Effect of substituent position on the phase separation of poly(4-methyl-1-pentene) in diisopropylbenzene

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The behaviour of poly(4-methyl-1-pentene) in a mixture of diisopropylbenzene isomers mimics that of the 1,4-isomer to an extent proportional to the amount of 1,4-isomer in the mixture. The 1,3-isomer gives the normal cloud-point curve behaviour, while the 1,4-isomer gives an anomalous one. This difference is reflected in the physical appearance of the foams obtained from the separated solutions. From an analysis of the solvent-to-polymer composition at the onset of this anomalous behaviour, a unique relationship is found for one 1,4-isomer molecule per methylpentene repeat unit. The observed results suggest special ordering of molecules during gelation.

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

INTRODUCTION

Poly(4-methyl-1-pentene) (PMP) has been used by our organization to prepare foams for use in inertial confinement fusion (ICF) targets and high-energy physics experiments. By phase separation of the polymer from various solvents, we have been able to prepare a wide range of foam densities. During a study of the phase behaviour of this polymer in diisopropylbenzene, we noted[1] that the phase-separation (cloud-point) curve did not decrease around 15% polymer, as expected, but began to rise sharply after levelling off. This behaviour was observed for a mixture of diisopropylbenzene (DIPB) isomers, and we indicated that the behaviour was probably isomer-dependent. Cloud-point/phase-separation curves for PMP in the 1,3- and 1,4-diisopropylbenzene isomers and isopropylbenzene (cumene) are reported herein and support that view.

EXPERIMENTAL

Sample preparation

All samples were prepared to contain the required weight of PMP to yield the desired density in 5 ml of solution. Solid PMP and the appropriate amounts of each solvent were added to a Pyrex test tube. The 20 cm long, 1.3 cm i.d., 1.5 cm o.d. test tube was previously necked down about 12 cm from the bottom to facilitate later sealing. 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. A g.p.c. analysis showed the *MW* to be ~500 000, i.e. ~6000 monomer units. The DIPB mixture was technical grade *o/m/p*: 10/50/40) from Kodak. The 1,3-DIPB (96% purity), the 1,4-DIPB (97%) and the cumene (99%) were obtained from Aldrich. Each solvent was used without further purification. The contents of the test tube were flushed with dry nitrogen, cooled externally with pulverized dry ice and the test tube sealed with an oxygen–natural gas torch.

Observation of the phase behaviour

Visual observations of phase changes were made in an apparatus previously described[1]. After the polymer was dissolved, the temperature was increased (generally 50°C above the cloud-point temperature) and maintained for a short period (generally 15–30 min) to ensure good dissolution. The maximum temperature could be above the boiling point of the solvent since the system was closed. After this dissolution process, the rotating test tube was stopped vertically in front of a high-intensity, fibre optics, white light beam. Visual observations were made 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, such as 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 were noted.

Gel extraction

When the oil bath neared room temperature, the test tube was removed and placed in an empty glass beaker for 12 h or more at room temperature. After cracking the tube open, the gel was carefully removed. A thin wafer about 0.5 cm thick was generally cut from the middle with a razor blade. Sometimes the mass was hard enough to need sawing; the sawed surfaces would then be smoothed with a razor blade. The cut wafer was then placed in a high-pressure, liquid CO_2 extractor[1]. Several days of extraction were usually sufficient to remove the solvents. After leaching at 1050 psi (~7.25 kPa) (below the supercritical point), the condenser of the extractor

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was turned off after the Soxhlet dumped its load of liquid CO_2 and the CO_2 was allowed to vaporize completely. The pressure was slowly vented to prevent solid CO_2 from forming. When the extractor was opened, the foam was dry and ready for density and SEM analyses[1].

RESULTS

The cloud-point/phase-separation curve of PMP in 1,3-diisopropylbenzene is displayed in *Figure 1*, with the exact response to the 200–300 mg cm^{-3} region being uncertain. The smooth response is quite similar to that found for atactic polystyrene with carbon disulphide[2]. Two different phenomena are at work. Below 200 mg cm^{-3}, gelation predominates; above 300 mg cm^{-3}, the glass transition of plasticized polymer predominates. A pronounced maximum in the gelation region has been found with atactic polystyrene in cyclohexane[3], and a discontinuity would be expected when the gelation and plasticization curves intersect. The cloud-point behaviour of PMP in isopropylbenzene (cumene) is similar (*Figure 2*) to that of PMP in 1,3-diisopropylbenzene. However, cumene is a better solvent for PMP than is 1,3-diisopropylbenzene; the cloud-point curve is ~15°C lower. The presence of the second isopropyl group in the *meta* position does not appear to change the general phase-separation behaviour of PMP significantly.

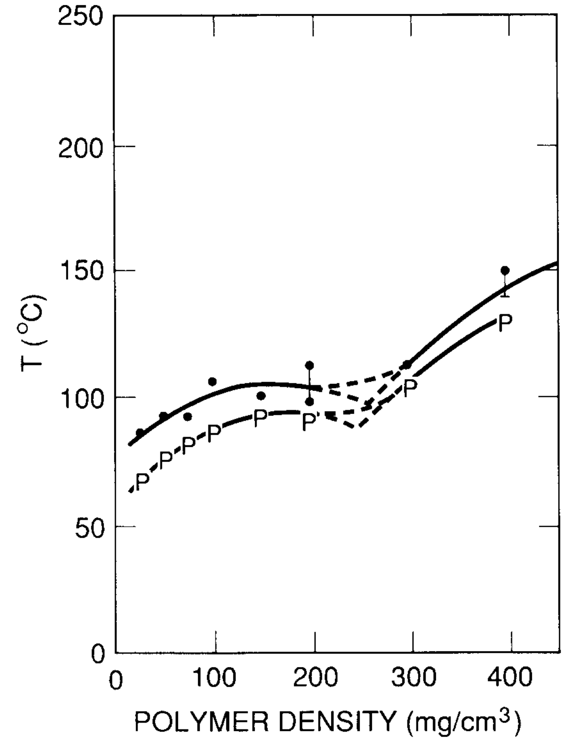

Figure 1 Visual cloud-point curve for PMP in 1,3-diisopropylbenzene. The P curve represents the temperature at which the separated polymer mass retracts from the container. The abscissa indicates the grams of polymer per cubic centimetre of solution

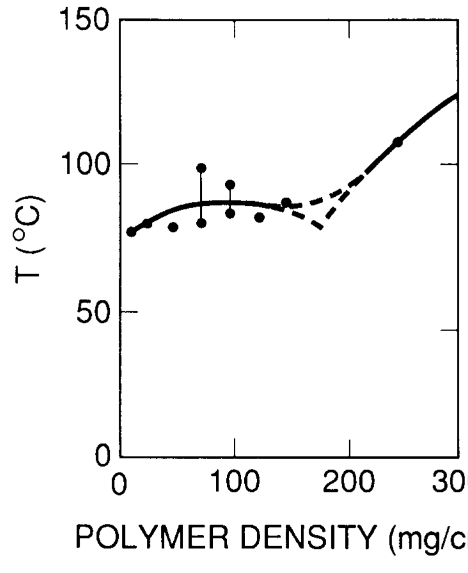

Figure 2 Visual cloud-point curve for PMP in isopropylbenzene (cumene)

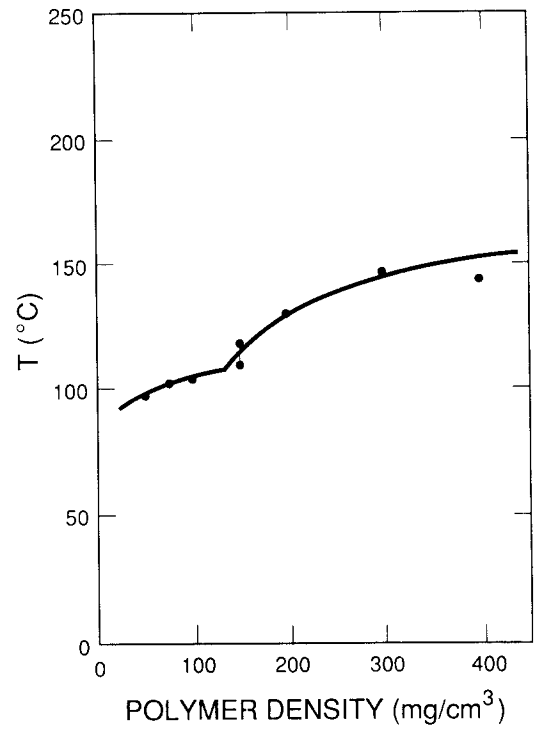

Figure 3 Visual cloud-point curve for PMP in 1,4-diisopropylbenzene

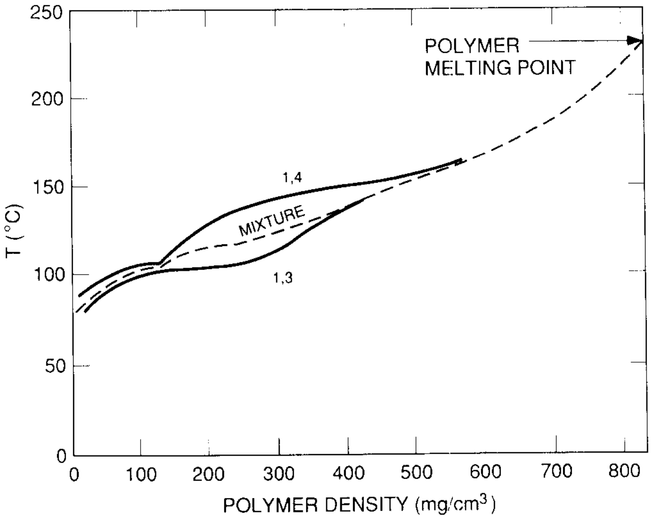

Figure 4 Visual cloud-point curves for PMP in isopropyl-substituted benzene solvents

Up to 125 mg cm^{-3}, the cloud-point curve of PMP in

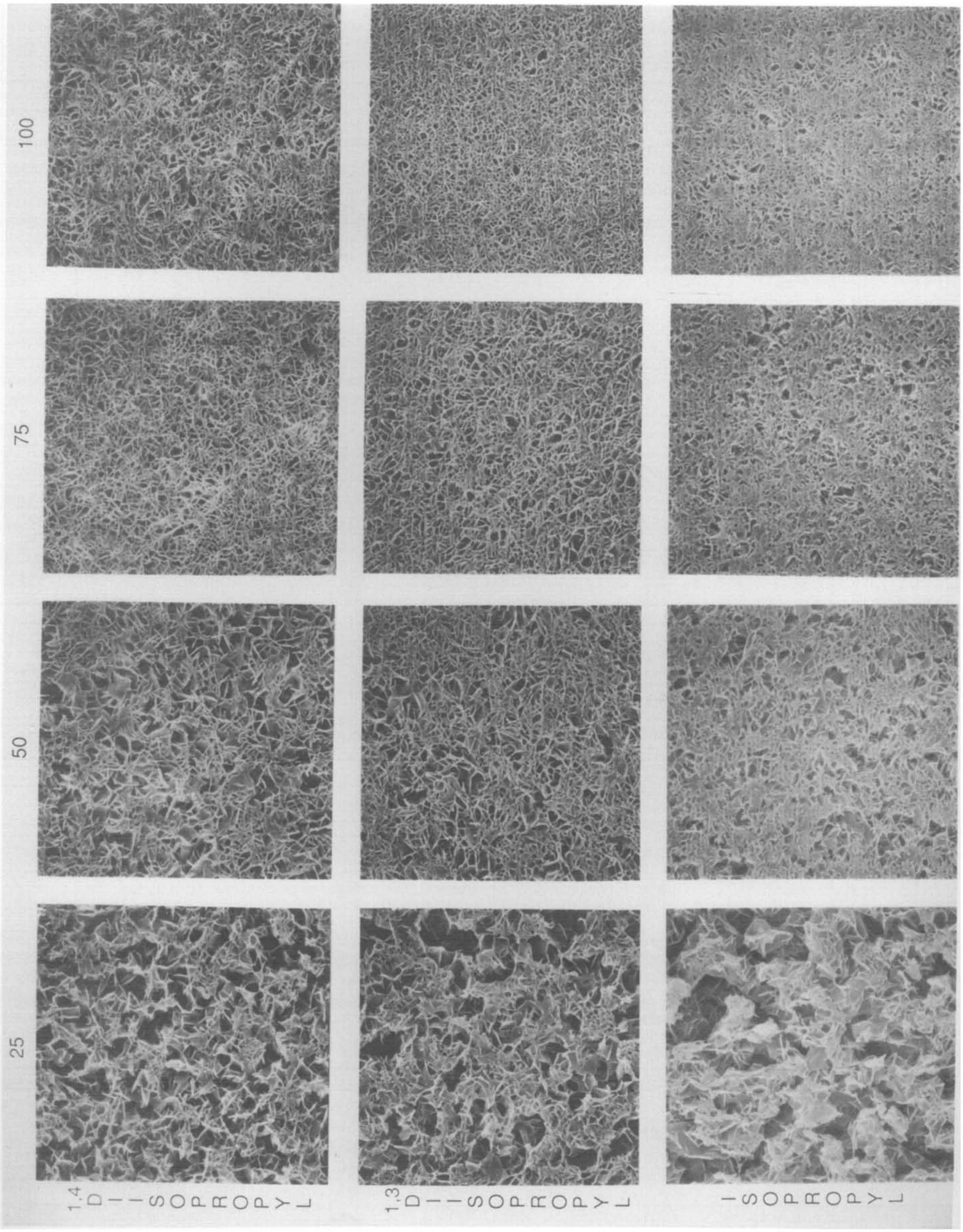

Figure 5 SEM micrographs of the PMP foams obtained at various polymer concentrations in isopropyl-substituted benzenes. The numbers above the micrographs indicate the mass of polymer in the original solution in mg cm^{-3}

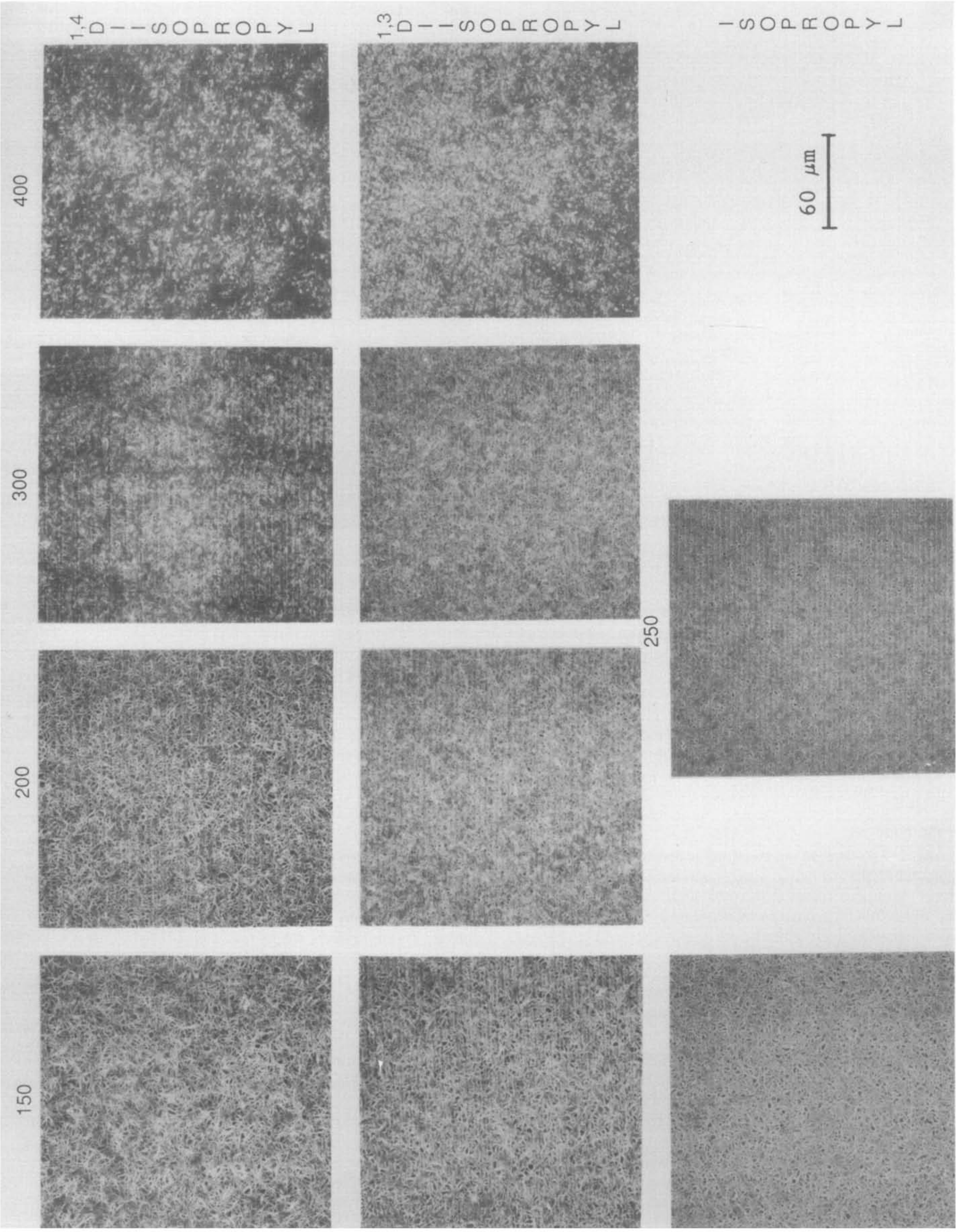

Figure 5 *contd*

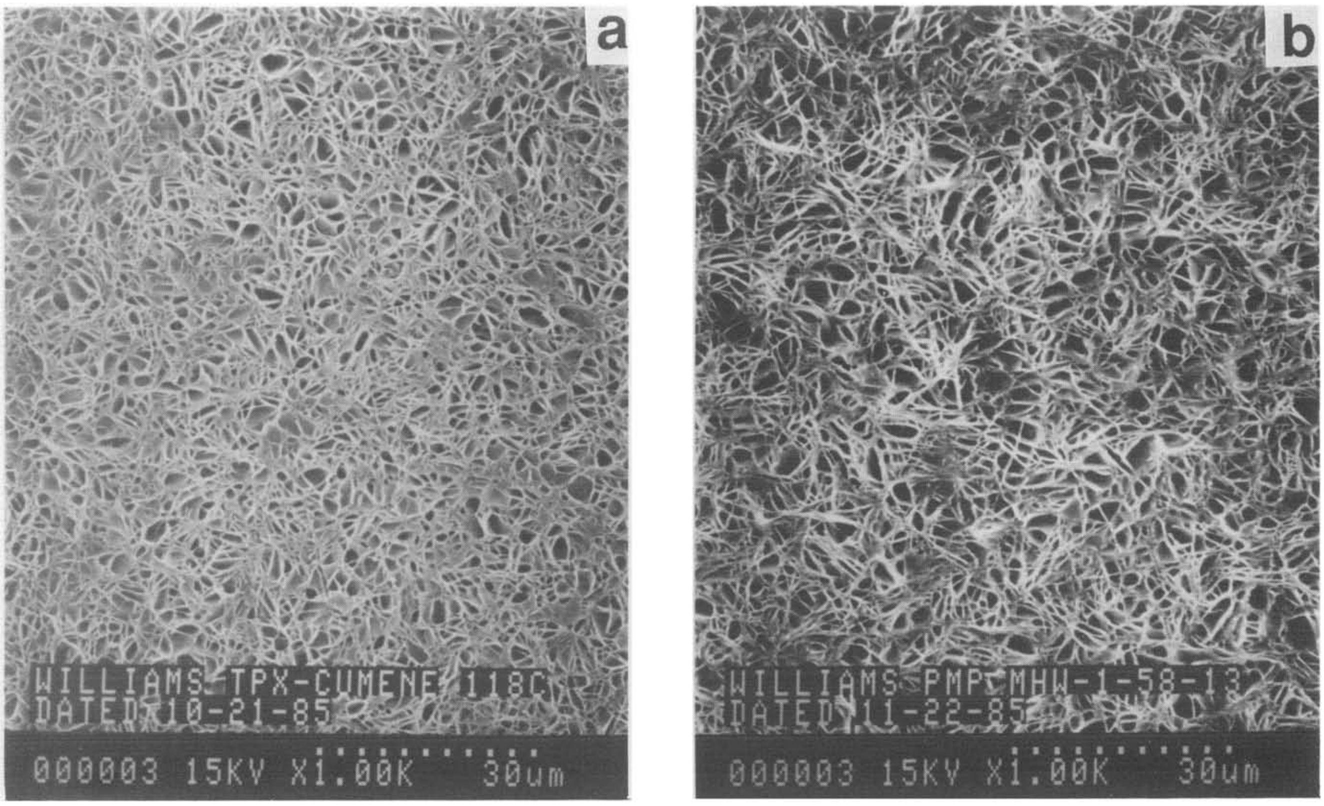

Figure 6 SEM micrographs of the PMP foams obtained at 150 mg cm^{-3} from (a) isopropylbenzene and (b) 1,4-diisopropylbenzene

1,4-diisopropylbenzene (*Figure 3*) is also similar to that of the 1,3-isomer, but a few degrees higher. Just before 150 mg cm^{-3}, however, the cloud-point curve makes a steep vertical rise. This abrupt change occurs at the same place as that reported earlier for the isomeric mixture[1]. The magnitude of the increase in the cloud-point curve for the pure 1,4-isomer, however, is greater than that of the mixture, which contained only 40% of the 1,4-isomer (see *Figure 4*). Indeed, the behaviour of the mixture seems to mimic that of the 1,4-isomer from 25 to about 300 mg cm^{-3}, but in proportion to the amount of 1,4-isomer in the mixture.

The 1,3-isomer gives a cloud-point curve behaviour typically expected when the plasticization and gelation phenomena are reasonably well separated. In contrast, the 1,4-isomer produces a different behaviour. This difference is reflected in the physical appearance of the foams (*Figure 5*) obtained from the separated solutions. Isopropyl- and 1,3-diisopropylbenzene solutions of PMP give foams whose general character does not change significantly from 25 to 300 mg of polymer/cm^3 (bottom two rows of *Figure 5*). At low polymer levels (up to 100 mg cm^{-3}), foams from the 1,4-isomer are similar. The foams from 150 and 200 mg of PMP/cm^3 solutions of 1,4-diisopropylbenzene are very different. They are quite fibrous-looking when compared to the others (*Figures 5* and *6*). This would imply that there is significantly more alignment of the polymer during phase separation from 1,4-diisopropylbenzene.

DISCUSSION

The phase-separation/cloud-point curve was determined as the temperatures at which the observer could be certain that a separation phenomenon (be it a colour change or clouding) was occurring. We frequently have the visual impression that 'something' was happening 10 to 30°C above this temperature as the solution, although still fluid, seemed to transmit light somewhat differently. In the case of the isopropyl-substituted benzene solvents, the separating solutions were clear and the observation was mainly a change in colour. The implication, therefore, is that we observed the gelation process first and that this was followed by other processes in the gel that led to translucent–turbid–opaque changes[1,4]. *Significant* ordering of the system must take place before the actual gelation event is observed. We have described elsewhere[5] a two-step process for polymer solvation and dissolution that has different solvent requirements for each step.

The abrupt rise in the phase-separation curve just before 150 mg cm^{-3}, when 1,4-diisopropylbenzene is the solvent, corresponds to 2.5 solvent molecules (exactly 2.5 at 147 mg cm^{-3}) per 4-methyl-1-pentene (4M1P) unit. The phase behaviour of the isomeric mixture also changes at this polymer-to-solvent ratio. In this case, however, there is only 1.0 molecule of 1,4-isomer per 4M1P unit; the other 1.5 molecules are 1,3- and 1,2-isomers. It seems reasonable, therefore, to conclude that one 1,4-molecule/PMP monomer unit in the pure 1,4-solvent is unique and that the other 1.5 molecules/PMP unit are not. It is implicit in this conclusion that the geometric arrangement of the isopropyl groups is not critical for the latter 1.5 molecules. Geometry appears to be very important, however, for exactly one molecule of 1,4-diisopropylbenzene solvent per 4M1P group.

Cumene serves as a benchmark to evaluate the disubstituted solvents. The prime molecular difference between the 1,3- and 1,4-diisopropylbenzene isomers is, of course, the position of the second isopropyl group

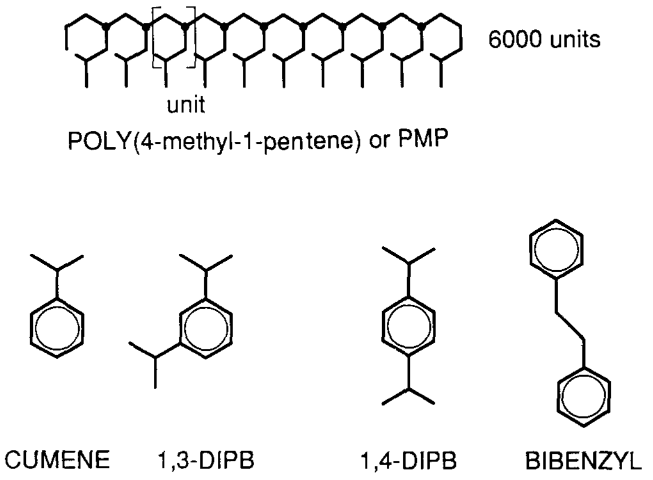

Figure 7 Models of some solvents and polymer. (Being isotactic, the polymer has long segments with the same configuration at the asymmetric carbon. These segments are followed by long segments of the opposite configuration)

relative to the first. The abnormality of the PMP separation from 1,4-diisopropylbenzene is thus believed to be related to the *para* (diametrically opposite) positioning of the isopropyl groups in the 1,4-isomer (*Figure 7*). This allows it to interact with other molecules in a more concerted fashion than is possible for the 1,3-isomer. This is reflected in the respective melting points of the isomers: m.p. = $-17°C$ for the 1,4-isomer; m.p. = $-63°C$ for the 1,3-isomer[6].

Colour changes similar to those in the separating solution of the 1,4-isomer (from purple to blue to yellow[1]) were observed when PMP was solvated by bibenzyl (i.e. 1,2-diphenylethane) in paraffin[5]. We believe that, in the latter case, bibenzyl also acted in a bidentate fashion, just like 1,4-diisopropylbenzene does here. Thus, this type of behaviour is not specific to 1,4-diisopropylbenzene, but is more general to solvent molecules with this type of symmetry. Errede[7,8] demonstrates significant dependence of the swellability of crosslinked polystyrene on small changes in solvent character. Interestingly, he shows that *m*-xylene provides a higher solubility than does *p*-xylene, but that their swellability parameters are very similar. We believe that, when the solvent is bidentate (axially symmetric), it introduces more interactions than would normally be expected between polymer and solvent.

SUMMARY

The behaviour of PMP in a mixture of diisopropylbenzene isomers mimics that of the 1,4-isomer, but to an extent proportional to the amount of 1,4-isomer in the mixture. The 1,3-isomer gives the normal cloud-point curve behaviour, while the 1,4-isomer gives an anomalous one. This difference is reflected in the physical appearance of the foams obtained from the separated solutions. From an analysis of the solvent-to-polymer ratio at the onset of this differing behaviour, we conclude that, in the pure 1,4-solvent, one solvent molecule per side-group (monomer unit) of the polymer is unique. The bidentate character of this molecule apparently allows it to provide more concerted interactions between components of the gel.

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