Solvation and Phase Separation in ABA Block Copolymers

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Synopsis

A conceptual scheme is presented for classifying the phase behavior of ABA block copolymers and solvents. The effect of solvent fraction ϕ_S on *microphase* separation is described for macroscopically homogeneous systems, but more attention is focused on the limits of solubility. A "miscibility map" is developed in terms of solubility parameters δ_A, δ_B, and δ_S and used to define regions of *macrophase* separation, complete miscibility, and partial miscibility. Combined with known triblock molecular structure, the miscibility map can be used to predict the character of solvated systems and guide the selection of solvents for special purposes. A survey of reports in the literature shows qualitative consistency with this treatment. New observations are reported on solvation of a polystyrene–polybutadiene–polystyrene polymer in numerous solvents; these are used to infer microstructural information and define the miscibility map more realistically.

INTRODUCTION

Thermodynamic incompatibilities of the A block and B block of block copolymers lead to microphase formation in the bulk polymer when temperature is reduced below T_s, the "separation temperature" defined by Leary and Williams.[1,2] This may occur also in the presence of a plasticizer or solvent (T_s is depressed in such cases[3,4]); but with solvent, a greater variety of phase separation possibilities can exist. The physical character of such ternary systems will depend on polymer molecular topology as well as on solubility phenomena.

We present here an outline of the spectrum of phase behavior and follow with a description of qualitative experiments performed with an ABA "thermoplastic elastomer" in a variety of solvents. This discussion establishes concepts and terminology which should prove useful with such systems in general and specifically illustrates restrictions on theoretical work published elsewhere.[3]

PHASE EQUILIBRIA CONCEPTS

Bulk Polymers

In the bulk copolymer, sufficient heating creates an assembly of *randomly* oriented blocks, even though mutual repulsion of A and B blocks within a single molecule provides some intramolecular orientation. This establishes an effective state of homogeneity, with no intermolecular correlation. Upon cooling, this assembly lapses at T_s into an ordered state wherein the A blocks of separate

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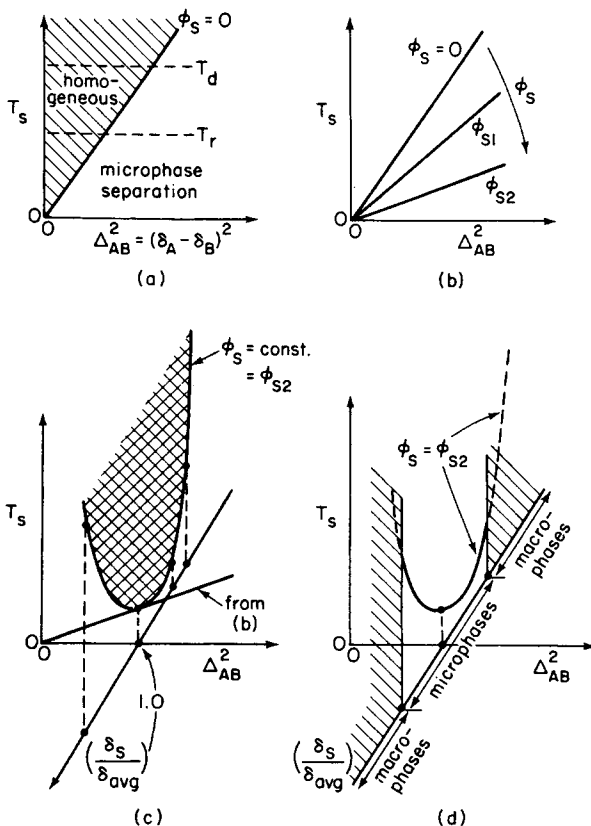
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Fig. 1. Variation of separation temperature T_s with several parameters for a copolymer with blocks of A and B and fixed molecular weight. (a) Dependence on A–B compatibility, approximated in terms of solubility parameters, for the bulk polymer. Note the importance of T_s relative to thermal decomposition and room temperatures, T_d and T_r, respectively. (b) Dependence on solvent content (ϕ_S) for a completely miscible system. (c) Dependence on solvent affinity for the two blocks for a fixed solvent content (e.g., ϕ_{S2}) in a hypothetically completely miscible system. Here, $\delta_{av} = (\delta_A + \delta_B)/2$, and T_s is minimized when $\delta_S = \delta_{av}$. (d) Limitations imposed by macrophase separation in poor solvents for a fixed solvent content.

molecules aggregate and the B blocks do likewise, forming a microstructure of characteristic dimension only slightly larger than the blocks themselves. Hence, this is termed *microphase* separation.

The high degree of long-range order in such systems permits geometric idealization of the aggregate morphology (m) whose formation from the random state occurs at $T_s{}^{(m)} = \Delta H_m/\Delta S_m$ when $\Delta G_m = 0$. Of the many geometries possible, the one formed first, i.e., with highest T_s, is expected to prevail at lower temperatures.

For bulk ABA copolymer, the dependence of T_s on the chemical nature of A and B is represented schematically in Figure 1(a). We use solubility parameters δ_A, δ_B, and later δ_S (for solvent) for chemical characterization,* and Figure 1a is influenced primarily by the fact that $T_s \sim \Delta H \sim M(\delta_A - \delta_B)^2$, where M is polymer molecular weight.[1]

* It should be realized that the forthcoming conceptual picture is not limited to the use of solubility parameters, which have well-known deficiencies.

Numerical calculations with any model show that T_s can be very high when M is large and $|\delta_A - \delta_B| > 1$, often well into the thermal decomposition range. To illustrate: a polystyrene–polybutadiene–polystyrene (PS–PB–PS) polymer with $M = (12.5 + 75 + 12.5) \times 10^3$, for which $(\delta_A - \delta_B) \approx 0.8$, has $T_s \approx 317°$C according to the Leary–Williams model[1] and a number of recent experiments.[2] But continued exposure of the PB block to temperatures in excess of 180°C causes[2] degradation and crosslinking. This limits processing to a temperature range T_p ($<180° < T_s$) where substantial microstructure exists, with great uncertainties in "melt" rheological properties. Reduction of T_s by the addition of a solvent might be desirable.

Conversely, a copolymer may be homogeneous even at room temperature if $T_s < T_{room}$. A sample of PS–PB–PS described elsewhere[2] has this property because of low M (49,000), and PS–poly(α-methylstyrene) block copolymers often described as homogeneous[5] are perceived this way because $|\delta_A - \delta_B|$ is small.

Solvated Block Copolymers

There are several reasons for studying carefully the role of solvent. Plasticizer or other solvent may be added deliberately in a commercial operation, or it may be a residue of polymer synthesis. Processing strategies may be influenced by how T_s and T_g (or T_m) vary with solvent volume fraction ϕ_S, the magnitude of these parameters relative to decomposition temperatures, and the nature of various phase separations. From a research standpoint, it is essential to have a framework to classify the great variety of experimental studies being reported.

We seek here to demarcate the boundaries of phase behavior for these ternary systems: coupled polymer blocks of A and B, with solvent S. This should place the study of solvated block copolymers of all types on a more systematic basis than seems to exist at present. For purposes of this discussion, it will be convenient initially to accept the familiar though naive criterion that complete miscibility of A and S can occur when $|\delta_A - \delta_S| < 1$, but phase separation— perhaps with partially solvated A plus supernatant S—exists when $|\delta_A - \delta_S| > 1$.

The simplest possible behavior is that solvent will act primarily as diluent, with no separation taking place on a macroscopic scale (*macrophase* separation). Such would be expected when δ_S is close to both δ_A and δ_B, which is possible only when δ_A and δ_B are themselves close together. Here, a *microphase* separation will occur upon cooling below T_s just as for bulk copolymer, but $T_s(\phi_S)$ is depressed[3,4] below the bulk polymer value (akin to a plasticizing effect on T_g), as shown schematically in Figure 1(b). The T_s depression is sensitive to solvent chemistry primarily in the sense that it is maximized when δ_S equals the average polymer solubility parameter δ_{av}, i.e., when $|\delta_A - \delta_S| = |\delta_B - \delta_S|$, in which case solvent is also distributed uniformly in the microphases [see Fig. 1(c)].

In the other extreme, when S becomes incompatible with both A and B upon cooling, a macrophase separation will occur before T_s for the whole system is reached. Distinct rich and lean phases will appear, the rich phase possibly endowed with a microphase structure because its T_s would be higher (with ϕ_S lower) than for the overall system. This behavior is shown in Figure 1(d) as a boundary constraint on the $T_s(\delta_S)$ envelope of Figure 1(c).

Between these two extremes lie a variety of interesting possibilities corresponding to *preferential* solvation, where S is compatible with either A or B but not both; e.g., $|\delta_A - \delta_S| < 1$ while $|\delta_B - \delta_S| > 1$. This presents a condition of partial miscibility which need not result in two classical macrophases, but rather a gross redistribution of solvent which, depending on polymer structure and solvent affinity, will produce either a colloidal fluid or a swollen gel with supernatant solvent. These possibilities are discussed in more detail below.

SOLVATION

We will subsequently be concerned with the addition of solvent to a bulk ABA copolymer, a process more easily discussed in terms of the "miscibility map" of Figure 2 despite the admitted shortcomings of solubility parameters in representing ΔH. Figure 2 fails to represent temperature and concentration effects and employs distinct linear boundaries rather than more realistic ones, but it serves to focus attention on the primary solvent phenomena.

The compatibility of solvent for blocks A and B is represented by $(\delta_A - \delta_S)$ and $(\delta_B - \delta_S)$, so these "solvent affinity coordinates" are chosen as axes in Figure 2(a). By arbitrarily taking $\delta_A > \delta_B$, we limit physical reality to the half-space below a 45° line through the origin. The region of hypothetically complete polymer/solvent miscibility, homogeneous on the macroscopic scale, is bounded by this line and the lines $(\delta_A - \delta_S) = 1$ and $(\delta_B - \delta_S) = -1$ to form the "miscibility triangle" (shaded). Total immiscibility is represented by the three crosshatched regions; there, two distinct macrophases should exist. The two intermediate regions running along the axes from the miscible boundary to infinity accommodate all intermediate cases. Dashed lines at 45° are loci characterizing the intramolecular block affinity, $\Delta_{AB} \equiv \delta_A - \delta_B$. The length of these lines contained *within* the miscibility triangle is indicative of the range of solvents (i.e., range of δ_S) compatible with both polymer blocks.

Discussion of solvation begins by presuming that *microphase* separation exists in a bulk ABA polymer at the given temperature, so $T < T_s$ ($\phi_S = 0$), and solvent is being progressively added. The physical nature of polymer/solvent mixtures will depend on both solubility phenomena [location of the A/B/S system on the map of Figure 2(a)] and on the microphase morphology. For convenience, we initially define two classes of solvent: those having *equal* affinity for blocks A and B, and those with strong affinity for one block but incompatible with the other.

I. Solvent Has Equal Affinity For Both Blocks

On Figure 2(a), this condition is represented by the dotted line emanating from the origin with slope −45°, meaning that δ_S is precisely intermediate between δ_A and δ_B so $(\delta_B - \delta_S) = -(\delta_A - \delta_S)$. This avoids all conditions of partial miscibility on the figure, implies that solvent must be uniformly distributed within any macrophase (including throughout each microphase structure), and has two types of limiting behavior:

(a) **Strong Affinity.** This can occur only when Δ_{AB} is itself small, near the base of the miscibility triangle, as shown on Figure 2(a) by a heavy superposed line. Complete miscibility prevails on the macroscale, but the preexisting mi-
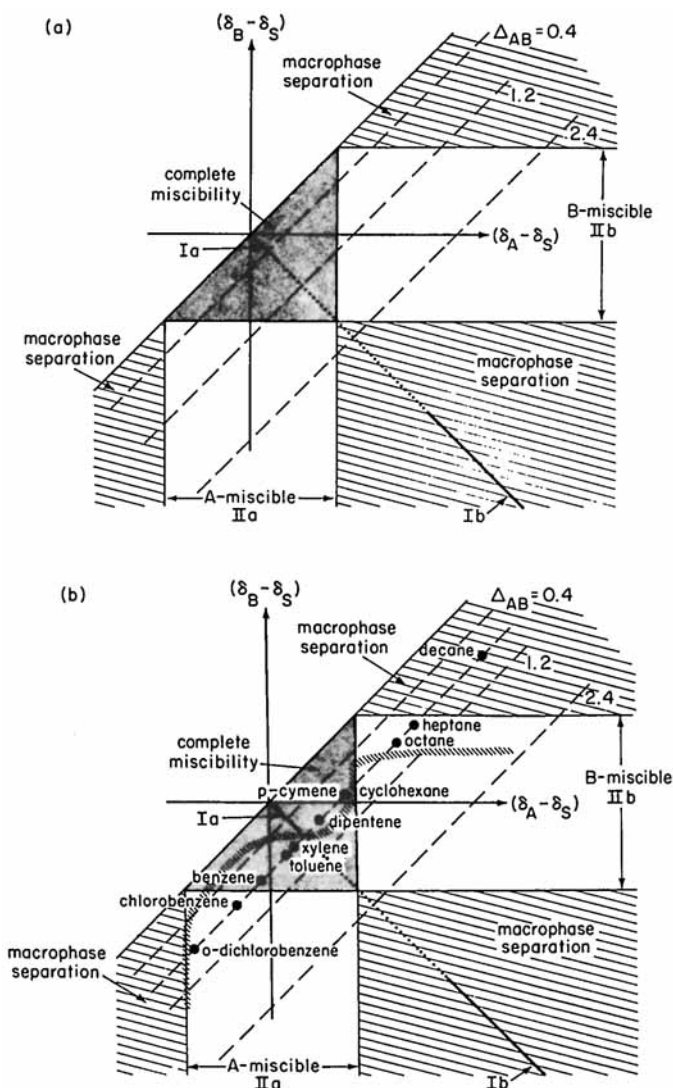
Fig. 2. Miscibility map for solvent S with polymer blocks A and B. (a) Idealized. (b) Accompanies discussion of Kraton 1101 (PS–PB–PS) solvation. The meandering fuzzy line (〰〰〰) represents the real miscibility boundaries implied by these solvation experiments.

crophases retain their identity as solvent is added. As ϕ_S increases, T_s is reduced [Fig. 1(b)] and mechanical properties weaken as the microphases are solvated. Eventually, $T_s(\phi_S) < T$ and the microphases vanish into a homogeneous solution. This thermodynamic transition can happen when solvent is still the minority component, and the polymer is still "concentrated" in conventional terms. (In special circumstances, a mechanical disruption of the microphases might occur somewhat sooner due to forces of solvent swelling and spatial restrictions.)

(b) **Strong Incompatibility.** In the limit, solvent could not penetrate the polymer at all and would remain as a supernatant macrophase with no polymer content. Actually, the polymer will take up a small amount of solvent, swelling slightly, and the macrophase separation will occur at very low ϕ_S. The poly-
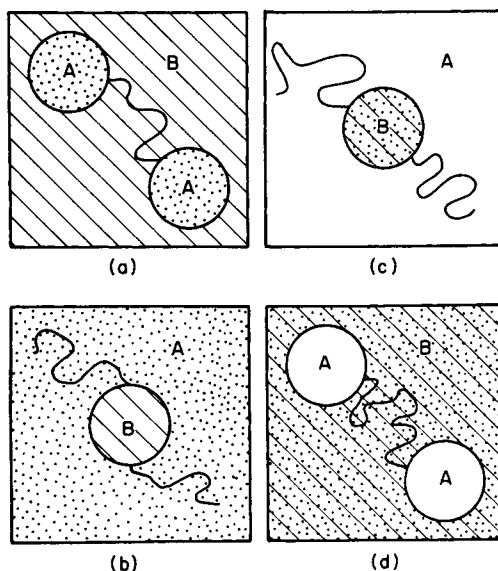
Fig. 3. Discrete morphologies (spheres or cylinders in continuous matrix) for ABA copolymers. Dots represent solvent molecules, phase A is white, and phase B is crosshatched. Shown are limiting class II system of solvent bias. (a) End A blocks favored, and form domains. (b) End A blocks favored, and form matrix. (c) Middle B blocks favored, and form domains. (d) Middle B blocks favored, and form matrix.

mer-rich phase will retain its microphase structure, slightly plasticized and mechanically only slightly weaker than bulk polymer. On Figure 2(a), such behavior corresponds to the heavy line in the immiscible region.

II. Solvent Strongly Biased

This case is represented by all the clear regions of Figure 2(a) and is richer in limiting possibilities than the previous one. We focus on an ABA polymer with B an elastomeric block and A a glassy block (a thermoplastic elastomer, e.g., PS–PB–PS), finding that ABA/S solvation behavior depends on whether the S-preferred block is a molecular end or middle *and* whether it forms the matrix or the domain of the microphase morphology.

(a) **End (A) Blocks Favored.** This is designated as region IIa in Figure 2(a), and two morphologies will be discussed.

1. *Ends in Domains* [Fig. 3(a)]: In the limit of absolute B/S incompatibility, no solvent could penetrate the matrix and an apparent (nonequilibrium) macrophase separation would occur. Even with more realistic B/S incompatibility, solvent permeation through the matrix will be quite slow. Ultimate polymer swelling will depend on how much spatial accommodation for the expanding A domains can be provided by the resilient matrix. The latter becomes limiting, in practice, if the rubbery microphase has sufficient strength. The result of further solvent addition is a supernatant fluid phase and a rubbery macrophase containing nonuniform solvent distribution within its microphases. (Of course, the rubber is above its T_g^{PB} and theoretically can relax in response to stresses produced by the swelling A domains. Given sufficient time, the microstructure

could disintegrate as $T_g^{PS}(\phi_S)$ drops and the glassy domains soften to permit disengagement of A blocks from the domains.)

2. *Ends in Matrix* [Fig. 3(b)]: Here, solvent uptake is not so restricted. After an initial delay, during which the favored matrix absorbs enough solvent to become plasticized and lose its glassy character, the matrix swells rapidly and becomes soft enough to make mechanical breakup (e.g., by stirring) very easy. When geometric limits on A block extensibility are reached, the polymer morphology is disrupted. There occurs a separation characterized by formation of micellar aggregates—having gel-like nature but retaining an internal microphase structure—which are dispersed in solvent. Further increase of ϕ_S serves only to move the micelles further apart, but does not affect their solvent content or size. These micelles could be quite large, containing many domains, and should cause considerable turbidity in the fluidized mixture. Mechanical means could, in principle, break them down to the size of a single-domain core surrounded by a solvated sheath of A blocks.

(b) **Middle (B) Block Favored.** See region IIb in Figure 2(a).

1. *Middle Block in Domains* [Fig. 3(c)]: Permeation of solvent through the glassy A matrix, which also is chemically incompatible, will be extremely slow. Solvent uptake in the compatible domains will be slight because of extreme mechanical resistance to B swelling in the rigid environment. Macrophase separation (not at equilibrium) will occur at very low ϕ_S, the system being composed of a still glassy plastic and supernatant solvent. In less extreme cases, when the glassy matrix is sufficiently plasticized, the plastic could crack or disintegrate under the internal pressure generated within swelling domains.

2. *Middle Block in Matrix* [Fig. 3(d)]: The rubbery matrix is favored and takes up solvent extremely rapidly, ultimately being limited by the existence of anchoring points (glassy domains of A) at both ends of the B block. The polymer will always be in the gel-like solid state, with maximum volume determined by the maximum attainable swelling of the middle blocks. Further increase of ϕ_S results in macrophase separation, with pure solvent plus a gel retaining its microphases.

Lamellar Microstructures. If polymer morphology is initially planar on the microphase level, with alternating lamellae of A and B phases, similar reasoning can be applied. Fewer alternatives need to be considered because A and B are equally accessible to solvent and there are no qualitative differences in exchanging A and B microphases. Class II thermodynamics are coupled to either (a) end-block favored, which leads to disruption of the network and creation of a turbid fluid system, or (b) middle-block favored, producing a swollen sandwich tied together by the rigid anchoring A lamellae. In reality, swelling would not be as great as this suggests because the actual morphology would consist of clusters of (possibly interlocking) planar structures with differing orientation, thereby providing additional volumetric restraints.

EXPERIMENTAL EVIDENCE

Review

A vast number of structural studies have been reported for ABA/S systems, but we shall focus here on rheological observations for reasons of novelty and

Table I
Solvents Tested with Kraton 1101

Solvent	δ_S, (cal/cm^3)$^{1/2}$[a]
n-Decane	6.6
n-Heptane	7.4
n-Octane	7.6
Cyclohexane	8.2
p-Cymene	8.2
Dipentene	8.5
Xylene	8.8
Toluene	8.9
Benzene	9.2
Chlorobenzene	9.5
o-Dichlorobenzene	10.0

[a] From reference 12.

brevity. Paul et al.[6] used a PS–PB–PS polymer with five solvents spanning the "good" range for both blocks, corresponding to the miscible triangle of Figure 2(a) along the line segment for $\Delta_{AB} \approx 0.7$ (= 9.1–8.4, according to them). We would predict that solutions should be easily made—similar to class Ia—and T_s greatly depressed, resulting in complete homogeneity at room temperature. Indeed, their systems all had $\phi_S > 0.7$, no turbidity was reported, and viscosities were entirely unexceptional, giving no hint of microstructural complications.

Identical results were reported by Nemoto et al.[7] for a PMMA–PS–PMMA polymer at $\phi_S = 0.83$ in chlorinated biphenyl (CBP). Since $\delta_{PMMA} \cong 9.4$ and $\delta_{PS} = 9.1$, and δ_{CBP} might be estimated as equivalent to chlorobenzene at 9.5, this system was also in the miscible triangle, on the $\Delta_{AB} = 0.3$ locus. However, in a mixed solvent with one component (DOP) unfavorable to PMMA, a fluid exhibiting viscometric anomalies characteristic of microstructure was obtained. This corresponds loosely to the partially miscible class IIb1, modified by the presence of the good-solvent component (70% DEP) which permitted sufficient solvation to achieve $\phi_S = 0.83$, avoidance of macrophase formation, and the fluid condition.

In a similar but somewhat broader investigation, Kotaka and White[8] tested mixtures of PS–PB–PS in decane ($\delta_{De} = 6.6$), decalin ($\delta_{Di} \cong 8.2$, estimated as equivalent to cyclohexane, solvent for both), and intermediate solvent blends over a range of ϕ_S. Macrophase separation was observed in high-decane content solvents, corresponding to the topmost crosshatched region of Figure 2(a), and no rheology was reported for these systems. Solvents of higher decalin content produced fluid systems whose properties could be measured. Extremely high viscosities existed with solvents just slightly better than those causing macrophase separation, which is consistent with behavior expected of the partially miscible class IIb systems; again, the decalin fraction served to fluidize the microstructure. With pure decalin (in the miscible triangle of Fig. 2), the polymer formed homogeneous solutions when ϕ_S was high, i.e., $T > T_s(\phi_S)$ in our interpretation, although microphase separation was reported at lower ϕ_S, consistent with $T < T_s$.

Elsewhere,[4] we have reported structural and rheological data on PS–PB–PS films plasticized with dipentene ($\delta_D = 8.5$). Data were interpreted in terms of

a theory[3] which presumes complete miscibility. Figure 2(a) indicates that these polymer/solvent systems lie in the miscible triangle, and thus the theoretical foundation was applicable.

Finally, brief mention can be made of selected nonrheological studies citing the variety of microstructures which can be formed when a block copolymer is cast from different solvents and dried. These studies involve cases of preferential miscibility, described above as class II, but usually have examined diblock (AB) rather than triblock copolymers; this eliminates some of the structural and rheological complications described above. Molau and Wittbrodt[9] surveyed results through 1967, reporting numerous instances of colloidal fluid systems at high ϕ_S. Inoue et al.[10] provided more experimental evidence and proposed a theory for high-ϕ_S AB/S systems to predict the size and geometry of micelles formed during solvent evaporation as the least-favored block undergoes microphase separation in class II. Sadron and Gallot[11] discussed the microstructural character of AB/S heterophases as ϕ_S was varied for numerous solvent–polymer systems. However, apparently no guidelines in terms of δ values have been presented for the problem of solvating a sample of bulk ABA polymer.

New Work

In conjunction with our other work,[3,4] it was desired to find a completely miscible ABA/S system. The strategy discussed above can be illustrated by the successful search for a solvent for Kraton 1101 (Shell Chemical Co.), a PS–PB–PS polymer with 25% PS and $M \cong 10^5$.

Solvents investigated are listed in Table I. A sample of bulk polymer in as-received condition was placed in a flask with solvent in 1:10 proportions, and qualitative observations were recorded at room temperature. Because Leary and Williams[2] recommended $\delta_{PB} = 8.3$ and $\delta_{PS} = 9.1$, the line for $\Delta_{AB} = 0.8$ in Figure 2(b) is taken to represent these tests. The 11 solvents of Table I are also displayed along this locus.

Liquids with low δ (decane, heptane, octane, all nonsolvents for PS end-blocks) produced obvious *macrophase* separation. Polymer particles swelled without losing their identity, as seen in Figure 4(b), and a clear supernatant liquid was seen. The position of these solvent δ values on Figure 2(b) suggests the existence of macrophases; the fact that octane and heptane lie in the partial-miscibility regime reflects fuzziness of the true solubility boundary and the role of temperature. The affinity of these latter fluids for PB (75% of polymer) caused solvent uptake to be fairly large. It is tempting to describe the gel macrophase as a class IIb2 system (PB matrix, PS domains), but the situation is not conclusive: Figure 4(b) could be showing the result of PB domains swelling in an imperfect (leaky) PS matrix which can be easily broken in its thinner regions by domain swelling. This would be more consistent with the predicted class IIb1 microstructure of bulk[1] and plasticized[3] copolymer. The decane gel, representing the greatest incompatibility of solvent with PS, could be made to flow only with heating well above 100°C; it is unclear whether this corresponded to softening of the glassy PS as $T_g{}^{PS}$ was exceeded or the passing of T_s for that phase.

For solvents of higher δ, the polymer/solvent system always formed fluid mixtures that were macroscopically homogeneous. This also agrees with Figure
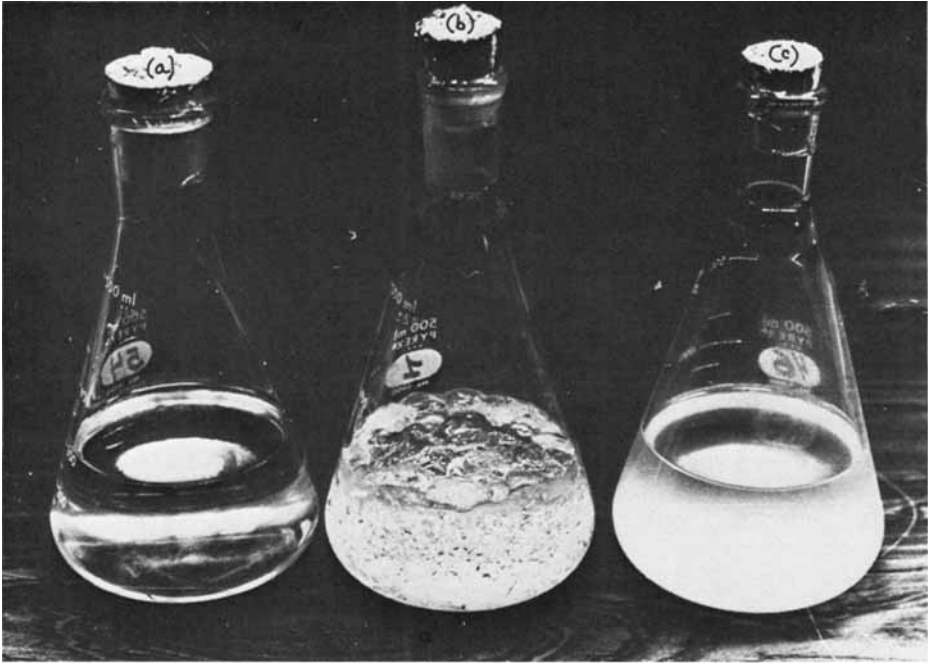
Fig. 4. Kraton 1101 with solvents ($\phi_S = 0.9$). (a) Dipentene, clear solution (class Ia). (b) Heptane, *macrophase* separation with a swollen gel phase (class IIb). (c) Chlorobenzene, turbid fluid (class IIa).

2(b); none of these solvents lies in a macrophase region, and even class IIa systems are capable of fluid behavior. However, detailed predictions associated with the miscibility triangle are not entirely correct; only mixtures with dipentene and cyclohexane formed clear solutions [Fig. 4(a)]. Other mixtures produced turbid fluids [Fig. 4(c)] associated with class IIa systems. Figure 2(b) would indicate this only for the two chlorobenzenes; we note that it occurred with all the aromatic solvents, which demonstrates greater incompatibility with PB blocks than the criterion $|\delta_{PB} - \delta_S| > 1$ would suggests. However, a certain consistency with the compatibility rating scheme of Figure 2(b) is found in the degree of turbidity of these fluids. Subjective turbidity ratings, on a scale 0 to
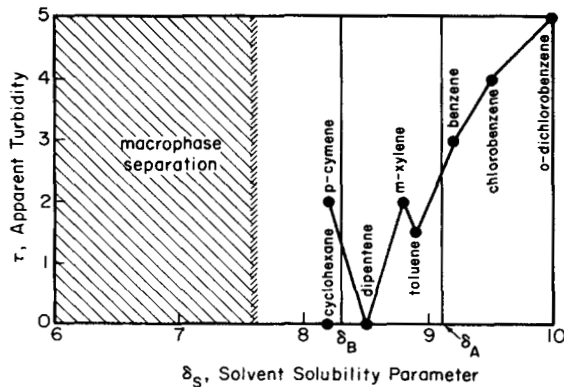

Fig. 5. Subjective turbidity rankings for mixtures of Kraton 1101 in various solvents.
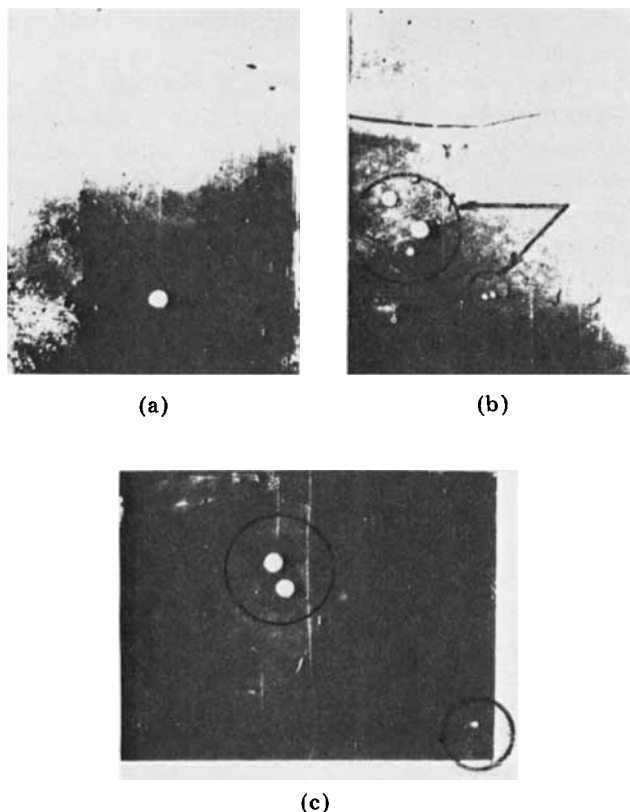
Fig. 6. Phase-contrast micrographs ($\times$100) of fluids similar to that shown in Figure 4(c), chlorobenzene in Kraton 1101. Kraton concentration: (a) 0.1 g/cm^3; (b) 0.2 g/cm^3; (c) 0.02 g/cm^3.

5, were made independently by three individuals with identical results, shown in Figure 5. The shape of Figure 5 parallels the $\eta_0(\delta_S)$ curve of Paul et al.[6] for similar mixtures, suggesting that some of their systems may indeed have had some class II microstructure which was not noticed.

The only inconsistent note here is with p-cymene, which should produce a clear solution like cyclohexane according to Figure 2(b). However, its closeness to the edge of the miscibility triangle makes class II behavior plausible, too. Cyclohexane may be an anomalously good solvent (being both saturated and cyclic), and p-cymene could be more representative of general block solubility.

Collectively, these results show that the miscibility "triangle" is likely to be much smaller than drawn in Figure 2 and not triangular either. The reason for the off-center solubility bias (the only true solvents, dipentene and cyclohexane, both had δ values closer to δ_{PB} than to δ_{PS}) is not clear; it might have been required by the excess of PB in the polymer. A relatively small adjustment in δ_{PB} and δ_{PS} would remove this bias. Using $\delta_{PB} = 8.1$ and $\delta_{PS} = 8.9$, retaining $\Delta_{AB} = 0.8$, would endow the miscibility region with much greater symmetry.

The great success of dipentene and cyclohexane as solvents seems to be related to their unusual structural similarities to both PS and PB, beyond mere δ considerations. This suggests that a search for ABA-miscible solvents should begin

with a screening according to δ_S and then be narrowed to those possessing molecular characteristics of both A and B.

It remains to interpret the fluidized class II mixtures. The five aromatic solvents, favoring the PS end blocks, produced fluid mixtures so easily that the latter are most plausibly interpreted as class IIa2 fluids which originate from a polymer with *PB domains* (or lamellae). This provides additional evidence that the equilibrium microstructure of this polymer does *not* have discrete PS domains as might be envisioned because of its low PS content. This agrees with electron micrographs presented by Leary and Williams[2] demonstrating a conversion to PB domains (or lamellae) upon thermal annealing of the bulk sample. The presence of solvent—here acting also as plasticizer of the glassy PS regions—would permit easy establishment of equilibrium conditions upon solvation.

The fluid condition of the p-cymene system is less easily explained. Since p-cymene favors the PB middle block, existing as domain material according to other evidence, it should produce a Class IIb1 system which is predicted to be a solid. However, p-cymene is very close to the miscibility triangle of Figure 2 and should thus be a reasonably effective penetrant of PS regions in the polymer microstructure. The resulting plasticization of PS would permit easy mechanical disruption of the microstructure by swelling forces in PB regions or by gentle stirring. This could be expected to produce a suspension of rather large particles, with a tendency to aggregate, and should scatter light with great effectiveness. This interpretation is reinforced by the exceptionally high turbidity of the p-cymene mixture, seen in Figure 5.

Two other observations are worth noting. First, the role of temperature in modifying the miscibility map (and behavior reported above) can be appreciable. At higher T, the miscible regions in Figure 2 should expand. This was verified by heating turbid p-cymene and chlorobenzene mixtures, representing opposite ends of the class II spectrum along the $\Delta_{AB} = 0.8$ line in Figure 2(b). With $\phi_S = 0.8$, the p-cymene system became clear at about 65°C and the chlorobenzene system, at about 90°C. [Note that greater heating was required for the system farther removed from the position of the best solvents in Fig. 2(b).] The change was entirely reversible and repeatable but not sharp, perhaps because the colloidal particles contained microphases representing a mixture of morphologies with slightly differing $T_s{}^{(m)}$. (A greater range of T_s has been observed in measurements of the dipentene-plasticized polymer, a class Ia system, and explained in similar fashion.[4])

Second, the particles responsible for turbidity in chlorobenzene mixtures were examined with phase-contrast microscopy. As seen in Figure 6, they are essentially spherical, with a wide distribution of sizes which are apparently independent of polymer concentration. This was predicted above for class IIa2 systems (PS matrix favored). Since the largest particle diameter is about 3 microns and a spherical PB domain of $M_{PB} = 75,000$ would have a diameter of about 200 Å, it is obvious that the particles are aggregates rather than individual domain cores surrounded by their own solvated matrix chains. The latter could be functioning as adhesive to hold the aggregate together; smaller particles would probably result from vigorous agitation.

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