tion highly efficiently as emulsifiers capable of stabilising both water-in-oil and oil-in-water systems. These properties have been characterised in some detail[25] and may also have relevance in the present catalytic studies.

More detailed investigations are required to achieve a full understanding of these systems and our work in this area is continuing.

References

1 Kunitake, T. and Okahata, Y. *Adv. Polym. Sci.* 1976, **20**, 159
2 Shimidzu, T. *Adv. Polym. Sci.* 1977, **23**, 55
3 Yamashita, T., Yasueda, H. and Nakamura, N. *Chem. Lett.* 1974, 585
4 Yamashita, T., Yasueda, H., Miyauchi, Y. and Nakamura, N. *Bull. Chem. Soc. Jpn*, 1977, **50**, 1532
5 Yamashita, T., Yasueda, H., Nakatani, N. and Nakamura, N. *Bull. Chem. Soc. Jpn*, 1978, **51**, 1183
6 Yamashita, T., Yasueda, H. and Nakamura, N. *Bull. Chem. Soc. Jpn.* 1978, **51**, 1247
7 Ise, N. *Adv. Polym. Sci.* 1971, 7, 536
8 Morawetz, H., 'Macromolecules in Solution', 2nd Edition, Interscience, New York, 1975
9 Okubo, T. and Ise, N. *Adv. Polym. Sci.* 1977, **25**, 136
10 Regen, S. L. *J. Am. Chem. Soc.* 1975, **97**, 5956
11 Cinquini, M., Colonna, S., Montanari, F. and Tundo, P. *Chem. Comm.* 1976, 392
12 Regen, S. L., Nigan, A. and Besse, J. *Tetrahedron Lett.* 1978, 2757
13 Mackenzie, W. M. and Sherrington, D. C. *Chem. Comm.* 1978, 541
14 Tomoi, M., Takubo, T., Ikeda, M. and Kakiuchi, H. *Chem. Lett.* 1976, 473
15 Chiellini, E., Solaro, R. and D'Antone, S. *Makromol. Chem.* 1977, **178**, 3165
16 Chiellini, E. and Solaro, R. *Chem. Comm.* 1977, 231
17 Hirao, A., Nakahama, S., Takahashi, M. and Yamazaki, N. *Makromol.Chem.* 1978, **179**, 915
18 Hirao, A., Nakahama, S., Takahashi, M. and Yamazaki, N., *Makromol. Chem.* 1978, **179**, 1735
19 Yamazaki, N., Hirao, A. and Nakahama, S. *Polym. J.* 1975, **7**, 402
20 Yamazaki, N., Hirao, A. and Nakahama, S. *J. Polym. Sci. (Polym. Chem.)* 1976, **14**, 1229
21 Kornblum, N. and Lurie, A. P. *J. Am. Chem. Soc.* 1959, **81**, 2710
22 Szwarc, M. 'Ions and Ion Pairs in Organic Reactions', (Ed. M. Szwarc), Wiley, New York, 1974, Vol 2, p 391
23 Toke, L. and Szabo, G. T. *Acta Chim. Acad. Sci. Hungaricae* (1977), **93**, 421
24 Yanagida, S., Noji, Y. and Okahara, M. *Tetrahedron Lett.* 1977, 2893
25 Reiss, G., Nervo, J. and Rogez, D. *Polym. Eng. and Sci.* 1977, **17**, No 8

A 'Feathered' polymer resin

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In the course of our on-going syntheses of new macromolecular supports for application in the solid phase method[1] of peptide and oligonucleotide assembly, we have prepared a crosslinked poly(*N,N*-dipropylacrylamide) with a remarkable macroscopic structure, which to the authors' knowledge has never been reported before. Polymerization was carried out in suspension as described below, in anticipation of producing a beaded polymer in the usual way. After the reaction was completed a sample of the suspended product was examined under an optical microscope. While the polymeric material did indeed consist of particles with essentially spherically symmetric cores, (~50 μm diameter), in addition, protruding in all directions from their surfaces were feather-like appendages (*Figure 1*). On leaving part of the reaction mixture to stand in a stoppered storage bottle the 'feathered' resin beads gradually settled. However, the volume occupied by the polymer was considerably larger than with conventional resins, presumably because the protrusions preclude close packing.

Examination of a sample allowed to dry out on a microscope slide showed that the 'plumage' had become detached from the central cores, and therefore has poor mechanical stability. Indeed when another sample was left in a shaker for 1 h many of the 'feathers' once again were detached. By repeatedly diluting this suspension with acetone followed, after settling, by decantation, the suspension medium was gradually changed. In this solvent the detached 'feathers' tend to remain in suspension much longer, and hence their separation from the remaining polymer fraction was readily effected. Infra-red analysis of the dried 'feathers' confirmed them to consist of an acrylamide-type polymer. Although no weight fractions were measured, the polymer 'plumage' appears to constitute a relatively minor fraction of the total mass of polymer.

The mechanism by which these structures are formed is not known, but a crucial factor may be the extent to which

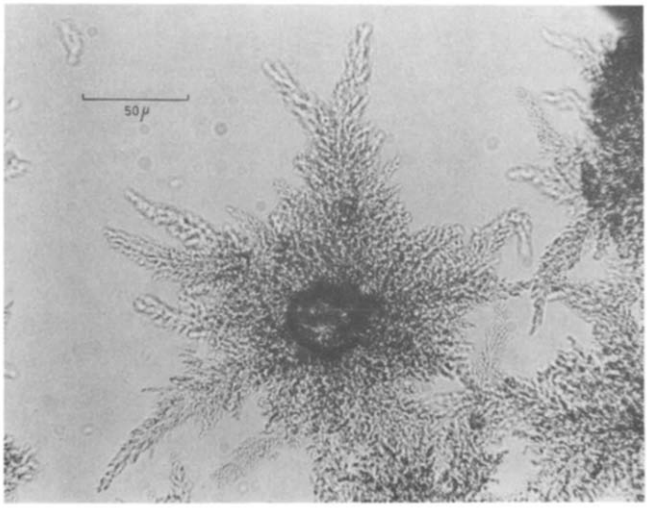

Figure 1 Optical photograph of a 'feathered' resin bead in suspension in water

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monomer and crosslinking comonomer are distributed between the suspended phase and the suspension medium, the feather-like species possibly arising from polymerization of monomers dissolved in the aqueous phase. Unfortunately time does not allow our own research efforts to pursue this matter further. However, the ability to generate such structures may have important consequences in the fields of colloid stability and polymer compatibility, and other groups may wish to examine this phenomenon in more detail.

Suspension copolymerization[2] was carried out as follows. *N,N*-methylenebisacrylamide (0.875 g) and *N,N*-di-n-propylacrylamide[3] (7.50 g) in toluene (10 ml) was suspended by rapid stirring (~800 rpm) in a previously prepared solution of poly(vinyl pyrrolidone) (1 g) in water (400 ml). After addition of the initiator, azobisisobutyronitrile (0.1 g), the reaction flask was flushed for 10 min with nitrogen gas and then stirred at 80°C for 3.5 h. Part of the product was retained in suspension for examination as described above, the remainder was collected by suction filtration and was washed consecutively with acetone, 50% aqueous acetone and finally water before being left to dry in air. The final product is a translucent amorphous solid.

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References

1 'Solid Phase Synthesis', (Eds E. C. Blossey and D. C. Neckers), Dowden, Hutchinson and Ross, Stroudsburg, 1975
2 Greig, J. A. and Sherrington, D. C. *Polymer* 1978, **19**, 163
3 Butler, K., Thomas, P. R. and Tyler, G. J. *J. Polym. Sci.* 1960, **48**, 357

Novel macroporous hydrogel adsorbents for artificial liver support haemoperfusion systems

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The clinical use of haemoperfusion in blood detoxification and in the treatment of uraemia is now well established. Problems still exist, however, particularly in the wider use of the technique as the basis of artificial liver support systems for the treatment of acture liver failure[1]. Many of these problems are associated with the nature of the adsorbent and the need exists for a range of biocompatible adsorbents showing some degree of specificity for various blood toxins. Although activated carbons have a high adsorbation capacity for many such toxins, especially those that are water soluble, the need to improve its blood compatibility and prevent the detachment of carbon microparticles entails its impregnation or encapsulation in a polymeric coating such as poly(2-hydroxyethyl methacrylate). One major disadvantage of homogeneous hydrogels of this type is that they effectively behave as a membrane, restricting the rate of adsorption and to some extent the size of species that are adsorbed. Thus a compromise between compatibility and adsorption properties must be accepted. An alternative group of materials are the macroreticular cross-linked polystyrene or acrylic resins used in ion exchange. These are effective in the removal of certain toxins (particularly the bile acids) but are of limited value because of their poor blood compatibility.

We have investigated the possibility of employing the principle of polymerization on a crystalline matrix (used by Krauch and Sanner[2] and extended by Halden and Lee[3] to the polymerization of 2-hydroxyethyl methacrylate) to provide a macroporous hydrogel bead having strength, blood compatibility and adsorption properties appropriate to use in haemoperfusion systems[4]. Since ice forms a convenient matrix for these systems, phase diagrams were constructed to establish solubility limits for mixtures of appropriate monomers and cross-linking agents in water and water–ethylene glycol mixtures. Rapid cooling of the homogeneous solutions, photopolymerization (in the presence of, for example, benzoin or uranyl nitrate) and subsequent hydration produced macroporous polymer gels. Initial work showed that variation in solvent: monomer ratio, the nature of the monomer and cross-linking agent and the cross-link density produced membranes having a range of equilibrium water contents. The properties of these membranes are different from their homogeneous counterparts in respect of strength, opacity, water binding properties (as measured for example by differential scanning calorimetry) and porosity (having mean pore diameters in the range 0.2–2.0 microns). The relevance of these differences is illustrated in the Figure which shows the variation in permeability of a series of macroporous membranes to bromosulphophthalein (BSP, a useful model compound in this work), as a function of water content. In contrast the permeability of homogeneous hydrogel membranes of similar water contents is seen to be vanishingly small; measureable permeabilities being shown only by membranes with high water contents (and consequently with low cross-link densities and strength). The blood clotting times of the hydrated macroporous membranes were found to be in the range 30–40 min and only slightly worse than that of hydrated poly-2-hydroxyethyl methacrylate which had a blood clotting time of around 45–50 min measured under the same conditions.

Macroporous beads were prepared by a modification of the foregoing technique involving the introduction of a stream of monomer solution (either dropwise or with a motorised syringe) into a stirred bath of non-solvent (e.g. heptane) cooled to −70°C by the addition of solid carbon dioxide. Variation in the rate of injection from 0.2 to

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