Microcellular foams: phase behaviour of poly(4-methyl-1-pentene) in diisopropylbenzene

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Microcellular foams are an important component of Inertially Confined Fusion (ICF) targets. The spatial distribution of the material is critical as the target implodes. In an effort to improve the spatial uniformity, we have explored the phase separation behaviour of poly(4-methyl-1-pentene) solutions with diisopropylbenzene solvent. The cloud-point phase-separation diagram from pure solvent to pure polymer is discussed. Microstructures of the various density foams and the need for a three-dimensional phase diagram are presented.

(Keywords: polymer; poly(4-methyl-1-pentene); diisopropylbenzene; phase diagram; foam; microcellular)

INTRODUCTION

Low density materials continue to be needed as 'structural air' and cushions in ICF targets. In 1980[1], these low density materials needed to be in the 50 mg cm^{-3} range with cells about 25 μm in size, have low Z composition (mainly hydrogen to carbon), be structurally sound, and be fabricated to high tolerances. A foam meeting these requirements was developed at Los Alamos using a phase separation technique in which the dissolved polymer separated from a hot organic solvent as the temperature was lowered[1]. The organic solvent was leached from the separated polymer–solvent mass to leave a foam structure. The polymer used was poly(4-methyl-1-pentene) or PMP. The best solvent at that time was a 90/10 mixture of bibenzyl and paraffin[2]. The most significant feature of that polymer/solvent system was the soap-like texture of the solvent-filled polymer mass. This physical property allowed the mass to be readily machined to high tolerances with standard tooling before the solvent was leached and a fragile foam produced.

By 1985, the properties needed for low density materials had become more stringent. The basic 1980 requirements were still needed, but designers now wanted smaller cell sizes (1 μm or less) and a foam that could withstand much harsher conditions. Recently Aubert and Clough[3] have reported success at making low density, microcellular polystyrene foams directed at achieving these goals. Like them, we have explored new polymer/solvent systems and have found that poly(4-methyl-1-pentene) produces a strong 50 mg cm^{-3} foam with near 1 μm cells when prepared from diisopropylbenzene (DIPB) solvent. Unlike previous efforts, the microcellular structure is uniform over very large (at least 10 cm in every direction) three-dimensional structures. We believe that the information gained from studying this system points the way to achieving the more stringent requirements listed above while shedding new light on the phase behaviour of polymer solutions in general.

EXPERIMENTAL PROCEDURES

Sample preparation

Solid poly(4-methyl-1-pentene) and the appropriate amount of solvent to give the desired polymer weight fraction and a total of 5 ml mix were added to a pyrex test tube. Also known as TPX, the PMP polymer was used in bead form, containing less than 5% other polymer homologues, and was produced by Mitsui Petrochemical Industries, Ltd, Japan, or Aldrich Chemical Company. The DIPB was technical grade with an isomeric ratio *o/m/p*:10/50/40 from Kodak. (The large fraction of 1,3- and 1,4-isomers caused significant effects in the phase separation behaviour, as will be discussed.) The 20 cm long, 1.3 cm i.d., 1.5 cm o.d. test tubes used in the cloud point studies were previously necked down about 12 cm from the bottom. The contents of each test tubes were cooled externally with pulverized dry ice and the test tubes closed off with an oxygen–natural gas torch.

Observation of phase behaviour

A sealed tube containing polymer and solvent was placed in the tube holder of the assembly shown in *Figure 1*. The tube was rotated as the oil bath was heated. After the polymer was dissolved, the temperature was raised somewhat higher (typically 50°C above the cloud point) and maintained for a short period (generally 15–30 min) to ensure good dissolution. After this dissolution process, the test tube was stopped vertically in front of a high intensity fibre optics white light beam. The beam was viewed visually from low (5–10°) to right (90°) angles in the horizontal plane. The temperature of the oil near the tube was measured with a thermocouple and plotted *versus* time on a strip chart recorder. Observations were generally concerned with the earliest certainty of clouding, the degree of system opacity, the colour and nature of the separating system, and the temperature at which the polymer mass (gel) pulled away from the test

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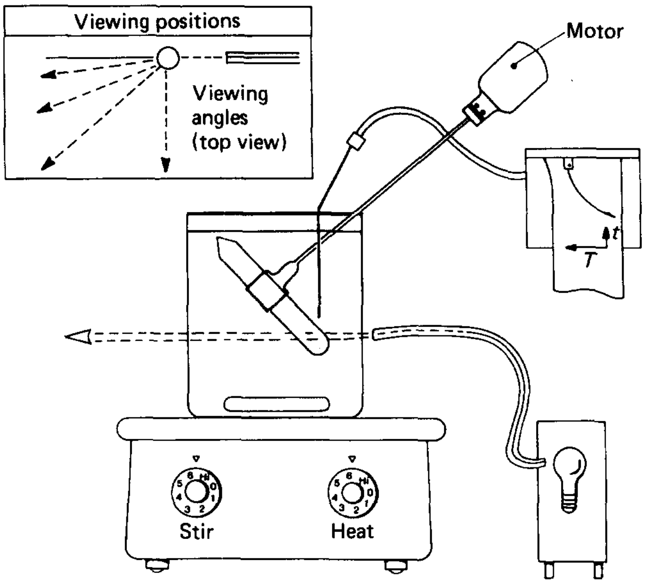


Figure 1 Schematic of cloud point observation equipment

tube. The use of a white light source allowed the visual effects of many frequencies to be observed. Although measurements made by eye have some inherent evaluative nature, all of our measurements were made by the same person in order to minimize this element.

Gel extraction

When the oil bath neared room temperature, the test tube containing the polymer/solvent gel was removed and placed in an empty glass beaker for 12 h at room temperature. The tube was then cracked open and the gel carefully removed. A wafer about 0.5 cm thick was generally cut from the middle with a razor blade. The cut wafer was then placed in a high pressure, liquid CO_2 extractor available from J&W Scientific, but modified with a viewport to allow the soxhlet dumping action to be observed. Overnight was generally sufficient time to complete the removal of the diisopropylbenzene. After leaching at 1050 psi (i.e., below the supercritical point), the 5°C condenser of the extractor was turned off when the soxhlet dumped and the CO_2 in the soxhlet was allowed to completely vapourize. The pressure was slowly vented to prevent solid CO_2 from forming in the foam. When the extractor was opened, the foam was dry and ready for density (by weight and volume) and scanning electron microscopy (SEM) analyses.

SEM analysis

The leached foam was mounted on a metal stalk with DUCO™ cement. After the cement was dried, a smooth surface was cut using a vibrating razor blade. The device used was a Vibratome Model 1000 sold by Ted Pella Inc. of Tustin, California. The sides of the foam and the mount were then coated with silver paint for conductivity. After the silver paint dried, the foam was coated with a thin layer (a few Ångstroms) of gold. The prepared foam was then analysed with a Hitachi Model S-520LB scanning electron microscope.

RESULTS

The diisopropylbenzene/poly(4-methyl-1-pentene) solvent/polymer system was initially investigated in an effort to study the phase separation phenomena by relating the phase diagram to the foams produced. The previously used[1] polymer (PMP) was again used because it continues to have the desired properties (only carbon and hydrogen with a high melting point). The solvent (DIPB) was chosen because of (1) its small-ring aromatic character, (2) its pendant isopropyl groups and (3) its low (−63°C) melting point. Nonfunctional group aromatic compounds have been noted here and elsewhere (notably by Lawrence Livermore National Laboratory ICF personnel) to produce better gels than acyclic aliphatic hydrocarbons. The isopropyl groups were desirable because of their similarity to the isobutyl group of the polymer. The low melting point of the solvent was desired so that this phase change would not enter into the region where polymer changes were expected, mainly above 20°C.

DIPB/PMP phase diagram

The phase behaviour was observed visually by watching the polymer/solvent system as it cooled in the closed glass tube suspended in an oil bath (*Figure 1*). *Figure 2a* shows the cloud points (marked C) and the colour changes observed. The cloud point was followed about 10°C lower by retraction of the gel (marked P in *Figure 2b*) from the glass tube. A number of colour changes occurred during the phase separation process. When clouding occurred above 105°C, the clouding solution had a highly translucent orange hue. A phase-separating solution would have a translucent purple hue between 105°C and 101°C; from 101°C to 96°C, it would

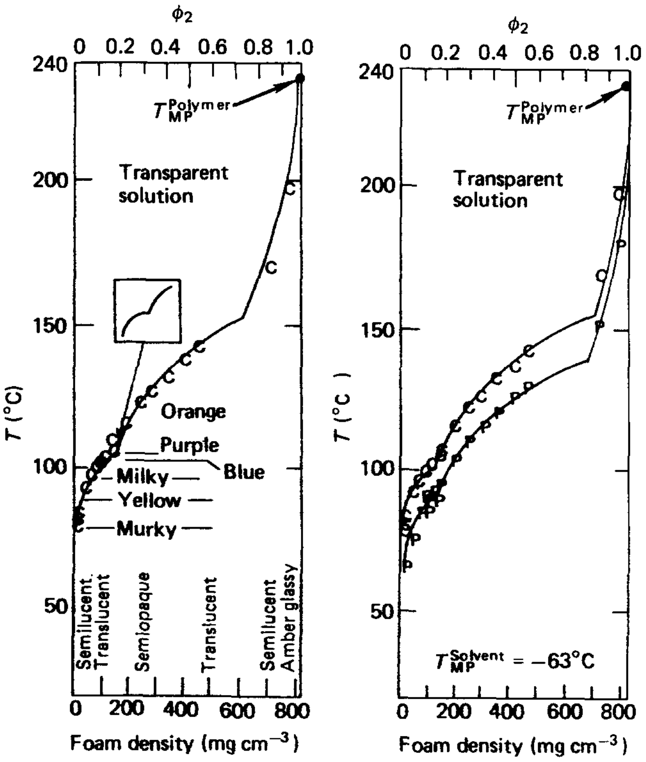


Figure 2 Phase behaviour of the DIPB/PMP system in closed tubes. Foam density varies linearly with ϕ_2, the weight fraction of polymer. Plotted points are C (the visually observed cloud point temperature) and P (the temperature at which the gelling mass retracts from the walls of the glass tube). [The insert of 2a denotes the discontinuity that occurs in the cloud point curve when the mixture changes from purple to blue. A similar discontinuity occurs in the retraction of the gel from the tube (2b)]

be translucent blue. At 96°C, the binary system would be less translucent than at higher temperatures, and then turn milky white. Around 80°C, it would become sufficiently non-transmitting as to be a murky white. Binary systems above 410 mg cm^{-3} did not pass through this purple–blue–white sequence as the temperature was lowered but those below 350 mg cm^{-3} did. The resulting gels were generally obtained without cracks or voids and were the most opaque around 250 mg cm^{-3} and the most transparent at very high (> 700 mg cm^{-3}) or very low (< 50 mg cm^{-3}) polymer densities (see *Figure 2a*). The gels produced in the range from 120 mg cm^{-3} to 140 mg cm^{-3} (corresponding to the initial separation in the purple region) were exceptions to the crack-free behaviour as they cracked catastrophically. Good, uniform gels about (5 cm)^3 can be produced in an open beaker by cooling through the cloud point at 0.5°C/min.

Programmable foam densities

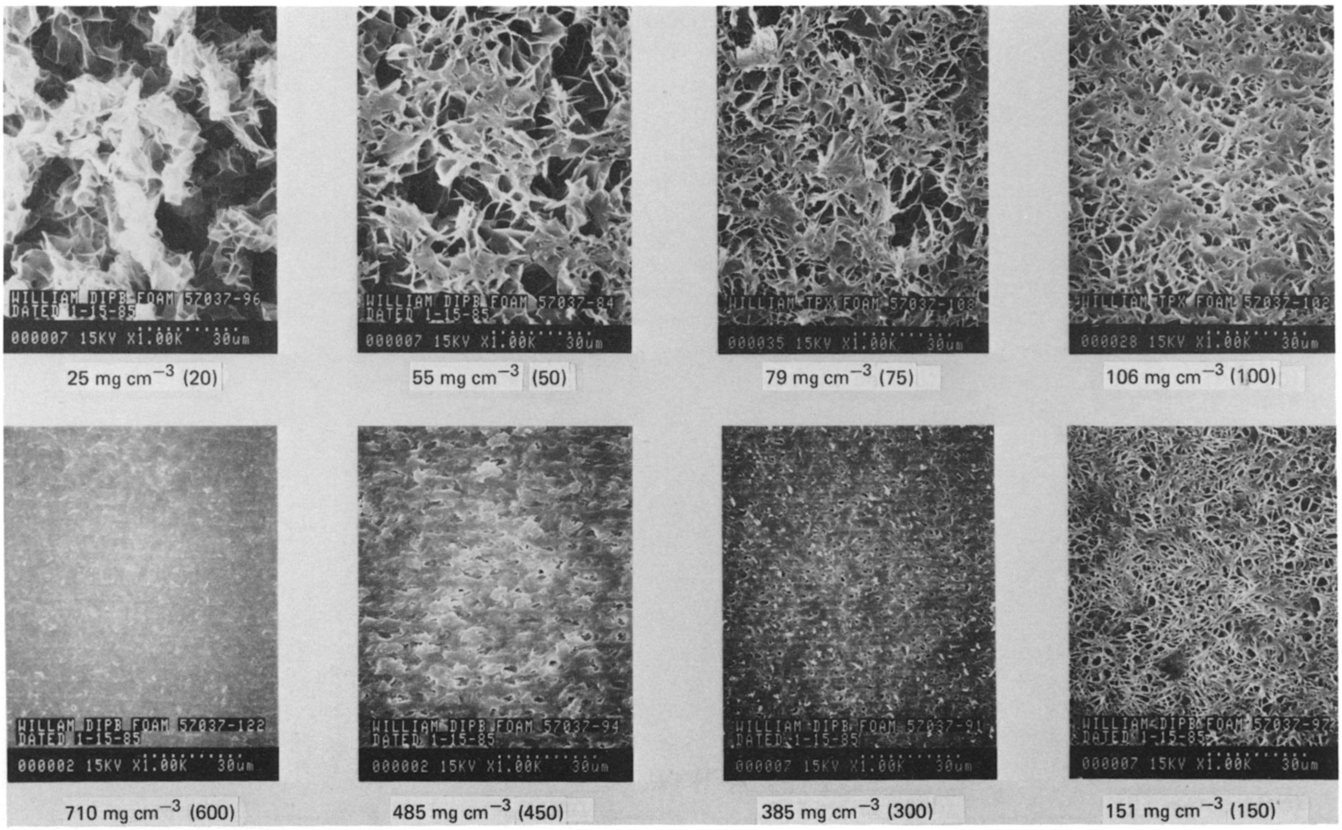
Because the poly(4-methyl-1-pentene)/diisopropylbenzene system gives good firm gels above 3% polymer content, it provides a means of producing foams that vary in density from 0.025 g cm^{-3} to 0.83 g cm^{-3} (the full density of the polymer). Unlike phase-separated gels produced from the PMP/dibenzyl/paraffin system studied earlier[2], however, gels produced from the DIPB/PMP system cannot be extracted with isopropyl or methyl alcohol. Neither can the solvent be removed by vacuum without the mass shrinking almost to the full density of the polymer. To overcome this, the gels were extracted with liquid CO_2. Generally, samples 0.2–0.8 cm thick could be extracted overnight, although some gels required several weeks to be extracted in the apparatus used here.

Scanning electron micrographs of the razor-cut surfaces of some of the foams produced are shown in *Figure 3*. (The 485 mg cm^{-3} sample shows the effect of using a dull blade as the surface is not cleanly cut and the micrograph of this sample is thus not truly indicative of the foam structure.) The numbers in parentheses of *Figure 3* are the targeted foam densities; those at the left of them are the observed densities. Significant open areas (> 10 μm) begin to occur when the density is decreased to 25 mg cm^{-3}. Below 20 mg cm^{-3}, the gels of this system are not sufficiently strong to be handled. Reasonably uniform foams, however, are available from the DIPB/PMP system with densities ranging from 3% (25 mg cm^{-3}) to 80% (710 mg cm^{-3}) of the bulk density (830 mg cm^{-3}) of poly(4-methyl-1-pentene).

Process variables in the DIPB/PMP system

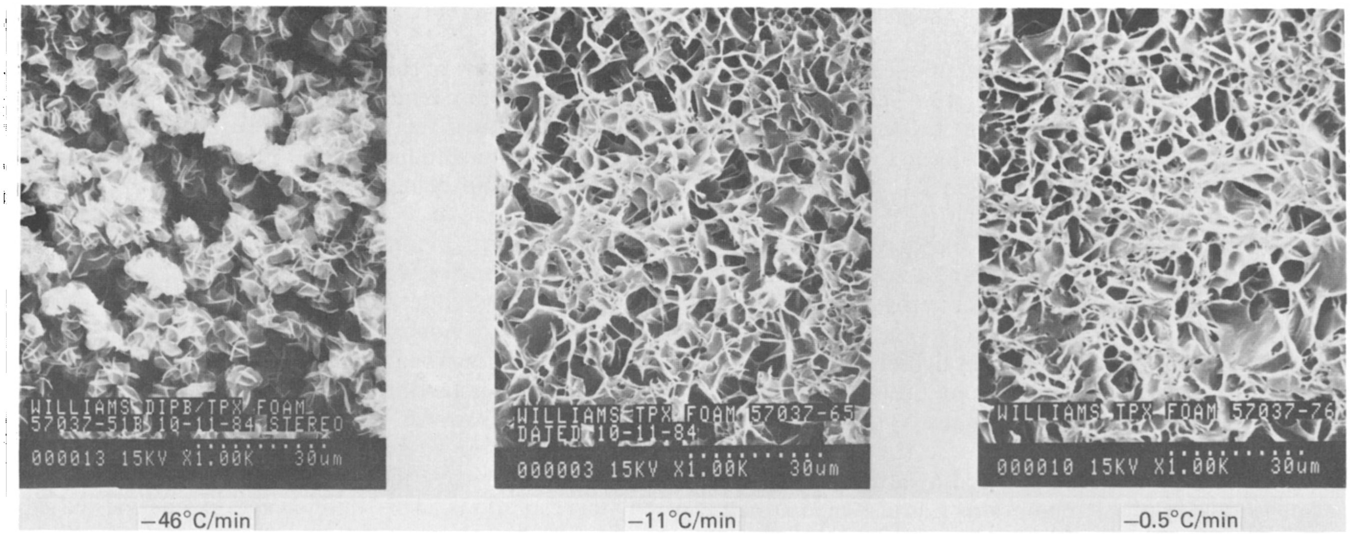
Several factors which influence the foam structure in other solvent/polymer systems are (1) the rate of cooling through the phase separation temperature (also called critical miscibility temperature or *CMT*) and (2) polymer variations. These two factors were studied for the DIPB/PMP system. In addition, the influence of performing the separation in a vessel open to the atmosphere *versus* performing it in a sealed vessel under pressure at the separation point was studied. We believe that the latter is the first example of using pressure to alter the structure of a microcellular foam by influencing the phase behaviour.

Rapidly cooling the DIPB/PMP solution through the *CMT* produced a foam which had very poor mechanical strength. Miles *et al.*[7] found similar behaviour for amylose in water. This is in sharp contrast to the results obtained by Aubert and Clough[3] for polystyrene in cyclohexane. The reason for our results can be found in *Figure 4* where the polymer is seen to be very poorly



25 mg cm^{-3} (20)
55 mg cm^{-3} (50)
79 mg cm^{-3} (75)
106 mg cm^{-3} (100)
710 mg cm^{-3} (600)
485 mg cm^{-3} (450)
385 mg cm^{-3} (300)
151 mg cm^{-3} (150)

Figure 3 Various density foams from the DIPB/PMP system (prepared from Mitsui RT-18 in closed glass tubes with ~2°C/min cooling)

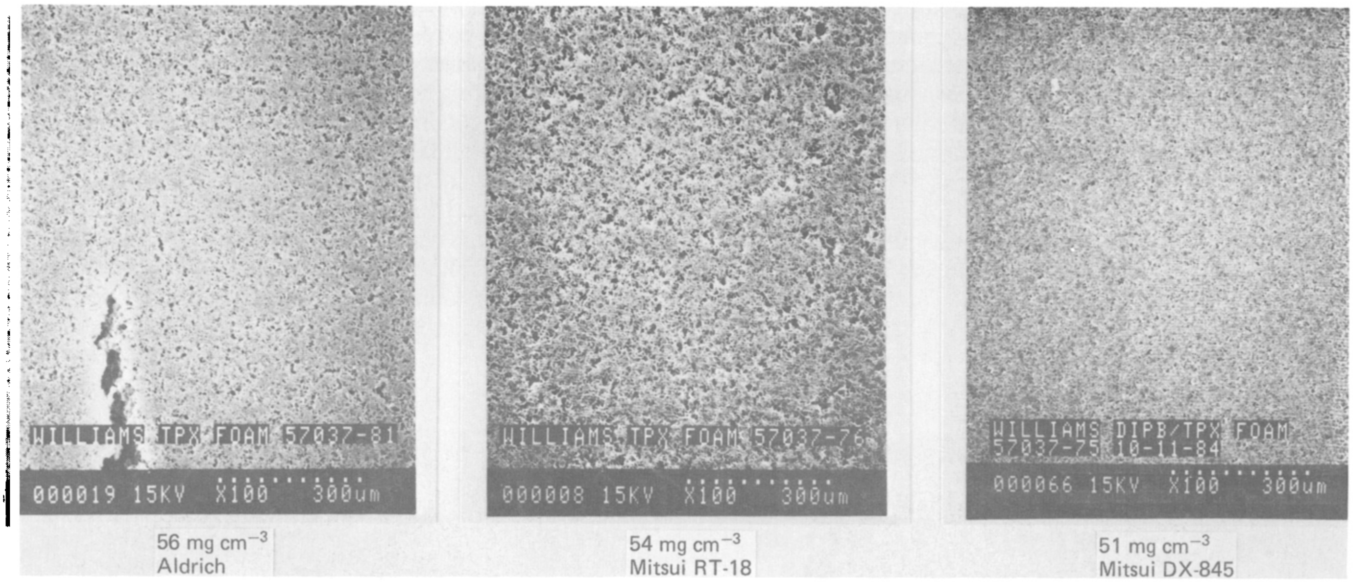


−46°C/min

−11°C/min

−0.5°C/min

Figure 4 Effect of cooling rate on the ultimate foam structure (prepared from Mitsui RT-18 in open vessels at 0.050 polymer g/ml. Results are the same for polymer concentrations ranging from 0.025 to 0.10 g/ml)



56 mg cm^{-3} Aldrich

54 mg cm^{-3} Mitsui RT-18

51 mg cm^{-3} Mitsui DX-845

Figure 5 Influence at PMP material on foam structure (prepared in open vessels at 0.050 g polymer/ml with ~0.5°C/min cooling. RT-18 has a higher melt index than the other two)

connected in the sample cooled rapidly at −46°C/min. We believe that after the polymer-rich phase is nucleated, deep quenching creates crystal formation at these nucleation points. Polymer in the solution flows towards these points. The residual polymer is thus incapable of stretching from one nucleation site to another and therefore results in the formation of spherules with polymer-deficient solution forming the continuous phase. Slower cooling allows the nucleation and separation to occur with either co-continuous phases or, as appears to be the case here, the polymer-rich phase as the continuous phase. This rate-related behaviour has occurred with PMP in each of the solvent systems (several) we have studied to date. The 11°C/min cooling rate (illustrated in *Figure 4*) may not be the fastest that one can use and still get good interconnected foam, but our experience favours maintaining the cooling rate below 5°C/min. We base this on producing samples 0.6 cm or thicker. The formation of thin (less than 200 μm) films and the behaviour of other polymer/solvent systems may be different because of gelling rates, for example.

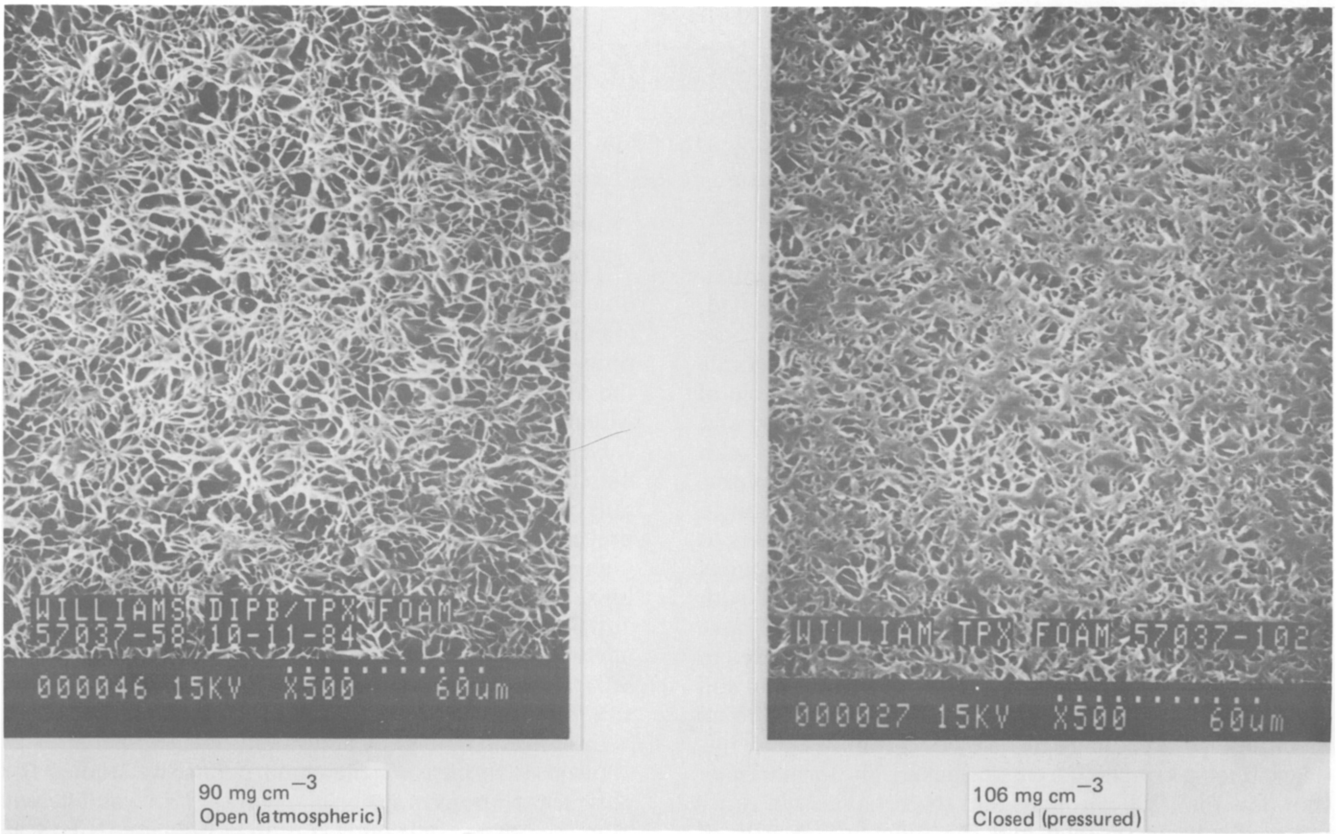
The polymer source has a small influence on foam quality. This is illustrated in *Figure 5* which shows the foams obtained from three different sources of PMP processed identically and at the same time. (The crack in the Aldrich sample is an artifact.) The best polymer is the Mitsui DX-845 material as it has been in all of our PMP/solvent systems. The poorest was the Mitsui RT-18 material which interestingly is manufactured with the tails of the molecular weight distribution removed to prevent 'cats eyes' during melt extrusion. RT-18 also has a higher melt index than the other two which means it has a lower average molecular weight. While one would anticipate that a narrower molecular distribution would narrow the temperature range over which phase separation might occur and hence might reduce the cell size, altering the molecular weight by chopping off the high molecular weight fraction did not help here.

In order to measure the cloud points, we studied the polymer solutions in sealed glass tubes. This was different from the open vessel conditions previously used[1]. To seal the tubes, the contents were first chilled through the glass with dry ice and then the tube was flamed closed at the neck. At elevated temperatures, this system was automatically pressurized, whereas an open vessel would always be at atmospheric pressure. The amount of polymer degradation (yellowing) at the high processing temperatures was also less in the sealed system. The result of performing the separation at elevated pressure is seen in *Figure 6* for Mitsui RT-18 PMP targeted for $100\,mg\,cm^{-3}$. The polymer boundaries with the open system are much better defined and encompass larger cells than are obtained with the closed system. The foam from the closed system looks much denser, but actually the polymer is spread out more. The denser looking areas are the walls of cells that have not yet been cut open. We envisage that the polymer is more swollen when it separates in the closed system than in the open one.

A comparison of foams produced by atmospheric and elevated pressure phase separations was also made using the best foam-producing PMP polymer (Mitsui DX-845). In this case, the targeted density was $50\,mg\,cm^{-3}$. This density was achieved with the open system (see the value in parenthesis in *Figure 7*) with 2–6 μm cells in a highly interconnected polymer network approaching a closed-cell structure. The foam from the closed system is much more nondescript (*Figure 7*). The density is higher than in the open system because the residual solvent could not be easily removed by liquid CO_2 extraction even when the foam slice was only 0.3 cm thick. The polymer is obviously highly swollen (see *Figure 7*, ×3.00 K magnification). Pressure thus has a significant influence on the solvation state of the polymer when separation occurs.

DISCUSSION

During the review of this paper, it became evident that a preface to the discussion that follows was needed. This need arose because there is a significant gap between the theoretical understanding and the practical application of polymer solution behaviour. 'Phase diagrams' abound with talk of cloud points, upper and lower critical miscibility points, binodals, spinodals, etc. The theorists, led by the extensive work of Koningsveld[4,5], Rehage[6], Šolc[7,4] and their colleagues, have recognized that cloud point curves are not synonymous with the coexistence phase curves described in elementary thermodynamics. This same understanding has not transferred to many of the rest of us, however. This has certainly been the case over the past five years among those of us involved in making foams by thermally-induced separation of polymer solutions. This misconception has existed in spite of the fact that in 1984 many of us participated in a three-day conference[8] entitled 'Applications of Phase Diagrams in Polymer Science' which featured P. J. Flory, Koningsveld and numerous other experts. Our particular misconceptions were certainly related to an imperfect understanding of the problem. A major cause of this has been our visualizing the similar shapes of cloud point and coexistence curves in a similar fashion and failing to appreciate the significance of the 'shadow curve' about which Koningsveld spoke. Our misconception has been continually fueled by literature that talks about binodals and cloud points in the same breath and without distinction. The following discussion shows how we grew from this muddled climate and is presented in hopes that



90 mg cm^{-3}
Open (atmospheric)

106 mg cm^{-3}
Closed (pressured)

Figure 6 Effect of open *versus* closed system on the foam structure (prepared from Mitsui RT-18 at 0.10 g polymer/ml)

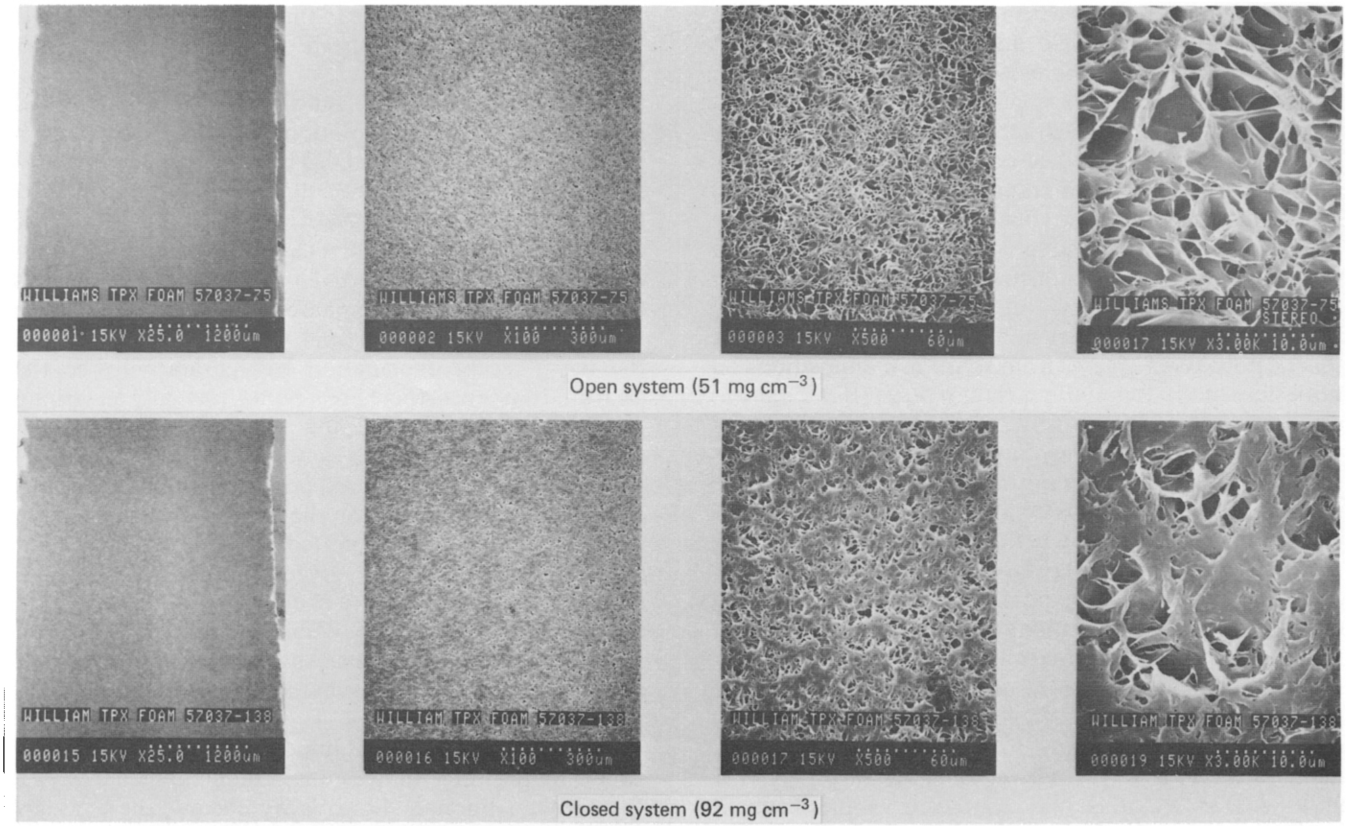


Figure 7 Effect of open *versus* closed system on the foam structure (prepared from Mitsui DX-845 at 0.05 g polymer/ml with 5°C/min cooling)

the gap between theorists and practitioners will be narrowed.

The conversion of polymer gels to foams through CO_2 leaching provides a view of the material distribution in the gel since the disruption of the thin membranes is minimal. With this data and the phase separation diagram, a physical description of the phase changes that occur in the phase diagram can be envisaged. When we first saw our foams, we were struck by the absence of polymer in the void areas and the denseness of the polymer areas (see *Figure 3*). This seemed strange considering that the traditional (thermodynamic) view of phase diagrams indicates that a polymer solution separating at point A of the binodal curve (*Figure 8*) should give a second phase of composition C. Since both of these phases would be highly solvated, one would anticipate getting a somewhat denser foam inside a somewhat less dense one. Such was not the case. As we began to study the problem more closely, we found that not only were:

(1) polymer areas not greatly bloated, and
(2) solvent areas (voids) devoid of polymer, but that
(3) solation occurred well above (>25°C) the cloud point,
(4) segmented structures (balls), not superfine laces, were formed when our semicrystalline polymer was rapidly cooled, and
(5) no differences in the foam structures were observed when the foams from the solvent-rich side of the 'binodal' (curve A in *Figure 8*) were compared with those from the polymer-rich side (curve C in *Figure 8*).

Viewing the cloud-point diagram in the traditional thermodynamic manner, one is hard pressed to explain these observations, although considerable attention has been given to the phase behaviour of polymer solutions since Flory's[9] initial work. Mathematical equations abound, e.g. see a recent formulation by Sanchez[10] to

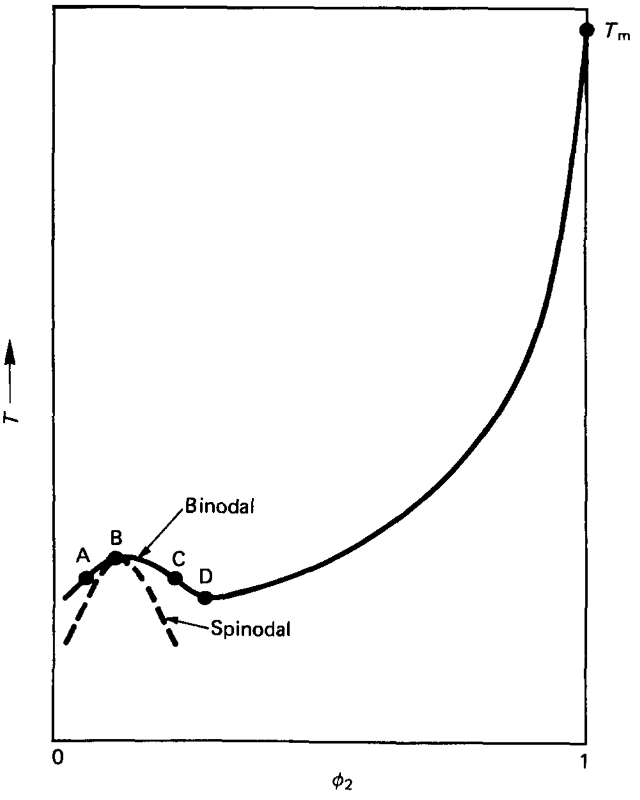


Figure 8 Typical cloud point diagram for a polymer in a theta solvent (ϕ_2 represents the fraction of polymer)

normalize for molecular weight behaviour and an earlier treatment by Koningsveld and Staverman[11]. Item (5) above is particularly problematical. One would expect a polymer-rich phase C to nucleate when composition A cools to the 'binodal' curve. Likewise, a solvent-rich phase should nucleate when composition C cools to the 'binodal' curve. No such transition occurs. The cells of our foams also show little roundish character (see *Figure 3*). If liquid–liquid demixing is occurring the separating phase should also be roundish, like droplets. The polymer areas are very dense looking and the voids have no polymer. Like us, Aubert and Clough[3] found that the atactic polystyrene foams from solution compositions on both sides of the 'binodal' maximum point (B in *Figure 8*) are 'identical' and 'insensitive to concentration' around the maximum point. (They have chosen to attribute this insensitivity to a quenching of their solution below the spinodal curve (see *Figure 8*) and subsequent 'ripening'.) The change in foams, whether from crystallizable or noncrystallizable polymer, is thus one of degree rather than kind. The traditional phase-separation (cloud point) diagrams of polymer solutions thus simply do not predict the correct physical arrangement of the components.

To explain the above results, we deconvoluted the planar representation (*Figure 8*) into the three-dimensional one of *Figure 9*. The nature of the third dimension is not yet clear and is purposely left undesignated. It must be related in some fashion, however, to a fundamental difference between the behaviour of very long and short molecules. The important feature of the 3-D plot is that none of the points of the cloud point curve lies in the same third plane as any other, and thus no coexistence phase boundaries are defined.

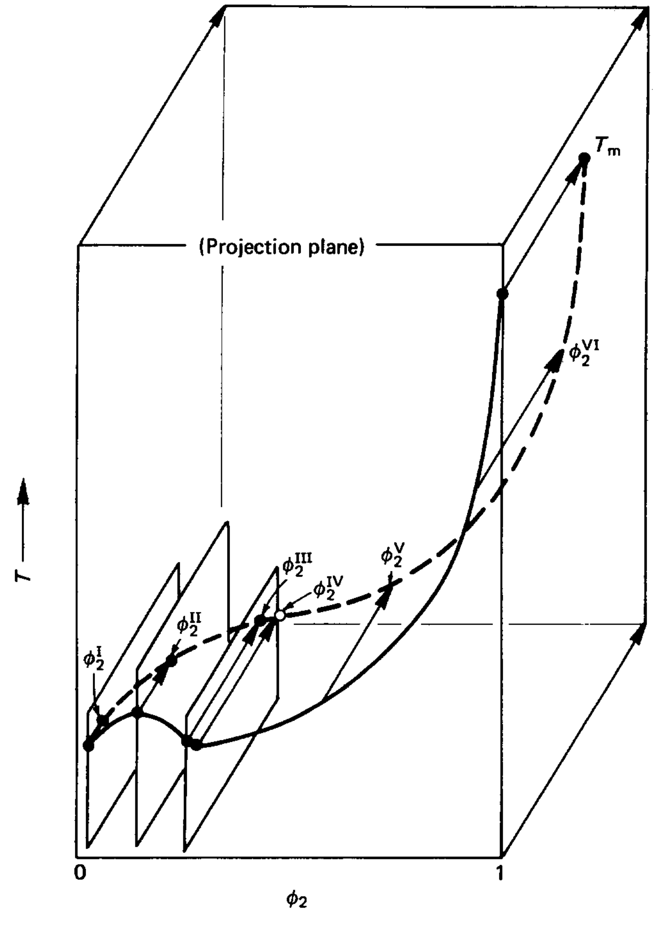


Figure 9 Pictorial deconvolution of a two-dimensional cloud point diagram into a three-dimensional one

Inspecting the literature, one finds that Tompa[12] noted in 1949 that a polymer solution cloud point curve does not coincide with the binodal. This distinction was clearly demonstrated by Rehage *et al.*[6] and more recently by Dobashi *et al.*[13]. Koningsvelt[11,14] has studied the issue extensively and states equivocally that 'miscibility gaps (cloud point curves) for given molecular distributions never represent coexisting phases'[4]. Just how the two are interrelated was described some years ago[6,11], but we find the more recent explanation by Kurata[15] to be the clearest. In essence, there are *n* points (actually an infinite number) on the cloud point curve. There are also *n* coexistence (binodal) curves with one (and only one) point coinciding with a cloud point. The other end of the binodal tie-line is a point on the curve that 'shadows' the cloud point curve. When plotted, everything (cloud point curve, shadow curve, and very few binodals for clarity) is always drawn coplanar. Since the binodal curves are themselves planes, they cannot exist in the same overlapping coplanar space. All of which brings us back to the three-dimensional character of the cloud point curve.

Illustrative coexistence (binodal) curves have been added to the three-dimensional cloud point curve (see *Figure 10*). Although shown fairly narrow, the binodals could be very broad with the separating phase very rich in polymer (high ϕ_2). The binodals need not be (and normally are not) symmetrical. The dotted portion of each binodal (above the cloud point) is inaccessible. The separating phases (S_1, S_2, S_3, S_4, etc.) form the 'shadow curve'. Projecting all of this onto the front plane of the 3-D phase diagram yields the coplanar diagram depicted by Kurata[15]. In *Figure 10*, the separating phase has a higher polymer content even when the cloud point curve peaks at ϕ_2^{II}. This is consistent with our experimental results. If the cloud point curve coincides with a binodal maximum (as at critical point C), a polymer solution with even greater polymer content will have a separating phase with a lower polymer content (note $\phi_2^{IV} \rightarrow S_4$). One would expect a change in the separating phase's behaviour at this point and *not* at the peak in the cloud point curve. A three-dimensional representation thus gives the viewer a clearer perspective of phase behaviour than is obtained from a two-dimensional one.

Some other features of the 3-D phase diagram are noteworthy. The vertical plane at 100% polymer will allow various forms of the polymer to be included if the third dimension is properly defined. This is especially important in our case, as PMP is known to exist in at least five crystal forms (at room temperature) that result when the polymer is crystallized (phase-separated) from different solvents[16]. It is envisaged that the melting point suppression curve in *Figure 9* ($\phi_2^{IV} - T_m$) has a similar shape in the 100% polymer plane and thus forms a surface instead of a line. Irreversibility (i.e., the solution temperature is much greater than the gelation temperature) in our system and others (amylose in water[17], PMP in cyclohexane[18], and isotactic polystyrene solutions[19]) is accommodated by the fact that, when the temperature is raised or lowered, the changes in the system do not have to occur in the same third-dimension plane. Indeed, fast and slow quenching can, from the same equilibrated solution point, give rise

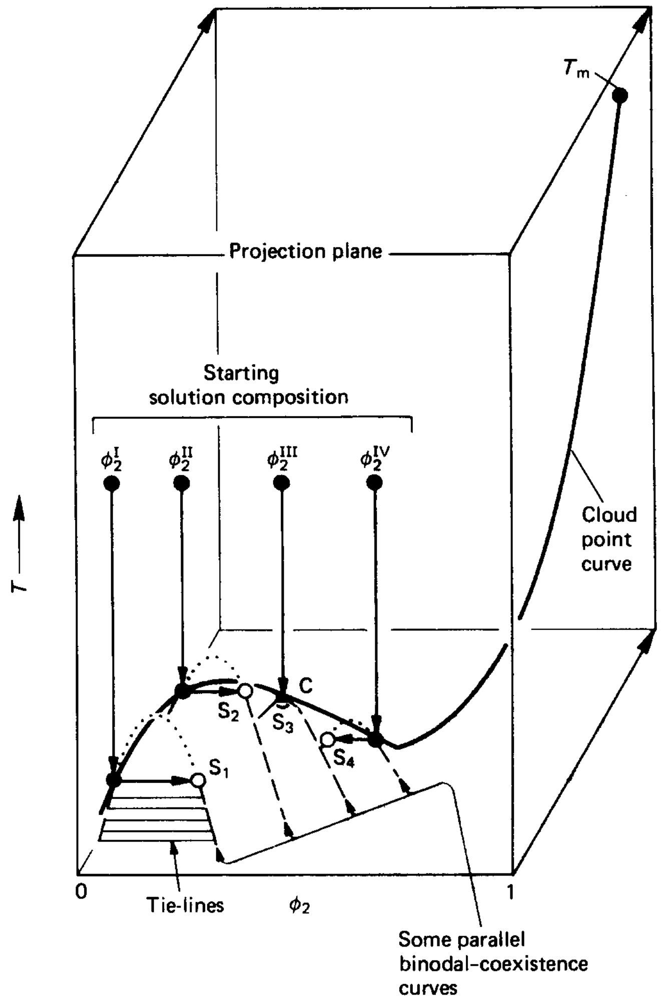


Figure 10 Illustrative coexistence (binodal) curves associated with a cloud point curve. The open circle points (S_x) are the separating phases associated with the solid circles on the cloud point curve at compositions ϕ_2^x. The S_x points define the 'shadow curve'

to phase separation behaviour in different planes as defined by the third parameter. The development of coexistence curves for different molecular weights of polystyrene in methylcyclohexane[10] also seems more appropriate in the context of the third dimension. But mostly, the three-dimensional representation provides a less confusing view of the cloud point and coexistence phase behaviour than is possible with the two-dimensional one. The explicit form of the third dimension is not clear, however, and we leave it to the theorists to define it for maximum usefulness.

The formation of beads during very rapid cooling of PMP/DIPB solutions is puzzling. Such a cooling technique was expected to give very fine (submicrometer) cellular structures. We now visualize the balls as starting from normally nucleated points. During deep quenching, the polymer at these nucleation points begin to crystallize immediately and the polymer between the points flows towards the nucleation points until the continuity between points ceases. During slow cooling the polymer between the points should crystallize about the same time that the polymer at the nucleation points crystallizes. We speculate that the weaker gels formed by the faster cooling of amylose/water solutions[9] result from similar behaviour. The non-crystallizing, atactic polystyrene/cyclohexane system studied by Aubert and Clough[3], on the other hand, can be rapidly cooled to a connected foam. There is little force to drive their polymer towards the nucleation sites, but, by the same token, the thin polymer membranes (observed in our system, but not theirs) are poorly stabilized and retract to the areas where joining membranes intersect. This would lead to the rib-like structure in their foams. Indeed, rapid cooling is the only way to prepare a foam from atactic polystyrene. Thus, while the occurrence of a polymer crystallization step can prevent a polymer solution from being rapidly cooled to a well-connected foam structure, the same step can allow that same solution to be slowly cooled to a well-connected one. A slow cooling process also permits one to produce larger foam pieces.

The cloud point behaviour of the PMP/diisopropylbenzene system studied here (*Figure 2*) does not decrease around 15% polymer as expected (*Figure 8*). Indeed, it begins to rise sharply after levelling out. This results from using a mixture of diisopropylbenzene isomers ($o/m/p = 10/50/40$). Data (to be presented elsewhere) show that the 1,3-isomer gives the 'normal' (full hump) cloud point curve behaviour (*Figure 8*), whereas the 1,4-isomer produces the anomaly (half hump, *Figure 2*). We believe that this abnormality arises from the fact that the isopropyl groups, located in the *para* position of the 1,4-isomer, interact with the polymer molecules in a significantly different fashion than do the isopropyl groups in the *meta* arrangement of the 1,3-isomer. The benefit or detriment of such interactions in foam formation and on phase separation behaviour is still to be determined.

SUMMARY

The foam structures derived from phase-separated-polymer solutions provide new insight into the mechanics of the phase separation process. Planar (two-dimensional), cloud point type, phase separation diagrams fail to predict the observed structures. The most significant deficiency is the implication that the kind of foam (i.e., phase-separated solution) will change as the polymer level is raised through the cloud point maximum. No such change is observed. This and other deficiencies have led us to propose a three-dimensional representation of phase behaviour. Such a diagram accounts for the data observed here and elsewhere. Mathematical treatments used with the two-dimensional diagrams are still useful, but their third dimensionality needs to be explored. The treatment of phase separation and plasticization appear to be separable although both are related to solvent–polymer interactions. We hope that those skilled in the art of phase diagrams can work out the details needed to satisfy the various thermodynamic laws and define the third-dimension parameter. We believe that, if two-dimensional cloud point diagrams are reported for solvent–polymer solutions, some method must be employed to caution the reader about the dangers of using tie-lines.

The DIPB/PMP system studied here can produce foams over a wide range of densities from near full density plastic ($830\,\mathrm{mg\,cm^{-3}}$) to light 'marsh-mallows' ($25\,\mathrm{mg\,cm^{-3}}$). Near one micrometer (2–6 μm) cells are obtained for $50\,\mathrm{mg\,cm^{-3}}$ foams; much smaller cells are obtained as the density is increased. The cell size for the $50\,\mathrm{mg\,cm^{-3}}$ foam produced here marks a 10-fold reduction when compared with that of the previous best foam produced from this polymer[1]. The new foam is much tougher than the previous: a 0.5 cm piece of the new foam can be bent almost 90° before breaking; the foam from bibenzyl/paraffin solvent [1] can only be bent 10° to 20°.

Good, highly interconnected, PMP foams with the minimum bulk dimension greater than 0.6 cm are best prepared by cooling the polymer solution through the phase separation region at rates less than 5°C/min. High cooling rates (greater than 10°C/min) lead to poorly (sometimes non-) connected foam structures. Subtle changes in the polymer can influence foam quality.

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