Communications to the Editor

Rigid Backbone Polymers. 5. Preliminary Ternary Phase Diagrams of Poly(isocyanates)

In a recent series of publications a statistical thermodynamic theory was developed by Flory[1-7] describing the behavior of mixtures of rodlike polymers. Accordingly, when a solution of rigid molecules separates into isotropic and anisotropic phases coexisting in equilibrium, the concentration of the polymer in the anisotropic phase, v_2', is higher than its concentration, v_2, in the isotropic phase. Also, the molecular weight of the polymer in the anisotropic phase is higher than in the isotropic phase.[1,2,4,5] Furthermore, the theory predicts that in a ternary mixture of one solvent and two polymers, the phase relationship depends on the rigidity of the polymers. In a solvent/rigid polymer/flexible polymer system, the solution is isotropic at concentrations below v_2^*, the critical concentration for the appearance of an anisotropic phase. Above v_2^* two phases, isotropic and anisotropic, coexist for all mixtures in which more than a negligible amount of both polymers is present.[6] It is obvious that v_2^* will depend on the relative amounts of the two polymers in the mixture and on their molecular weight. In a solvent/rigid polymer/rigid polymer system, the solution will be isotropic at all concentrations below v_2^*. At polymer concentrations, v, above v_2^*, two phases coexist, and at even higher v, the isotropic phase disappears and a single, anisotropic, phase obtains.[1,3]

Using concentrated solutions of mesogenic poly(isocyanates), we have demonstrated in previous papers[8,9] that the first of the theoretical predictions, viz., partition of a higher concentration and higher molecular weight fractions of the polymers into the anisotropic phase, indeed occurs. Similar observation was reported by Kwolek et al.[10] on solutions of poly(1,4-benzamide) in tetramethylurea–LiCl.

In this communication, preliminary and partial ternary phase diagrams are presented which, in our opinion, substantiate Flory's theory. Due to the experimental difficulties associated with the extremely high viscosities of the investigated systems, the range of total polymer concentration is limited to less than 50% by volume. In all cases, the solvent was tetrachloroethane (TCE), and the temperature was 25 °C.

Figure 1 is for poly(octyl isocyanate) of intrinsic viscosity of about 2.4 dL/g in chloroform, polystyrene (PS) of $M = 4000$ (lot No. 11b of Pressure Chemical Co., $M_w/M_n < 1.10$), and TCE. Figure 2 is for poly(50% butyl + 50% *p*-anisole-2-ethyl isocyanate) of intrinsic viscosity of 0.93 dL/g in chloroform, PS of $M = 4000$, and TCE. Figure 3 is for a mixture of the two poly(isocyanates) above with TCE. The phase diagrams were constructed from microscope observations using cross-polarized light. Depending on their concentration and viscosity, samples corresponding to each datum point in the phase diagrams were observed after up to 2 weeks from the time of their preparation. In this way it was hoped that a state of equilibrium was attained.

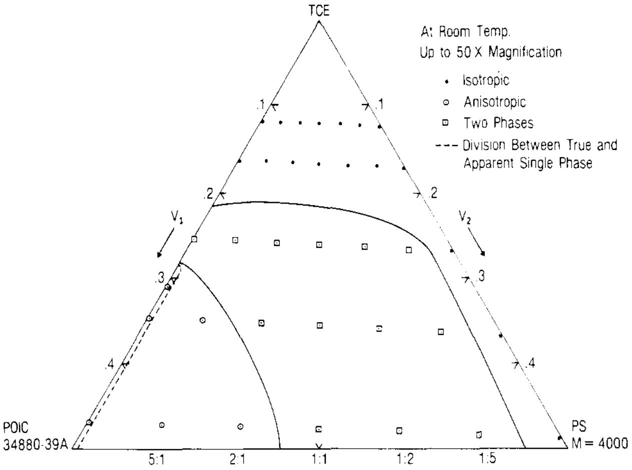

Figure 1. Ternary phase diagram of poly(octyl isocyanate)/PS/TCE at 25 °C up to 50× magnification: (●) isotropic phase; (⊙) anisotropic phase; (□) two phases; --- division between true and apparent anisotropic single phase.

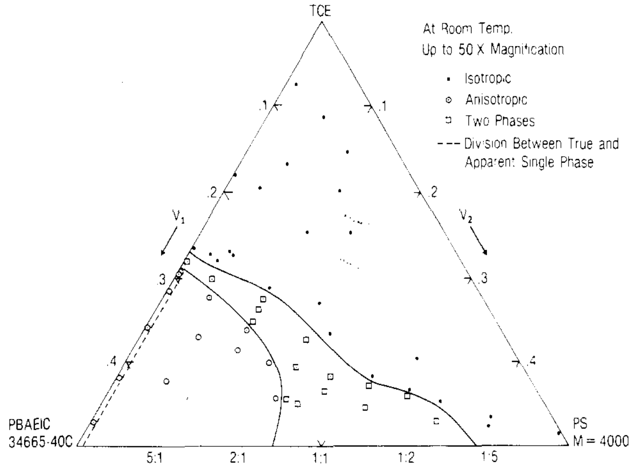

Figure 2. Ternary phase diagram of poly(50% butyl + 50% *p*-anisole-2-ethyl isocyanate)/PS/TCE. Same conditions and same legend as in Figure 1.

In Figures 1 and 2 there exists in the poly(isocyanate)-rich part of each diagram a region that appears to be a single, anisotropic phase when observed with the naked eye or under magnification lower than 50×. Under higher magnification, one may observe occasional minute isotropic inclusions in the anisotropic matrix. This region of the phase diagrams is bound on one side by the range clearly exhibiting two phases and on the other side by a truly single anisotropic phase, in which the PS concentration approaches zero. The dashed lines in Figures 1 and 2 are not accurate with respect to concentration and are merely drawn to indicate that a single anisotropic phase indeed exists at the limit where the concentration of the polystyrene becomes vanishingly small. The solid lines, especially in Figures 1 and 3, are drawn about halfway between experimental data points, but the exact position of the phase boundary between the relevant points is not known for sure as of now.

The preliminary data presented above indicate a general agreement between the experimental observations on poly(isocyanates) and the theoretical predictions. The regions of apparently anisotropic single phase in Figures 1 and 2, brought about by the occlusion of minute isotropic droplets in the anisotropic matrices, are apparently a result of the very high viscosity of the systems. It was previously shown that such inclusions tend to reach an equilibrium size.[9] It may well be that only repeated centrifugation will

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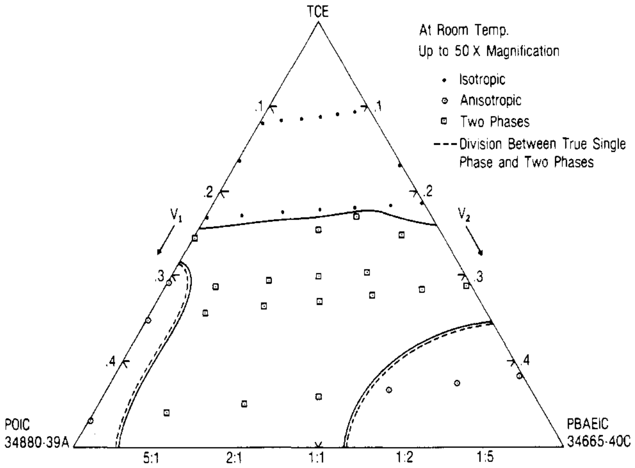

Figure 3. Ternary phase diagram of poly(octyl isocyanate)/poly(50% butyl + 50% *p*-anisole-2-ethyl isocyanate)/TCE. Same conditions and same legend as in Figure 1.

remove the isotropic inclusions completely.

The anisotropic single phase in Figure 3, containing substantial amounts of both poly(isocyanates), appears under high magnification as a truly single phase. Furthermore, the corresponding samples produced NMR spectra indicating them to belong to a single anisotropic phase on the molecular scale level. A detailed discussion of the NMR spectra of poly(isocyanates) in these and in additional phase diagrams is soon to be published.[11]

The existence of a single anisotropic solution containing substantial amounts of both poly(isocyanates) strongly supports, we believe, Flory's theory.[1-7]

References and Notes

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Hysteresis Behavior in Polyether Poly(urethaneureas) Based on 2,4-Toluene Diisocyanate, Ethylenediamine, and Poly(tetramethylene oxide)

Thermoplastic poly(urethanes) and poly(urethaneureas) are linear segmented copolymers which consist of alternating hard (aromatic urethane or urea) and soft (aliphatic polyether or polyester) segment units. The properties of these materials depend largely on the extent of microphase segregation of soft and hard segments which arises from their thermodynamic incompatibility. Compositional variables such as the symmetry in the diisocyanate structure,[1] the chain extender,[2] the molecular weight, and the molecular weight distribution[3] of the soft and the hard segments are known to have a strong influence on the extent of phase segregation, the domain organization, and thus the polymer properties.

Table I
Characterization of Polyether Poly(urethaneureas) Based on 2,4-TDI, Ethylenediamine, and Poly(tetramethylene oxide)

sample	$M_n \times 10^{-3}$	e	T_g,[b] °C	T_g,[d] °C
2,4-TDI-ED-PTMO 1000				
2:1:1[c]	21	29	−53	192
3:2:1[c]	28	39	−54	190
4:3:1[c]	33	47	−58	190
5:4:1[c]	43	53	−55	180
6:5:1[c]	27	57	−61	184
2,4-TDI-ED-PTMO 2000				
3:2:1[c]	36	24	−75	180
4:3:1[c]	34	30	−74	190
5:4:1[c]	35	36	−73	186
6:5:1[c]	25	40	−78	191

[a] Hard-segment content is equivalent to total urea content. [b] T_g of the soft-segment phase. [c] No crystallinity observed in these samples. [d] T_g of the amorphous hard segment domain. [e] Hard-segment content in wt % (footnote *a*).

The presence of the hard segment domains is widely recognized as being responsible for the high tensile strength and modulus exhibited by these materials. However, the presence of the domains was also throught to be responsible for the stress softening, a serious deficiency in many applications under cyclic loading conditions due to the heat buildup.[4] Several attempts to minimize this problem have been made.[5] One successful method was to cross-link the polymer with triol.[4] This treatment disrupts the domain structure, thereby reducing hysteresis under cyclic loading. However, this also leads to a reduction in the modulus and the tensile properties. Moreover, the polymer is no longer thermoplastic. An alternate way has been reported where orientation followed by heat setting is used which presumably breaks the interconnectivity of the domain and reduces the heat buildup problem.[6]

In our continuing studies of segmented poly(urethanes) and poly(urethaneureas) toward establishing structure–property relationships, we have recently reported that the incorporation of the urea linkage via ethylenediamine (ED) as a chain extender leads to a drastic improvement in microphase segregation and domain structure, even with asymmetric diisocyanate such as 2,4-toluene diisocyanate (2,4-TDI).[2,7,8] For example, in polyether poly(urethaneureas) consisting of 2,4-TDI, ED, and PTMO (poly(tetramethylene oxide), mol. wt. 1000 or 2000), the phase segregation and domain structure were greatly improved as compared with diol extended analogues.[2] This was evidenced by the lower T_g of the soft-segment phase and the higher T_g of the amorphous hard-segment domain. The presence of the amorphous domain was also supported by small-angle X-ray scattering studies.[2] Between the PTMO 1000 and the PTMO 2000 series, polymers containing 2000 molecular weight polyether exhibited better phase segregation, as illustrated in Table I. The T_g of the soft-segment phase for the PTMO 1000 series is around −55 °C, while that for the PTMO 2000 series is −75 °C which is only a few degrees higher than the T_g of the free soft segment. This result indicates that the amount of the solubilized hard segment in the soft segment phase in the PTMO 2000 series is very small if any, because tying down both ends of the soft segment would likely contribute to

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