erized monolayers was particularly efficient for enhancing the barrier capacity of very thin multilayers.

Registry No. B, 116910-53-3; C, 116926-37-5; KBr, 7758-02-3.

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Sensitivity of Ternary Phase Diagrams of Miscible Polymer Pairs in Common Solvents to Traces of Water: Solvent–Poly(ethyl acrylate)–Poly(vinyl propionate) and Solvent–Poly(methyl acrylate)–Poly(vinyl acetate) Systems

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Received March 4, 1988;
Revised Manuscript Received June 22, 1988

A miscible polymer pair in a common solvent gives rise to clear solutions at all compositions, or the triangular phase diagrams of the solvent (1)–polymer (2)–polymer (3) contain closed immiscibility loops.[1-3] Quite a few of these diagrams have been published in the literature.[3-9] The miscibility of closely similar polymer pairs has been studied in this laboratory for some time.[7,10,11] The phase diagrams of solutions of one such pair, poly(methyl acrylate) (PMA)–poly(vinyl acetate) (PVAc), in solvents such as toluene and 1,2-dichloroethane have been published from this laboratory by Nandi et al.[7] The phase diagrams contained closed immiscibility loops. While continuing these studies using an analogous miscible polymer pair, poly(ethyl acrylate) (PEA) and poly(vinyl propionate) (PVPr), we discovered that traces of water which remain in the systems under the usual experimental conditions, unless extremely stringent precautions are taken, bring about inhomogeneity in some of the ternary solutions at subambient temperatures. The closed immiscibility loops observed in the phase diagrams in the paper of Nandi et al. referred to above resulted from the presence of traces of water in the systems. Under the stringently dry conditions these do not appear. In this note we report the results of phase studies for the miscible polymer pair PEA + PVPr in common solvents with special reference to the effect of traces of water on the homogeneity of the ternary solutions.

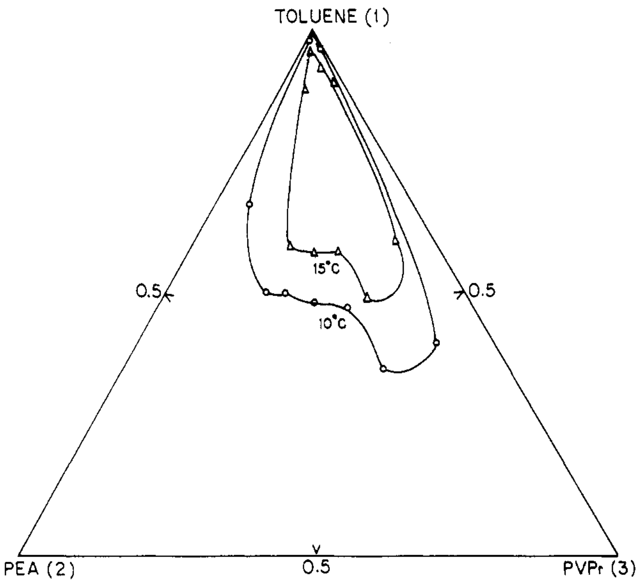

Figure 1. Ternary phase diagram of toluene (1)–PEA (2)–PVPr (3) at the indicated temperatures (normal sealing technique).

Experimental Section

PEA ($\bar{M}_n$ = 773 000) and PVPr ($\bar{M}_n$ = 34 700) were whole polymers prepared in the laboratory.[10] The solvents used were of analytical reagent grade. They were purified by standard methods,[12] dried over Drierite, and distilled before use. Two different procedures were adopted for making the ternary solutions. In the first method (the normal technique), a polymer blend (blended by dissolution in a common solvent and casting film) was weighed into a tared dry Corning glass tube (7 mm × 20 cm), the required amount of a dry solvent was added, and the tube was sealed without cooling the solvent. The small loss of solvent during sealing was determined from the weights of the sealed-off parts and the initial weights and due correction in composition was made. In the second method (vacuum line transfer technique), dry and degassed (freeze–thaw process) solvent was stored over Drierite (with indicator) in one section of a greaseless vacuum manifold. A polymer blend was weighed into a tared Corning glass tube (7 mm × 20 cm) provided with a flange. The tube was attached to the vacuum line through a flange joint, evacuated to $\sim 10^{-5}$ Torr, and pumped for 1 h. The solvent was then transferred into the tube from the reservoir to a predetermined level. The tube was then sealed. The sealed-off parts were weighed, and the amount of solvent transferred was estimated from these weights and the initial weight of the tube with the polymers.

The tubes sealed by both methods were kept at 70–80 °C for 4 days to ensure dissolution of the polymers. They were then slowly cooled, and the cloud points were visually noted as reported previously.[7]

Results and Discussion

The common solvent solubility of the blends was studied in the following solvents; ethyl acetate, ethyl propionate, acetone, methyl ethyl ketone, chloroform, benzene, 1,2-dichloroethane, toluene, and chlorobenzene. First, the clarity of the solutions of the 1:1 blend at 10 and 50 wt % concentrations prepared by the normal sealing technique was examined. The solutions were found to remain clear over the temperature range −30 to 100 °C except for toluene and chlorobenzene, where cloudy solutions were obtained at subambient temperatures. The cloud points of solutions of various other compositions in these two solvents were then determined, and the phase diagrams shown in Figures 1 and 2 were constructed. These diagrams were very similar to those obtained by Nandi et al. for the solvent–PMA–PVAc system and may be explained

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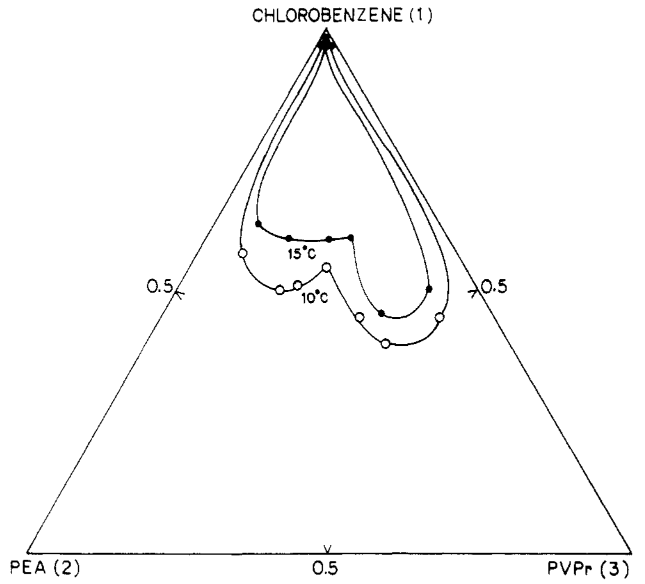

Figure 2. Ternary phase diagram of chlorobenzene (1)–PEA (2)–PVPr (3) at the indicated temperatures (normal sealing technique).

in the same way as Nandi et al. did.[7]

However, subsequent experiments revealed that the phase separation at subambient temperatures in toluene and chlorobenzene was very sensitive to traces of water.[11] Thus, when the vacuum line transfer method was used to prepare the solutions the closed immiscibility loops shown in Figures 1 and 2 no longer appeared at 10 and 15 °C but moved to lower temperatures through 30 or 40 °C. However, even this latter procedure failed to yield solutions dry to the level effected by Drierite since it was found that even the two pure solvents so prepared become cloudy at temperatures much above the freezing points of the solvents at around −20 to −30 °C, which are not reproducible, and addition of a small piece of Drierite (8 mesh) in the tube prior to sealing eliminates the cloudiness. Like the pure solvents the ternary solutions did not turn cloudy even when they were cooled to temperatures close to the freezing points of the solvents (−95 °C for toluene and −45 °C for chlorobenzene) if a small piece of Drierite was added to the system before sealing by using either of the two methods of sealing. On the other hand, when toluene saturated with water was used as a solvent, the cloud points of the ternary solutions increased to values 20–30 °C higher (depending on composition) than those of the solutions containing traces of water (normally sealed situation, Figure 1).

Essentially similar results were obtained by us for the analogous system toluene–PMA–PVAc previously studied by Nandi et al.[7] for which they reported phase diagrams with closed immiscibility loops as mentioned in the introduction.

The inhomogeneity or incompatibility of a miscible polymer blend in a ternary solution has been explained by Patterson et al.[1,3] They showed both theoretically and experimentally that a cloudy ternary solution results when the difference in strength of interaction of the solvent with the polymer (i.e., $|\chi_{12} - \chi_{13}| = |\Delta\chi|$) exceeds a critical value that is dependent on χ_{1i} as well as the segment numbers of the polymers, which in turn depend on the molecular weights of the polymers and the solvent, which serves as a reference (segment number unity). For $\chi_{23} = 0$ these critical values are called the tolerated $|\Delta\chi|$. These values given in Table I for the present system have been calculated according to Patterson et al. by using χ_{12} or χ_{13} values that have been determined by us using the inverse gas chromatographic (IGC) method (values extrapolated to 30 °C were used[11]). Table I also shows the experimental $|\Delta\chi|$ values obtained by way of extrapolation to 30 °C of the IGC-determined χ_{1i} values obtained at four temperatures, viz., 60, 80, 100, and 120 °C. From the data given in Table I it is predicted from the $|\Delta\chi|$ theory that clear solutions will be obtained at room temperature (30 °C) in all the studied solvents except toluene, ethyl propionate, and chlorobenzene. However, obtaining clear solutions in these latter solvents under real dry condition does not necessarily invalidate the $|\Delta\chi|$ theory. Previously, Nandi et al. showed that $|\Delta\chi|$ varies markedly with polymer concentration,[7] the $|\Delta\chi|$ being lower for dilute solutions than for concentrated solutions so that viscometrically determined $|\Delta\chi|$ fails to support the $|\Delta\chi|$ theory, whereas the IGC-determined $|\Delta\chi|$ does support it.[7] In view of this composition dependence of $|\Delta\chi|$, the IGC-determined $|\Delta\chi|$ would not be appropriate for testing the $|\Delta\chi|$ theory, particularly when the values are small.

Table I
Experimental $|\Delta\chi|$ and Tolerated $|\Delta\chi|$ (Theoretical) Values

solvent	$d|(\Delta\chi)|/dT \times 10^4$ [a]	$|\Delta\chi|$ at 30 °C[b]	tolerated $|\Delta\chi|$
benzene	3	0.04	0.09
toluene	−3	0.10	0.08
acetone	10	0.03	0.08
methyl ethyl ketone	5	0.02	0.09
ethyl acetate	0	0.06	0.10
ethyl propionate	−2	0.11	0.08
chloroform	−7	0.08	0.12
1,2-dichloroethane	−3	0.04	0.12
chlorobenzene	−7	0.14	0.12

[a] Calculated from χ_{12} and χ_{13} values determined by IGC at 60, 80, 100, and 120 °C. [b] Extrapolated value.

However, the cloudy solutions in presence of traces of water in toluene and chlorobenzene may be explained in the following way. An examination of the χ_{1i} data published in the literature reveals that for a given polymer pair and a series of solvents the IGC-determined $|\Delta\chi|$ is largest with the poorest solvents for both polymers.[7,13] The solvent with a trace of water in it could be treated as a single solvent with the difference that the water makes it a poorer solvent for both the polymers. This may result in an increase in the values of $|\Delta\chi|$. The theoretically calculated tolerated $|\Delta\chi|$ for solvent (1)–PEA (2)–PVPr (3) systems, obtained by using arbitrary χ_{12} or χ_{13} values, showed that as the solvent becomes poorer (i.e., χ_{12} or χ_{13} values are increased with χ_{23} fixed) the tolerated $|\Delta\chi|$ decreases only marginally. We therefore hypothesize that inhomogeneity in some of the ternary solutions is due more to the effect of the moisture-induced poor solvent increasing the values of $|\Delta\chi|$ rather than to decreasing tolerated $|\Delta\chi|$. However, the present results should not be used to interpret that all the closed immiscibility loops reported in the literature are caused by traces of moisture. The closed immiscibility loops in many reported systems are associated with much larger $|\Delta\chi|$ values than found here. Reference 3, for example, reports $|\Delta\chi|$ values like 0.45 − 1.05 for the solvents that showed closed immiscibility loops. These values are much larger than the tolerated $|\Delta\chi|$ and the immiscibility loops will arise because of these intrinsically large $|\Delta\chi|$ values, and the results will not be qualitatively altered by the presence of traces of moisture.

Finally, it should be noted that although $|\Delta\chi|$ for ethyl propionate solvent at 30 °C is comparable to that of toluene (Table I), a trace of water does not induce phase separation when the former is used as the solvent. This fact may suggest that the sensitivity of cloud points to traces of water becomes greater the lower the solubility of water in the solvent.[14]

Conclusion

From the results presented here it turns out that the real dry ternary solutions of the blend system PMA–PVAc investigated by Nandi et al. and the newly discovered miscible pair PEA–PVPr are homogeneous at all compositions in the solvents investigated, testifying to the compatibility of these blend systems. The inhomogeneity of some of the ternary solutions reported by Nandi et al. earlier was due to the presence of traces of water in the systems.

Acknowledgment. Thanks are due to Prof. D. Patterson of McGill University, Canada, for helpful discussion.

Registry No. PMA, 9003-21-8; PVAc, 9003-20-7; PEA, 9003-32-1; PVPr, 25035-84-1; toluene, 108-88-3; chlorobenzene, 108-90-7; water, 7732-18-5.

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End-Confined Polymers: Corrections to the Newtonian Limit

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Received March 21, 1988; Revised Manuscript Received May 26, 1988

In recent papers Milner et al.[1,2] described a new method to determine the statistics of "end-confined" polymers, such as polymers densely grafted to a surface. The method augments the established approaches of Helfand and Wasserman[3,4] and of Scheutjens and Fleer.[5] These authors reduce the many-chain problem to that of a single chain in a space-dependent monomer chemical potential. This chemical potential must be determined self-consistently in terms of the local concentration of monomers. The statistical mechanics of such a polymer was shown by Edwards[6] to be equivalent to the quantum mechanics of a Schrödinger particle moving in a potential proportional to the monomer chemical potential. The Helfand–Wasserman and Scheutjens–Fleer treatments provide explicit procedures for solving this self-consistent quantum-mechanics problem. Our new method amounts to the observation that for large molecular weight the quantum mechanics reduces to classical Newtonian mechanics. The new method then solves the Newtonian problem without further reference to the underlying quantum mechanics.

The new approach leaves some important formal issues unsettled. Since the connection to Newtonian mechanics is made at the most general level, it is not clear how the Newtonian solution of ref 1 emerges explicitly from the quantum-mechanical description. In particular, our Newtonian description treats the probability density of the free chain end as a quantity to be determined self-consistently, in addition to the chemical potential profile. This end density may vary *independently* of the potential. Thus for chains of given molecular weight and coverage, the potential profile is a fixed parabola, but the required end density is different for a melt, for an Edwards solvent,[7] and for a Flory–Huggins equation of state. This contrasts with the quantum description, where only the potential is to be determined; the free-end probability density is fixed in terms of this potential. The two pictures appear mutually contradictory; one implies that there are two independent functions to be determined; the other states that there is only one.

The purpose of the present paper is to resolve this apparent contradiction. We show that the end density profile in the Newtonian limit is indeed determined by the potential. But variation in this potential required to shape the end density profile becomes indefinitely small relative to the potential as calculated in ref 1. The required perturbing potential may be expressed as a simple integral transform of the logarithm of the end density.

An end-confined polymer of N statistical segments with one end attached at the position $z = 0$ may be described by its Edwards propagator $G(n;z,z')$. This G is the partition function for a section of n segments beginning at height z and ending at height z', relative to the overall partition function of a free random walk of n segments. The propagator G for an end-confined chain is nontrivial because the chain interacts with the other chains. Each monomer of the chain in question displaces other chains; the free energy cost to place a monomer at z amounts to a position-dependent monomer chemical potential, which we denote $V(z)$ (in units of kT).

The Edwards propagator of a chain in the potential $V(z)$ obeys the heat or Schrödinger equation:

$$\partial G/\partial n = \nabla_z^2 G + V(z)G$$

Thus G behaves much like the wave function of a quantum particle in the potential $-V$. From this G one may calculate the local monomer concentration $\phi(z)$ and finally impose the requirement of consistency between the local monomer chemical potential $V(z)$ and the local concentration $\phi(z)$; e.g., $V(z) = \sigma w \phi(z)$, where σ is the number of chains per unit area and w measures the strength of the interaction.

Once a self-consistent $V(z)$ has been found, the free energy of the chain passing from the attachment point to some z_0 is simply $[\log G(N; 0, z_0)]$. For large N and fixed coverage σ we found[1] that the "quantum" propagator G attains the limiting behavior describing classical Newtonian motion. Then the free energy of a chain becomes the action $S(z_0)$ of a Newtonian particle of unit mass starting from rest at z_0 in the potential $-V(z)$ and ending at $z = 0$. We found that $V(z)$ must be parabolic with a curvature independent of σ in this limit. For this parabolic potential, the action S is independent of z_0 and is of order N. But viewed in another way, $S(z_0)$ cannot be completely independent of z_0, since the free energy of a chain at z_0 controls the probability $\epsilon(z_0)$ that a chain ends there:

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