

# Effect of several dual solvents on the phase separation of poly(4-methyl-1-pentene)

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Phase separation of isotactic poly(4-methyl-1-pentene) (PMP) from various solvents gives polymer masses which can be converted into foams that vary from crumbly powders to well-connected, strong, flexible solids. The composition of the solvent is an important parameter in determining the nature of the separated polymer phase. The influence of solvent (or non-solvent) on the temperature and character of the phase separation event and on the resulting foam structure is addressed in this paper. Thus differing ratios of two poor solvents for PMP, bibenzyl and paraffin, were found to give variable foam structures and surprising phase behaviour. Thermochromism is sometimes observed as the polymer separates.

(Keywords: poly(4-methyl-1-pentene); bibenzyl; paraffin; diisopropylbenzene; phase behaviour; foam; microcellular)

## INTRODUCTION

Isotactic poly(4-methyl-1-pentene) or PMP has been used to prepare foams by phase separation for use as cushion materials in ICF (inertial confinement fusion) targets<sup>1</sup>. This is done by dissolving the polymer and subsequently allowing it to phase separate into a structure that can be converted into a foam. Bibenzyl is one solvent that has been used. Since both the solvent and the polymer are solids at room temperature, the entire mass becomes solid and can be machined with conventional milling tools. To prevent crumbling however, paraffin wax has been added to give the mass a smooth, soap-like texture<sup>2</sup>. Neither bibenzyl nor paraffin is a particularly good solvent based on their high cloud point temperatures. In our continuing effort to understand the processes involved in the phase separation of polymeric solutions, we studied the phase behaviour and resulting foams generated by adding a poor PMP-solvent (paraffin) or a good PMP-solvent (diisopropylbenzene, DIPB) to a poor-PMP solvent (bibenzyl).

## EXPERIMENTAL

### Sample preparation

All samples contained 0.25 g PMP in 5 ml of solution. (This is equivalent to 50 mg of polymer  $\text{cm}^{-3}$ .) Solid poly(4-methyl-1-pentene) and the appropriate amounts of each solvent to give the desired weight fraction and a total volume of 5 ml were added to a Pyrex test tube. The 20 cm long, 1.3 cm inside diameter, 1.5 cm outside diameter test tube used was previously necked down about 12 cm from the bottom to facilitate later sealing. The contents of the test tube were cooled externally with pulverized dry ice and the test tube closed off with an oxygen-natural gas torch. Also known as TPX, the PMP polymer was in bead form, contained less than 5% other monomers and was produced by Mitsui Petrochemical Industries Ltd, Japan, as type DX-845 TPX. The bibenzyl was obtained from Sharp Chemical; DIPB was technical grade (*o/m/p*:10/50/40) from Kodak; the paraffin was Cullen Wax (Cullen Industries, Huntington Valley, PA).

### Observation of phase behaviour

Visual observations of phase changes were made in an apparatus previously described<sup>3</sup>. After the polymer was dissolved, the temperature was raised (generally to the 200–250°C range) and maintained for a short period (generally 15–30 min) to ensure good dissolution. After this dissolution process, the test tube was held vertically in front of a high intensity, fibre optics, white light beam. Visual viewing was begun from low (5–10°) to right (90°) angles in a 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 generally concerned 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 tube.

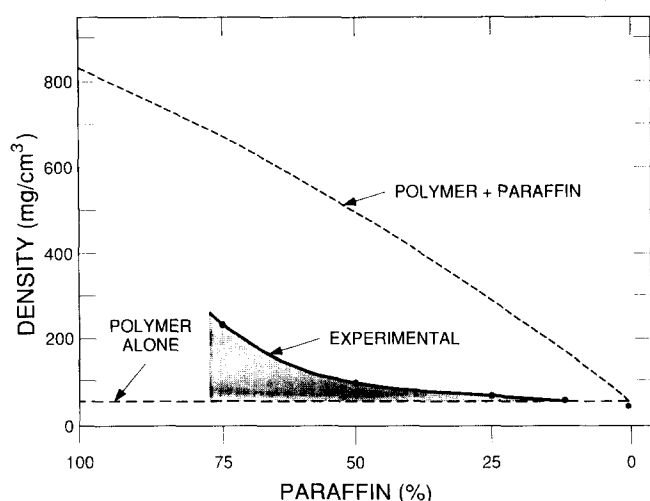


Figure 1 Foam densities obtained from paraffin/bibenzyl/PMP mixtures. (All mixtures had 50 mg of PMP polymer  $\text{cm}^{-3}$ . The broken 'polymer + paraffin' line indicates the expected density of the foam piece, if only the bibenzyl component were removed from the solidified mass. The broken 'polymer alone' line indicates the expected density, if both paraffin and bibenzyl were removed.)

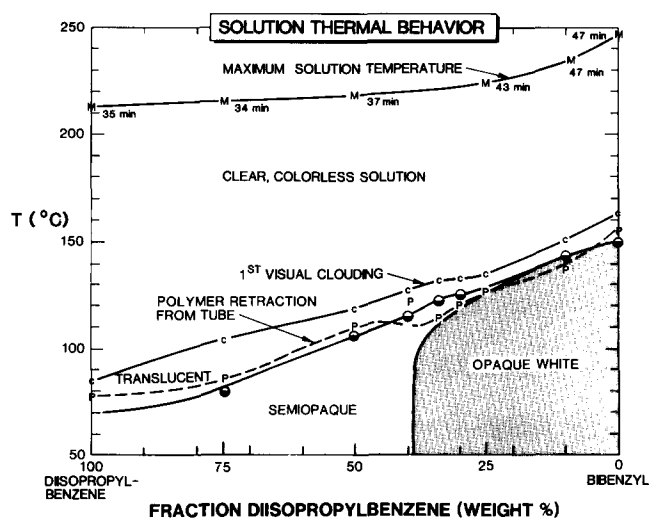


Figure 2 Phase behaviour of 50 mg cm<sup>-3</sup> PMP in diisopropylbenzene/bibenzyl mixtures

### Gel extraction

When the oil bath neared room temperature, the test tube was removed and placed in an empty glass beaker for 12 h at room temperature. After cracking the tube, the gel was carefully removed. A thin wafer about 0.5 cm thick was cut from the middle with a razor blade. Sometimes the mass was hard enough to need sawing; the sawn surfaces would then be smoothed with a razor blade. The cut wafer was placed in a high pressure, liquid CO<sub>2</sub> extractor<sup>3</sup>. Several days were needed to remove the solvent from the pure bibenzyl and bibenzyl/DIPB solvent systems. Wafers with low levels of paraffin could be extracted with several weeks of leaching (Figure 1). Those with high levels of paraffin required leaching periods longer than a month. The shaded area of Figure 1 indicates a higher density than expected from polymer alone. The extra mass is attributed to unextracted paraffin. After leaching with liquid CO<sub>2</sub> at 1050–1150 psi and with the bottom half of the pressure vessel at 34.5°C, the 5°C condenser of the extractor was turned off after the soxhlet dumped, and the CO<sub>2</sub> was allowed to completely vaporize. The pressure was slowly vented to prevent solid CO<sub>2</sub> from forming. When the extractor was opened, the foam was dry and ready for density and scanning electron microscopy analyses<sup>3</sup>.

## RESULTS AND DISCUSSION

### DIPB/bibenzyl/PMP system

As expected, additions of a good PMP-solvent (DIPB) to bibenzyl lowered the temperature at which the initial clouding point occurred (Figure 2). All initial cloudings had a whitish cast except the 100% DIPB one which had a slight bluish hue. More dramatic, however, was the influence on the gel appearances and the structure of the resulting foams (Figure 3). With additions of up to 25% DIPB, the gelling solution turned an opaque white about 10°C below the temperature at which the solution began to cloud. Above 40% DIPB, no such opacity was observed and the gels remained semi-opaque even at room temperature. After several days, large crystals of bibenzyl were observed growing out the side of the 50/50 sample gel. The change in opacity behaviour suggests that a significant change in the behaviour of the polymer occurs with increasing level of good solvent.

The scanning electron micrographs (SEMs) (Figure 3) of the foams produced by this solvent/polymer system show three distinct types of foam structures. These were:

- (1) a partially connected, corn-flake structure [0% DIPB, 100% bibenzyl];
  - (2) a well-connected, large (10–20 μm) cell structure [10% DIPB, 90% bibenzyl], and
  - (3) a well-connected, small (1–6 μm) cell structure [> 35% DIPB].
- Adding a small amount of good PMP solvent, e.g., DIPB, seems to give the phase-separating polymer enough continuity to remain intact around the developing solvent areas. Adding a large amount (50% or more) of DIPB appears to dramatically change the character of the phase separation. Large pockets of solvent no longer develop. An abrupt change in behaviour, rather than a gradual one, is favoured as the 25/75 DIPB/bibenzyl sample attempts to form two different structures, but with catastrophic results. Not only is the cell structure non-uniform, some of the solvent cannot be removed (note the density, *D*, in Figure 3). The change from large cell foam to small cell foam coincides with the cessation of the gelling mass to turn opaque white soon after clouding begins. This change in behaviour suggests that polymer crystallization is retarded by DIPB, because the polymer remains in a more highly swollen state.

### Paraffin/bibenzyl/PMP system

Both paraffin and bibenzyl are poor solvents for PMP (as indicated by the very high phase separation temperature). At low (1%) PMP concentrations in an open vessel, polymer is observed to settle from the cooling solution much like a crystallizing solid. Thus, one would anticipate that adding paraffin to bibenzyl would simply make the ultimate foam less interconnected and eventually not interconnected at all. Such is not the case. Adding a small (10 wt%) amount of paraffin to the bibenzyl/PMP mixture actually improves the cell structure of the final foam (Figure 4). Unlike the crumbly polymer gel produced at room temperature by the bibenzyl solvent alone, the addition of paraffin (10%) gives a smooth, soap-like, machineable mass, as was demonstrated by Young *et al.*<sup>2</sup>. The mass produced here in a closed vessel is considerably harder than the ones produced in open vessels. Further increases in the paraffin content (to 25%) produce more uniform, smaller, and rounder cells. The unleached gelled mass is not as hard and is waxier than that made with 10% paraffin. The contrast between the foam formed here in a closed system with 25% paraffin added and that reported for an open system is dramatic too. Here we have a well-formed foam structure that is patently unlike the 'platelet-rosette' structure reported for the open system<sup>2</sup>. As we reported previously<sup>3</sup>, only slight increases in the pressure of the system can make remarkable changes in the phase separation process and thus the ultimate foam structure.

When the paraffin level is raised above 25%, a marked change occurs in the foam structure. A significant drop in the maximum cell size occurs (Figure 5) and the cells become more angular (Figure 4). The very thick areas represent unleached paraffin. Because of the poor solubility of paraffin in liquid CO<sub>2</sub>, the densities (Figure 4) of the foams that result after only 1 week of CO<sub>2</sub> extraction increase with increasing paraffin level. Attempts to improve the paraffin extraction by making the CO<sub>2</sub>

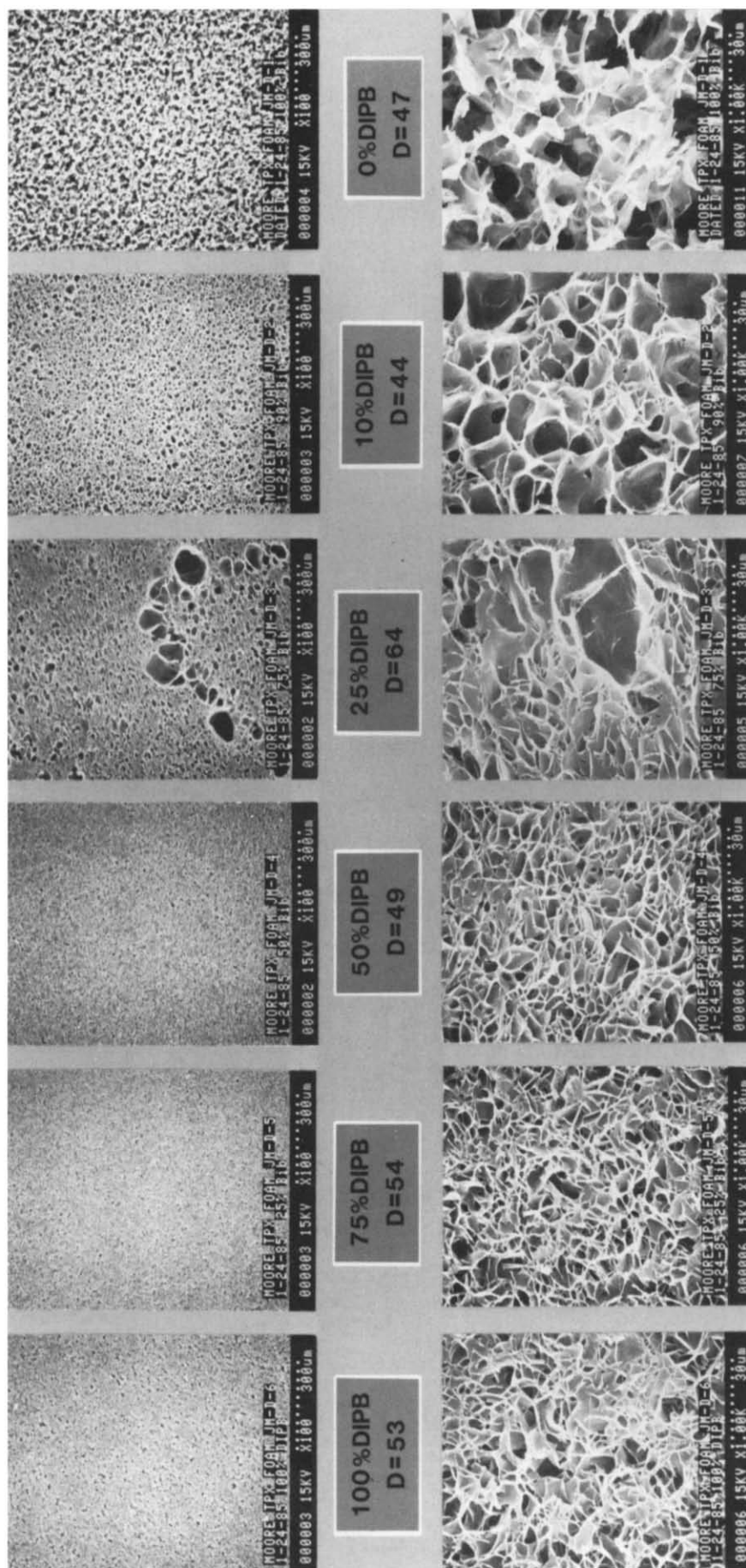


Figure 3 SEMs of foams from PMP/diisopropylbenzene/bibenzyl system. (The D values are the densities of the leached foam which nominally contain 50 mg of PMP cm<sup>-3</sup>.)

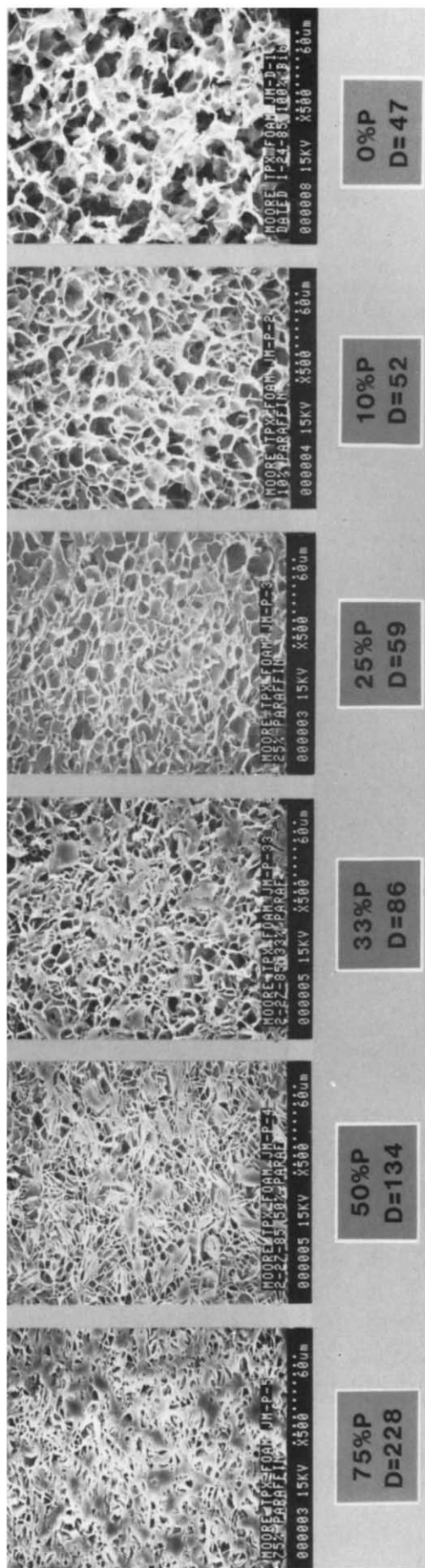


Figure 4 SEMs of foams from PMP/paraffin/bibenzyl system. (The D values are the densities of the leached foam which nominally contain 50 mg of PMP cm<sup>-3</sup>.)

medium supercritical resulted in highly shrunken, shrivelled pieces of foam. With 100% paraffin, the phase-separated sample is highly fractured with the texture of paraffin wax. Unlike the pure solvent mixes, all the paraffin-plus-bibenzyl mixes show good continuity with no microcracks at room temperature. At room temperature, the gelled masses are Teflon-like near 33% paraffin, become softer and opaque with increasing paraffin content. The change in the cell structure is related to a change in the phase separation behaviour.

The phase behaviour for the paraffin/bibenzyl/PMP system is quite complex (Figure 6). The first visual clouding may occur between 180°C and 150°C. Two minima occur: one at 55% paraffin and another around 20% paraffin. The improved cell structure, noted when a small amount (10%) of paraffin is added to the bibenzyl, coincides with a drop in the temperature of the first visual clouding point. As the temperature drops further, the solution turns to an opaque white. Between 30% and 33% however, this second clouding phenomenon disappears abruptly; this event coincides with the change in cell structure noted above. The gel eventually turns opaque white when the bibenzyl crystallizes at 50°C or below. Continued additions of paraffin lead to gels that may be colourless, orange, purple, blue, or white and translucent at the onset of clouding. For a given paraffin level, the gel systematically moves from one colour sequence to another as the temperature is lowered. For example, at 60% paraffin the clouding solution is first orange, then turns purple, and then blue before becoming a translucent white. The gel generally pulls away from the glass tube about 10°C after the first visual clouding. The change in cell structure at 33% paraffin coincides with the appearance of a blue hue in the clouding, instead of only white as observed with lower amounts of paraffin. Smaller cells are noted for the 50% (than for 33%) paraffin foam which had a longer temperature period in the blue gel stage than did the 33% paraffin sample. Sufficient foam structure data are not available to evaluate the effects of phase changes above 75% paraffin.

The colour changes in the 33–60% paraffin region are very similar to those observed with increasing polymer concentration in the DIPB/isotactic PMP system<sup>3</sup>. In that particular case, a symmetrical solvent molecule

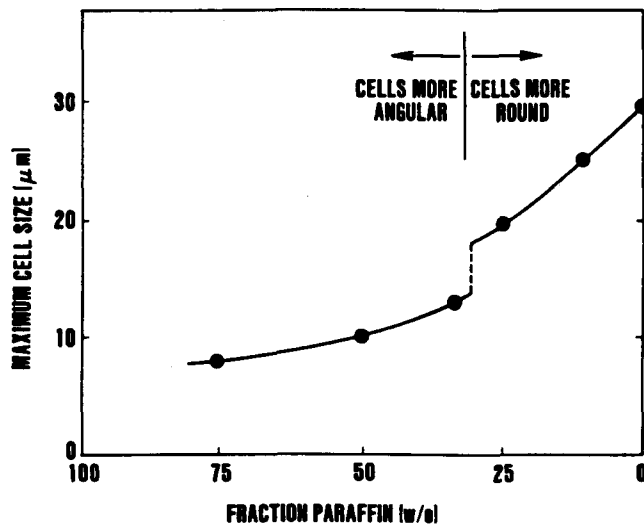


Figure 5 Effect of paraffin/bibenzyl ratio on cell size and shape

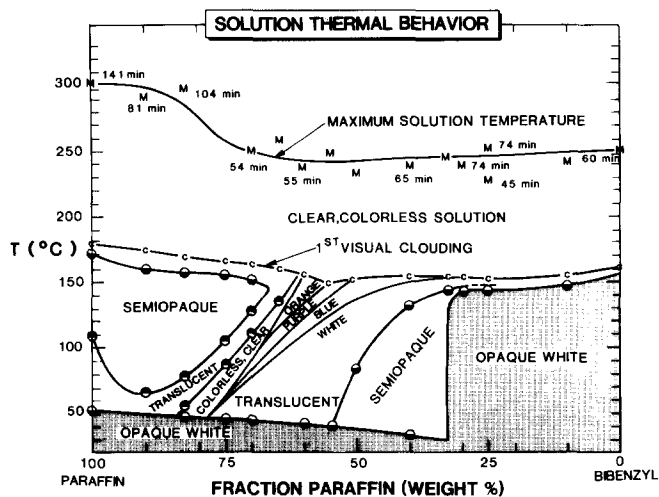


Figure 6 Phase behaviour of  $50 \text{ mg cm}^{-3}$  PMP in paraffin/bibenzyl mixtures. The orange, purple and blue zones are coloured, translucent gels

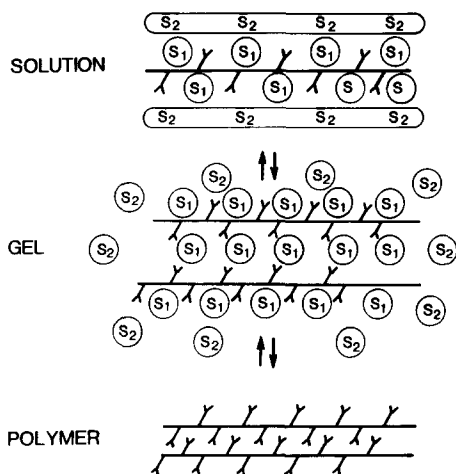


Figure 7 Simple visualization of dual solvent needs in foam making. (Temperature increases upwardly.)

(1,4-diisopropylbenzene) was identified as instrumental in joining PMP chains into 'twin' chains. Thermochromism of isotactic propylene gels in benzene has been observed<sup>4</sup>: a change from blue to yellow with increasing temperature up to 70–80°C. Atactic polypropylene, on the other hand, did not exhibit thermochromism<sup>4</sup>. This behaviour also resembles that of optically active, cholesteric liquid crystals<sup>5</sup>. The correlation here is remarkably similar to the DIPB/PMP behaviour if added paraffin is ignored; that is, if by adding paraffin one considers that the concentration of polymer is increasing relative to the amount of bibenzyl present. Thus at 45 wt% paraffin, the concentration of PMP relative to bibenzyl is  $104 \text{ mg cm}^{-3}$ ; at 50%,  $116 \text{ mg cm}^{-3}$ ; at 60%,  $150 \text{ mg cm}^{-3}$ , and so on. Starting in the solution phase at any one of these paraffin levels and dropping the temperature, the same colour

changes occur that occurred in the DIPB/PMP system<sup>3</sup> at the same polymer concentration that is defined by the PMP/bibenzyl ratio. The correspondence would suggest that polymer chains are in increasingly closer proximity as the level of paraffin increases. This would imply that significant ordering of the polymer molecules has already taken place at the moment the first visual clouding is observed. Indeed, we frequently have the visual impression that 'something' is happening 10–30°C above the first visual clouding. The solution seems to transmit light somewhat differently. We have not yet accurately pinpointed or detailed this situation.

## CONCLUSIONS

A simple visualization of the solvation–desolvation of a polymer is given in Figure 7 where temperature increases in the upward direction. As viewed by us, the solvent performs two functions: a short-ranged one in which the polymer is intimately solvated (as depicted by  $S_1$ ) to effect a swollen polymer (gel); and a long-ranged one wherein the solvated polymer units are dispersed (as depicted by  $S_2$ ). The solvation requirements for the two events are sufficiently different that although one solvent might perform both operations, a multicomponent (binary, tertiary, etc.) solvent is more likely to provide the necessary flexibility to properly manipulate the phase behaviour and physical alignment of the polymer. As we view the situation, bibenzyl operates primarily in the  $S_1$  arena and paraffin in the  $S_2$  arena. A small amount of paraffin changes the  $S_2$  character of the bibenzyl solution sufficiently to extend the polymer. With further additions of paraffin, the polymer is probably extended sufficiently to form more interconnected gels, instead of more precipitate-like networks. Bibenzyl may actually facilitate the interaction of individual polymer chains by being bidentate. The DIPB used was a mixture of isomers and was sufficient to operate in  $S_1$  and  $S_2$  modes. The differing behaviour of the isomers is reported elsewhere. As further research is reported, a better understanding and quantifications of the solution factors will allow us to specify polymer/solvent conditions for preparing better foams and polymer solutions in general.

## ACKNOWLEDGEMENTS

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