Preparation and glass transition temperatures of elastomeric PolyHIPE materials

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Highly porous elastomeric PolyHIPE materials have been prepared by polymerisation of the continuous phase of high internal phase emulsions (HIPEs) containing styrene, divinylbenzene and varying amounts of either 2-ethylhexyl acrylate or the corresponding methacrylate monomer. The glass transition temperatures of the resulting copolymers were investigated by differential scanning calorimetry (DSC). For each series, T_g was found to vary non-linearly with copolymer composition. By consideration of the comonomer unit sequencing along the polymer backbone, as deduced from reactivity ratios, the relationship between T_g and composition in each case has been qualitatively explained. Comparison between experimental results and values calculated using an entropic approach have been made. It is thought that the (meth)acrylate comonomers reduce the overall T_g by three mechanisms: by introducing large amounts of free volume, due to their bulky side groups; by providing a much higher degree of flexibility to the polymer chains; and by reducing the proportion of adjacent styrene units, which display particularly unfavourable steric interactions.

PolyHIPE[1] polymers belong to a class of materials known as emulsion-derived foams. Their preparation involves the polymerisation of the continuous (external) phase of a high internal phase emulsion (HIPE), consisting of a large volume of porogenic liquid dispersed in a relatively small volume of monomer(s) or monomeric solution. The volume fraction of the dispersed phase must be at least 0.74, this being the maximum volume that can be occupied by uniform undeformed spheres, and can be as high as 0.99. The HIPE is stabilised by a sufficiently high concentration of a carefully chosen surfactant, such that inversion to the corresponding dilute emulsion is prevented. Following polymerisation, the dispersed phase is removed yielding, generally, an open-cellular, low-density foam.

A considerable volume of literature exists on PolyHIPE polymers, most of which deals with styrene/divinylbenzene (S/DVB) materials. In this case, an aqueous droplet phase is dispersed in a mixture of monomers plus nonionic surfactant (*e.g.* sorbitan monooleate). A water-soluble free-radical initiator, such as potassium persulfate, is used to facilitate polymerisation. The open-cellular morphology of the resulting material can clearly be seen by scanning electron microscopy (Fig. 1). Compared to conventional gas-blown polystyrene foams, the cells are more spherical and of smaller size.

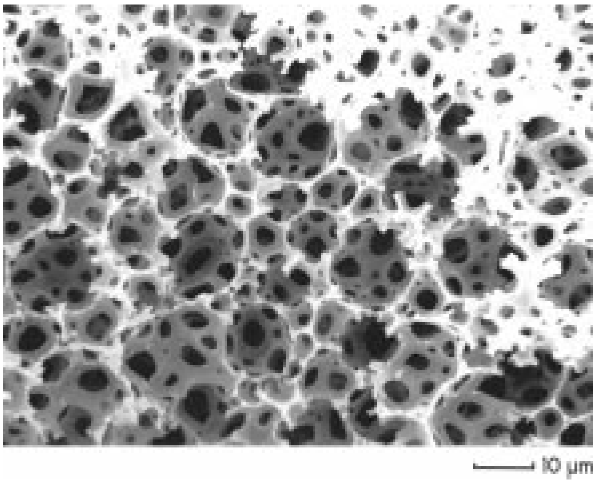


Fig. 1 Scanning electron micrograph (SEM) of typical poly(styrene/DVB) PolyHIPE (bar ≡ 10 μm)

Investigations into the factors which affect the cellular structure and morphology of PS/DVB PolyHIPE polymers revealed that surfactant concentration plays a pivotal role,[2] particularly in determining whether an open- or closed-cell structure is formed. The volume fraction of the water droplets is less critical in this context. Recent cryo-SEM studies[3] have shown that the appearance of holes between adjacent water droplets corresponds to the gel-point of the polymerisation. The cell sizes of PS/DVB PolyHIPE polymers were found to be strongly affected by the concentration of electrolytes in the aqueous phase,[4] increasing salt concentration tending to lower the cell-size. The presence of salts is known to enhance water-in-oil emulsion stability *via* inhibition of the Ostwald ripening process, due to the decreased miscibility of the oil and aqueous phases.[5] Additionally, electrolytes lower the interfacial tension thus giving greater surfactant adsorption at the interface and an increased resistance to droplet coalescence.[6]

Open-cell PolyHIPE polymers are characterised by a low bulk density, typically less than 0.1 g cm^{-3}, and cell sizes range between 5 and 100 μm, depending on the preparation conditions, as mentioned above. Consequently, the internal surface areas tend to be much lower than those observed in typical PS/DVB resins, 5 m^2 g^{-1} being an average figure. However,[7] using porogens in the monomeric phase allows PolyHIPE materials with surface areas up to 350 m^2 g^{-1} to be prepared, in which the cell walls have pores similar in size and character to those observed in conventional macroporous polymer resins.[8]

PolyHIPE materials have recently been successfully employed as supports in solid phase peptide synthesis, in which the porous structure acts as a scaffold for a soft polyamide gel.[9] Additionally, PolyHIPE monoliths have been used to immobilise flavin,[10] and granulated PS/DVB PolyHIPE has been used as a catalyst support.[11] The preparation, properties and applications of PolyHIPE polymers have recently been comprehensively reviewed.[12]

PS/DVB PolyHIPE polymers have similar overall mechanical properties to gas-blown PS foams, although the smaller size and increased spherical symmetry of the cells results in higher compressive strengths.[2] They are, however, rather hard and brittle, due to the relatively high glass transition temperature (T_g) of polystyrene (100 °C). The mechanical properties of PolyHIPE polymers might be improved by introducing an elastomeric comonomer to reduce the overall T_g and thus lend some flexibility to the material. This comonomer must also be sufficiently hydrophobic to form stable HIPEs, should copolymerise readily with styrene and DVB and preferentially should be available commercially at low cost. Both 2-ethylhexyl acrylate (EHA) and methacrylate (EHMA) possess these requirements. The T_g values of the homopolymers are 223 and 263 K, respectively.[13] Acrylates giving low T_g polymers are often used as comonomers to plasticise harder materials.[14]

In this publication the preparation of PS/DVB PolyHIPE materials incorporating increasing quantities of either EHA or EHMA is described. In addition, the thermal properties of the resulting foams are investigated by means of differential scanning calorimetry (DSC).

Experimental

Materials

Styrene (Fisons), divinylbenzene (55% DVB, tech. grade, Aldrich), (±)-2-ethylhexyl acrylate (Aldrich), (±)-2-ethylhexyl methacrylate (Aldrich), sorbitan monooleate (Span 80, Koch-Light), potassium persulfate (Fisons) and calcium chloride hexahydrate (Fisons) were used as received.

Synthesis of poly[styrene/2-ethylhexyl (meth)acrylate/-DVB] PolyHIPE copolymers. Two series of materials were prepared, with varying contents of EHA or EHMA, relative to the total monomer content. A procedure for the preparation of a material containing 40% v/v EHMA is given below.

Styrene (5 ml, 0.05 mol), DVB (1 ml), EHMA (4 ml, 0.02 mol) and Span 80 (2.0 g) were placed in a 300 ml wide-necked polyethylene bottle, and were stirred with a glass stirring rod fitted with a D-shaped PTFE paddle, connected to an overhead stirrer motor, at 300 rpm. The aqueous solution, comprising potassium persulfate (0.2 g, 0.7 mmol) and calcium chloride hexahydrate (2.0 g, 9.1 mmol) in de-ionised water (90 ml) was added dropwise, with constant stirring, to form the HIPE. As the aqueous phase was added, the bottle was lowered to maintain stirring just below the surface of the developing HIPE, ensuring that no water pockets formed. Once all the aqueous phase had been added, stirring was continued for a further 5 min, to produce as uniform an emulsion as possible. The HIPE was then transferred to a reusable polymerisation mould. This consisted of a PVC cylinder, itself composed of two halves, which were screwed together, with separate screw-on base and lid. When assembled, the mould had an internal height of 14 cm and an internal diameter of 4.5 cm. Prior to use, the inner surfaces were sprayed with PTFE spray to prevent the polymer from adhering. The HIPE was poured into the assembled mould, which was then immersed in a water bath at 65 °C for 48 h, to form the PolyHIPE. The polymer monolith was retrieved by disassembling the vessel and was then extracted in a Soxhlet apparatus with water, for 24 h, to remove inorganic materials, followed by a lower alcohol, for a further 48 h. The bulk of the liquid was removed from the porous material *in vacuo* at room temp., and drying was completed *in vacuo* at 50 °C for 24 h.

Instrumentation. The T_g values of the copolymers were determined by DSC using a DuPont 910 Differential Scanning Calorimeter fitted with a DuPont 9900 Computer/Thermal Analyser unit, under a steady flow of nitrogen and at a heating rate of 5 °C min^{-1}. Monolithic PolyHIPE samples were ground to a powder and dried in a vacuum oven at 40 °C for 2 h prior to DSC analysis. Each DSC sample contained between 5 and 10 mg of polymer material.

Results and Discussion

Upon cleaning and drying, the EH(M)A PolyHIPE materials appeared identical to their PS/DVB analogues. The open-cellular morphology was confirmed by SEM (Fig. 2). The copolymer T_g values were determined by DSC; plots of T_g against composition are given in Figs. 3 and 4. Each T_g value was obtained from an average of two or three runs.

Theoretical treatments

The T_g values of alkyl acrylate and alkyl methacrylate homopolymers are largely governed by the nature of the alcoholic moiety of the ester; T_g decreases as the number of carbon atoms in the *n*-alkyl series increases. However, as the chain

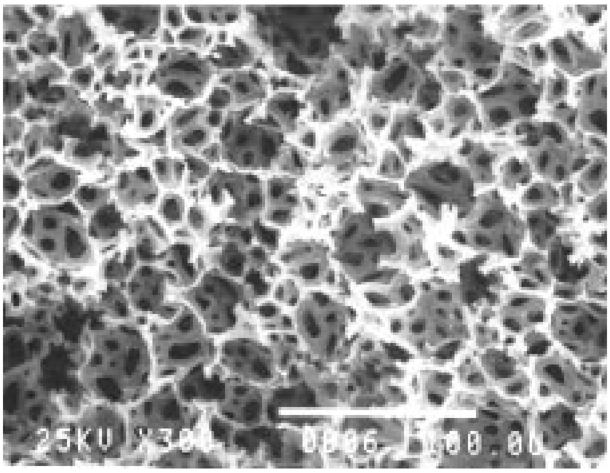


Fig. 2 Scanning electron micrograph (SEM) of poly(styrene/DVB/EHA) PolyHIPE (vol%: S, 70; DVB, 10; EHA, 20. Internal Phase vol% = 90) (bar ≡ 25 μm)

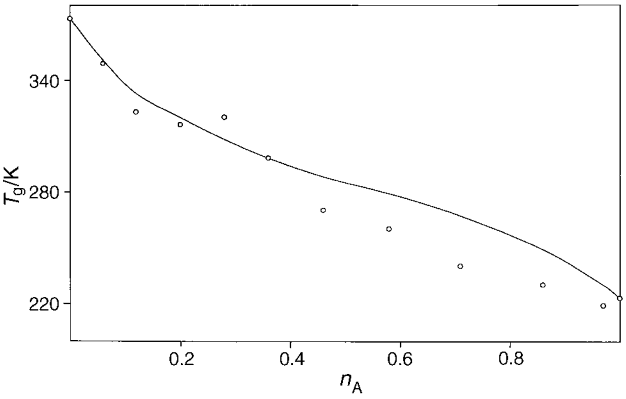


Fig. 3 T_g *vs.* EHA content of poly(styrene/DVB/EHA) PolyHIPE copolymers: (○) experimental values and (—) values predicted by Barton's model

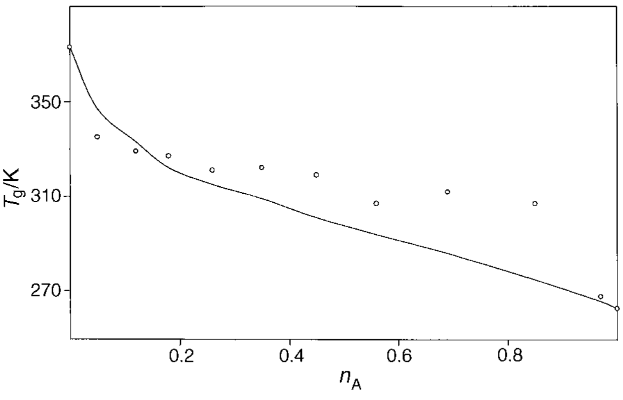


Fig. 4 T_g *vs.* EHMA content of poly(styrene/DVB/EHMA) PolyHIPE copolymers: (○) experimental values and (—) values predicted by Barton's model

length increases beyond a certain value, crystallisation of the side-chain occurs and T_g starts to increase once more. Branching of the alcohol chain restricts the rotation of the side-chain bonds so T_g is raised. Thus, PEHA has a T_g of 223 K compared to that of poly(*n*-hexyl acrylate) which is 216 K.[13] Polymethacrylates are harder and therefore have higher T_g values than the corresponding acrylates, due to increased restriction to rotation of the polymer backbone from the methyl group. For this reason, PEHMA has a T_g of 263 K, higher than that of PEHA.

The glass transition temperatures of random copolymers were initially described by a simple additive formula, known as the Fox equation [eqn. (1)],[15]

$$\frac{1}{T_g}=\frac{W_1}{T_{g_1}}+\frac{W_2}{T_{g_2}}+\ldots+\frac{W_i}{T_{g_i}} \tag{1}$$

where W_i is the weight fraction of monomer i in the copolymer and T_{g_i} is the glass transition temperature of its homopolymer. However, DiMarzio and Gibbs[16] suggested that the T_g of a copolymer would be determined largely by the stiffness of the polymer chains, and arrived at the following relation (eqn. 2),

$$n_a\alpha_a(T_g-T_{g_a})+n_b\alpha_b(T_g-T_{g_b})=0 \tag{2}$$

where n_i is the mole fraction of repeat unit i, α_i is the number of rotatable bonds in repeat unit i and T_{g_i} is the glass transition temperature of the homopolymer of i.

In reality, many copolymers were found to deviate from these simple linear relationships. Barton[17] modified the theory of DiMarzio and Gibbs to take account of the sequencing of monomer units in a random copolymer. An AB-type copolymer has four possible pairs of repeat units, or diads, which can be expressed as aa, ab, ba or bb. The properties of an ab or ba diad may indeed differ from those of either an aa or bb sequence; the linear expression can therefore be extended to give eqn. (3),

$$T_g=n_{aa}'T_{g_{ab}}+n_{bb}'+(n_{ab}'+n_{ba}')T_{g_{ab}} \tag{3}$$

where n_j' is given by eqn. (4),

$$n_{ij}'=n_{ij}\alpha_{ij}/\sum_{ij}(n_{ij}\alpha_{ij}) \tag{4}$$

and n_{ij} is the molar fraction of ij sequences, α_{ij} is the number of rotatable bonds in sequence ij, $T_{g_{aa}}$ and $T_{g_{bb}}$ are the T_g values of the respective homopolymers and $T_{g_{ab}}$ is the T_g of an exactly alternating 1:1 copolymer of a and b. This can be rearranged to eqn. (5).

$$T_g-n_{aa}'T_{g_{aa}}-n_{bb}'T_{g_{bb}}=(n_{ab}'+n_{ba}')T_{g_{ab}} \tag{5}$$

$T_{g_{ab}}$ can then be found from the slope of the plot of the left-hand side of eqn. (5) against $(n_{ab}'+n_{ba}')$. The sequencing of diad units is controlled by the reactivity ratios of each monomer in the copolymer feed, therefore the T_g values of the copolymers are also affected.

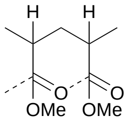
Similarly, the Fox equation was modified by Johnston and co-workers[18] to include the influence of monomer unit sequencing on copolymer T_g [eqn. (6)].

$$\frac{1}{T_g}=\frac{W_aP_{aa}}{T_{g_{aa}}}+\frac{(W_aP_{ab}+W_bP_{ba})}{T_{g_{ab}}}+\frac{W_bP_{bb}}{T_{g_{bb}}} \tag{6}$$

W_i is the weight fraction of i in the copolymer, P_{ij} is the probability of unit ij occurring in the copolymer chain and $T_{g_{ij}}$ is the contribution to the overall T_g of unit ij. These expressions, or modifications thereof, have been shown to be applicable to a wide range of copolymer systems.

Rather surprisingly, T_g values of styrene/2-ethylhexyl (meth)acrylate linear copolymers could not be found in the literature. However, the relatively similar styrene/*n*-butyl acrylate system has been studied. Illers[19] observed a non-linear S-shaped curve in the graph of T_g against composition, with an inflection point at around 60% styrene. Interestingly, this was the only copolymer system examined by Barton which would not conform to his theory, which predicted a negative deviation from linearity. Recent work[20] with styrene/*n*-butyl methacrylate copolymers indicated that the T_g-composition relationship is a simple curve of negative curvature. In this case, the experimental results were found to coincide with theoretical predictions.

The negative curvature predicted by Barton[17] for styrene/*n*-butyl acrylate copolymers, and observed by Schellenberg and Vogel[20] in styrene/*n*-butyl methacrylate systems, can be explained qualitatively by the reduction in steric hindrance between adjacent copolymer chains, due to the increase in free volume on incorporation of comonomers with long *n*-butyl side chains. In comparison, styrene/methyl acrylate systems show a positive curvature in T_g-composition plots. The much smaller methoxy groups do not disturb the chain packing to such a great extent, so steric hindrance to backbone motion is still encountered. The positive deviation has been attributed by Barton to the ability of methyl acrylate diads to form a ring-type conformation:



Experimental results

The T_g-copolymer composition plots for both the acrylate- and methacrylate-containing copolymers are non-linear. The transition temperatures of the EHA materials decrease steadily until about 12% EHA content, followed by a plateau region up to 30%. After this, the T_g falls steadily towards that of PEHA (223 K). With the EHMA copolymers, however, there is an initial dramatic decrease in T_g upon addition of only 5% comonomer; subsequently, hardly any decrease is shown over almost the entire composition range, before a further sharp drop at the highest EHMA content. Barton's copolymer T_g model[17] was used to predict the T_g value of the PolyHIPE copolymers, employing eqns. (3)–(5). For the EHA/S/DVB system, $\alpha_{aa}=22$, $\alpha_{ab}=14$ and $\alpha_{bb}=6$, whereas for the EHMA/S/DVB system, $\alpha_{aa}=24$, $\alpha_{ab}=15$ and $\alpha_{bb}=6$. Since the materials in the present study are all crosslinked and ~100% converted, the following assumptions have been made: (1) for determining α values, DVB (and Et-styrene isomers) units have been ignored; (2) the concentrations of styrene and DVB in the comonomer feed are combined to give a value for styrenic monomers, designated species b in this case; (3) the mole fraction of each monomer incorporated in the copolymer, n_a, is equal to the mole fraction of monomer in the feed, n_A.

T_g values for the 1:1 alternating copolymers ($T_{g_{ab}}$) were calculated using the linearised Barton eqn. (5), as described in the previous section. This gave $T_{g_{ab}}=282$ K for EHA copolymers and 310 K for the EHMA materials. These parameters were then used in eqn. (3) to calculate the theoretical T_g at each feed ratio. The results of the model predictions are shown with the experimental data in Figs. 3 and 4.

Both the experimental and model results indicate that the introduction of only 5% (meth)acrylate comonomer causes a considerable decrease in copolymer T_g. This could be due to an increase in free volume caused by the bulky ethylhexyl side chains, reducing the temperature at which the onset of local segmental motion occurs. In addition, the introduction of some (meth)acrylate units into the backbone reduces the number of styrene–styrene diads, which experience unfavourable steric interactions between adjacent phenyl groups, thus also lowering the T_g. However, further increases in EH(M)A content causes only a slight decrease in the T_g since the packing of the chains is already severely disrupted.

After approximately 30% EH(M)A monomer content, differences start to appear between the curves of acrylate and methacrylate copolymers. From Fig. 3, it can be seen that the rate of decrease of T_g with increasing EHA content increases after a mole fraction of 30%. This can be explained as follows. The distances between adjacent chains do not increase greatly; however, the chance of bb diads of EHA occurring increases. The reactivity ratios of styrene (M_1) and EHA (M_2) are reported as being $r_1=0.91$ and $r_2=0.29$.[13] Therefore, at low EHA content, it is highly probable that no EHA diads exist, only ab styrene-EHA sequences. As the EHA concentration increases, EHA diads become increasingly more probable. Since EHA monomer repeat units possess many more rotatable bonds than styrene units, the introduction of EHA diads would result in a large enhancement of the freedom of rotation and motion of the polymer chain. Thus, the T_g starts to decrease more quickly.

The T_g values of the methacrylate copolymers (Fig. 4) do not drop rapidly after 30% EHMA content, but remain more or less constant. This reflects the hindrance to rotation of the polymer backbone in the vicinity of EHMA units, caused by the α-methyl groups. The reactivity ratios of styrene and EHMA could not be located in the literature. However, for styrene (M_1) and *n*-hexyl methacrylate (M_2) the corresponding values are: $r_1=0.45$ and $r_2=0.65$,[13] *i.e.* each polymer radical type has approximately equal reactivity. Assuming styrene and EHMA have similar *r* values to those above, at low EHMA content bb EHMA diads are quite possible. Both intermolecular (chain spacing) and intramolecular (rotation of groups in the backbone) effects therefore occur even at low EHMA content, so initially there is a large drop in T_g (Fig. 4). Subsequently, interchain spacing does not drastically increase, while the content of EHMA diads grows steadily, resulting in a gradual drop in T_g with increasing EHMA content.

Comparison of the experimental and model results indicates that, in this case, Barton's theoretical treatment is only partially successful at predicting copolymer T_g. However, a number of observations can be made. First, the trends shown by the experimental results are generally reproduced, that is to say that the EHA copolymer series is expected to have an S-shaped T_g-copolymer composition relationship, whereas the EHMA series shows simple negative curvature. Second, the model predicts a sharper initial drop in T_g for the methacrylate series, which is also observed experimentally. Fig. 3 indicates that the experimental T_g values of the EHA copolymers above $n_A=0.4$ fall below the model curve. This may be due to plasticisation by residual surfactant, which is notoriously difficult to remove from PolyHIPE materials.[21] This could counteract any raising of T_g caused by crosslinking, which is probably the reason for the underestimation of the T_g results by the model in Fig. 4.

Crosslinking affects the glass transition temperatures of copolymers by two independent mechanisms:[22,23] (1) the crosslinking effect, which invariably raises T_g, and (2) the copolymer effect, due to the chemical nature of the crosslinking species. The latter can either raise or lower T_g. Since DVB is almost identical chemically to styrene, the copolymer effect can largely be neglected,[24] especially for the low crosslink density of the materials in the present study. Recently, it has been reported that approximately 5% of crosslinked PS/DVB resins have T_g values about 25 K higher than linear polystyrene.[25] In the same publication, however, model calculations indicate that, for a given crosslink density, the increase in T_g caused by crosslinking is reduced as the flexibility of the polymer backbone increases. For the copolymers investigated here, this implies that increasing the concentration of the more flexible component lessens the crosslinking effect. This is the opposite to the trend shown in Fig. 4, which may reflect the shortcomings of the various models (composition-T_g and crosslinking-T_g) in adequately describing such complex systems. The copolymers containing the highest amounts of EH(M)A, which consequently are only 1% crosslinked, would be expected to mimic the model behaviour more closely. This may explain why the T_g of the most lightly crosslinked sample at high EHMA content coincides with the calculated value.

Conclusions

The preparation of elastomeric PolyHIPE polymers from high internal phase emulsions containing styrene, DVB and 2-ethylhexyl (meth)acrylate has been described. The glass transition temperatures of the resulting materials, as determined by DSC, were found to vary in a non-linear fashion with composition. It is proposed that the (meth)acrylate comonomer units influence T_g in three ways: first, they introduce significant amounts of free volume due to their bulky side-groups; second, the high flexibility of the side-groups results in increased segmental motion; and third, introduction of EH(M)A units dilutes the concentration of sterically unfavourable styrene–styrene diads. All of these effects conspire to lower the T_g values further than is predicted by the Fox equation. The shapes of the individual curves have been explained qualitatively by considering the comonomer unit diad sequencing, which can be predicted from the corresponding reactivity ratios. Comparisons with T_g values calculated using Barton's model indicate that the overall T_g-composition trends are reproduced in each case, despite the lack of exact correlations. The complexity of the systems studied here may preclude the accurate use of any predictive model.

NRC gratefully acknowledges the (then) SERC for the provision of a CASE studentship and Unilever Research, Port Sunlight, the Cooperating Body. The discussions with Dr D. Gregory are particularly appreciated.

References

1 D. Barby and Z. Haq, *Eur. Pat.* 0,060,138 (1982) (to Unilever).
2 J. M. Williams and D. A. Wrobleski, *Langmuir*, 1988, **4**, 656.
3 N. R. Cameron and D. C. Sherrington, *Colloid Polym. Sci.*, 1996, **274**, 592.
4 J. M. Williams, A. J. Gray and M. H. Wilkerson, *Langmuir*, 1990, **6**, 437.
5 J. Kizling and B. Kronberg, *Colloids Surf.*, 1990, **50**, 131.
6 M. P. Aronson and M. F. Petko, *J. Colloid Interface Sci.*, 1993, **159**, 134.
7 P. Hainey, I. M. Huxham, B. Rowatt, D. C. Sherrington and L. Tetley, *Macromolecules*, 1991, **24**, 117.
8 A. Guyot, *Synthesis and Structure of Polymer Supports*, in *Syntheses and Separations using Functional Polymers*, ed. D. C. Sherrington and P. Hodge, Wiley, New York, 1988, ch. 1.
9 P. W. Small and D. C. Sherrington, *J. Chem. Soc., Chem. Commun.*, 1989, 1589.
10 H. F. M. Schoo, G. Challa, B. Rowatt and D. C. Sherrington, *React. Polym.*, 1992, **16**, 125.
11 E. Ruckenstein and L. Hong, *Chem. Mater.*, 1992, **4**, 122.
12 N. R. Cameron and D. C. Sherrington, *Adv. Polym. Sci.*, 1996, **126**, 163.
13 *Polymer Handbook*, ed. J. Brandrup and E. H. Immergut, 2nd edn., Wiley Interscience, USA, 1975.
14 B. B. Kine and R. W. Novak, *Acrylic and Methacrylic Ester Polymers*, in *Encyclopedia of Polymer Science and Engineering Vol. 1*, Wiley-Interscience, USA, 1985.
15 T. G. Fox, *Bull. Am. Phys. Soc.*, 1956, **1**, 123.
16 E. A. DiMarzio and J. H. Gibbs, *J. Polym. Sci.*, 1959, **40**, 121.
17 J. M. Barton, *J. Polym. Sci., Polym. Symp.*, 1970, **30**, 573.
18 N. W. Johnston, *J. Macromol. Sci., Rev. Macromol. Chem.*, 1976, **C14**, 215 and references therein.
19 K. H. Illers, *Kolloid-Z.*, 1963, **190**, 16.
20 J. Schellenberg and J. Vogel, *J. Polym. Sci. B, Polym. Phys.*, 1995, **32**, 1969.
21 D. P. Gregory, Unilever Research, Port Sunlight, personal communication.
22 S. Loshaek, *J. Polym. Sci.*, 1955, **15**, 391.
23 L. E. Nielsen, *J. Macromol. Sci., Rev. Macromol. Chem.*, 1969, **C3**, 69.
24 T. G. Fox and S. Loshaek, *J. Polym. Sci.*, 1955, **15**, 371.
25 J. Bicerano, R. L. Sammler, C. J. Carriere and J. T. Seitz, *J. Polym. Sci. B, Polym. Phys.*, 1996, **34**, 2247.

Paper 7/02030I; *Received* 24*th March*, 1997