pairs studied, and assess quantitatively the miscibility level for the components of the system.

For most of the PEO/PMMA blends, the parameter

Table 1 Scattering intensity I_0[a] for PEO/PMMA and PVDF/PMMA samples

	$w=0$	0.1	0.2	0.4	0.9	1.0
PEO-2/PMMA, $T=393$ K	7.11	10.43	15.74	–	17.05	2.37
PEO-125/PMMA, $T=393$ K	5.64	13.25	19.89	37.28	19.61	2.37
PVDF/PMMA, $T=453$ K	22.11	25.28	38.36	–		3.55

[a] $I_0\times10^{-23}$ (el^2 cm^{-3})

χ_{12} decreases with increasing pressure. For some of the blends PEO-2/PMMA, $(d\chi_{12}/dP)_T$ changes sign from negative to positive over the pressure range studied, due to the change of the 'sign' of the thermal pressure coefficient; evidently, this is related to variations of the network of specific interactions. The weak temperature dependence of the parameter $\chi_{12}<0$ at $(d\chi_{12}/dT)_p>0$ evidences the presence of a high LCST in the system PEO/PMMA. The parameter χ_{12} for blends PVDF/PMMA increases with pressure due to deterioration of the miscibility of the components. The temperature and pressure dependences of χ_{12} $(d\chi_{12}/dT)_p<0$, $(d\chi_{12}/dP)_T>0$ points to the existence of an UCST that is relatively close (from below) to the temperature range under consideration.

In spite of the components' miscibility at a 'macro-level', the blends studied exhibit significant composition fluctuations at a segment level, which manifest themselves in positive deviations of electron density fluctuations from additivity.

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