Synthesis and Ultrastructural Studies of Styrene–Divinylbenzene Polyhipe Polymers

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ABSTRACT: A range of Polyhipe polymers have been prepared by polymerization of the styrene–divinylbenzene continuous oil phase of a number of high internal phase emulsions (HIPE). The aqueous internal, or discontinuous, phase constituted ~90% by volume in each case and was in the form of small droplets ~10 μm in diameter. Complete removal of each aqueous phase was achieved after polymerization by exhaustive extraction with hot ethanol, leaving monolithic Polyhipe polymers with completely interconnected cellular structures of overall very low bulk density. By adjustment of the level of cross-linker (divinylbenzene) and by use of either a precipitating porogen, petroleum ether, or a solvating porogen, toluene, in the comonomer oil phase, a secondary pore structure has been generated within the cell "walls" of the Polyhipe polymers. Overall surface areas deduced from a BET treatment of N_2 sorption data of between 3 and 350 $m^2\ g^{-1}$ have been achieved. Scanning (800× and 6400×) and transmission (7000× and 50 000×) electron micrographs have confirmed the cellular structure of the Polyhipe polymers, and the porous structure of their walls. Superficially the observed porosity correlates positively with the measured surface areas.

Introduction

High internal phase emulsions (HIPES) of water dispersed in a continuous oil phase can be formed readily by adding water slowly to a stirred solution of a surfactant of low hydrophilic–lipophilic balance (HLB) dissolved in the oil phase. Internal phase volumes (water) up to 99% are readily achievable, and in this state the droplets of the dispersed phase presumably interact strongly![1] Particularly useful surfactants in this context are amphiphilic block copolymers.[2,3] Where the continuous oil phase is composed of, in part or in whole, a polymerizable monomer, in principle the continuous phase can be polymerized to form a solid polymer. The term Polyhipe has been coined to describe such polymers.[4] This approach has been used in an attempt to produce "water-extended" styrene–unsaturated polyester materials[5,6] and to "extend" other polymeric solids.[7] Indeed, a number of other reports exist regarding the polymerization of HIPES.[8-14] It appears that, in all of these cases, however, the solid polymer "foam" that is produced is essentially of the closed-cell type and that the internal aqueous phase is trapped within the cellular structure and can be removed only slowly.

In 1982, however, Unilever scientists demonstrated that, by using relatively simple low HLB surfactants, HIPES composed of a styrene–divinylbenzene continuous phase could be polymerized to form open-cell Polyhipes. Furthermore, the aqueous dispersed phase could be readily and quickly removed to form a highly porous polymeric block material with a very low dry density of less than 0.1 g/cm^3.[15] Extension of this technology to include Polyhipes composed of a wide range of polycondensation polymers has also been reported recently,[16] and likewise a very detailed study of the originally disclosed system has been reported by Los Alamos scientists.[17] Potential uses of these materials include low-technology applications such as bulk liquid containment or as a sorbent for the trapping of waste organic liquids or vapors and also higher technology situations, e.g., as a component of a number of filtration technologies, as a matrix for the immobilization and growth of viable cells, and as a support, or component of a support, for use in "solid phase" chemistry.[18]

The cell size in Polyhipe polymers is typically in the range 1–20 μm, and not surprisingly, therefore, the surface area (as calculated from a BET treatment of N_2 sorption data) is typically rather small, ~5 $m^2\ g^{-1}$. For many potential applications of these polymers, a much higher surface area would be a major advantage, and we now report on our attempts to prepare such polymers and on our porosity and electron microscopic studies of the products.

Experimental Section

Materials. Styrene (general purpose reagent (GPR); Fisons), commercial divinylbenzene (55 vol % *m*- and *p*-divinylbenzenes, 45 vol % *m*- and *p*-ethylstyrenes; BDH), Dow divinylbenzene (80 vol % *m*- and *p*-divinylbenzenes, 20 vol % *m*- and *p*-ethylstyrenes), petroleum ether (GPR, bp 80–100 °C; A and J Beveridge), toluene (GPR; Strathclyde Chemical Co.), Span 80 (sorbitan monooleate; Sigma), potassium persulfate (GPR; Fisons), and calcium chloride (GPR; BDH) were used as supplied.

HIPE Preparation and Polymerization. Typically, the monomer phase (10 mL) was made up of the comonomers and porogen (when used), and to this was added Span 80 (3 mL). The aqueous phase (90 mL) contained potassium persulfate (0.2 g) and calcium chloride (1.0 g). (Note: We have *chosen* to call this a HIPE of 90% internal phase volume. In practice the 3 mL of surfactant has not been accounted for because its location is problematical. Much of it clearly resides in the interface of the emulsion, and most of remainder probably resides in the oil phase.) The organic phase was placed in a polyethylene bottle (300 mL) and was stirred with a D-shaped Teflon paddle driven by an overhead stirrer motor (~300 rpm). The neck of the bottle was covered with a polyethylene film to reduce evaporative losses, and then the aqueous phase was added dropwise through an aperture in the film, over a period of ~60 min. Throughout this time the stirrer paddle was gradually moved upward as the volume of the bottle contents gradually increased. A creamy white, rigid, high internal phase emulsion (HIPE) slowly formed. After all the aqueous phase was added, the stirrer paddle was gently withdrawn and the bottle top was sat loosely on top of the container. The latter was then clamped in a water bath at 60 °C for 48 h. After this period the polyethylene bottle was cut away from the Polyhipe polymer using a scalpel and the exposed

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Table I
Composition of Polymerized Hipes and Surface Area and Porosity Data of Resultant Polyhipe Polymers

				Polyhipe characteristics				
	HIPE composn[a]			surface	pore vol., mL g^{-1}			
polyhipe polymers	styrene + ethyl styrene, vol %	divinylbenzene, vol %	monomer/ porogen	area m^2 g^{-1}	Hg intrusion	H_2O imbibition	CH_3OH imbibition	toluene imbibition
X5PV90	95[b]	5[c]		3.8	0.8	2.3	2.4	4.7
X20PV90	80[b]	20[c]		22	3.5	1.9	5.0	8.6
X20PV90(0.5PE)	80[b]	20[c]	1/0.5 petroleum ether	33	5.9	1.9	3.7	7.7
X55PV90(0.5T)	45[b]	55[c]	1/0.5 toluene	137	9.6	0.3	3.5	5.4
X55PV90(1T)	45[b]	55[c]	1/1 toluene	264	13.6	0.4	5.4	9.3
X80PV90(1T)	20[d]	80[d]	1/1 toluene	354	9.7	0.7	3.3	4.9

[a] PV90 = organic phase–water phase (10/90, v/v); organic phase = comonomers + porogen (when used). [b] *m*- and *p*-Ethylstyrenes originate from commercial divinylbenzene (see *c*). [c] Calculated assuming commercial divinylbenzene = 55 vol % *m*- and *p*-divinylbenzenes, 45 vol % *m*- and *p*-ethylstyrenes. [d] Calculated assuming Dow divinylbenzene = 80 vol % *m*- and *p*-divinylbenzenes, 20 vol % *m*- and *p*-ethylstyrenes.

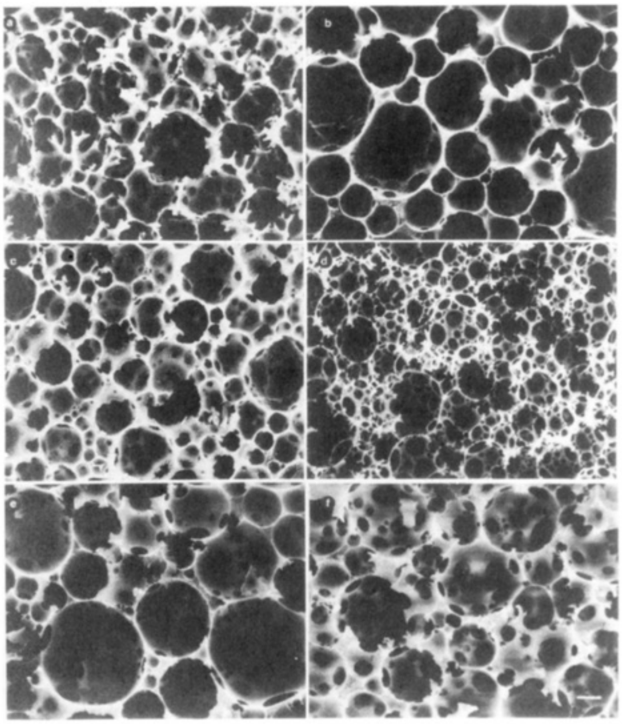

Figure 1. Scanning electron micrographs of Polyhipe polymers, scale bar 15 μm: (a) X5PV90; (b) X20PV90(0.5PE); (c) X20PV90; (d) X55PV90(0.5T); (e) X55PV90(1T); (f) X80PV90(1T).

monolithic block was cut into disks ~1 cm in thickness. These were then exhaustively extracted with refluxing ethanol in a Soxhlet apparatus (typically 2–3 days). The disks were dried in a vacuum oven at room temperature.

Characterization of Polyhipe Polymer Physical Parameters. Surface Area. The surface area of each sample (~0.3 g) was calculated from N_2 adsorption data by using a BET model. The adsorption data were obtained by using a Micromeritics Accusorb 2100E instrument, and the sample was in the form of particles each ~0.03 cm^3 in volume.

Porosities. The pore volume of each sample was determined by using a variety of measurements. Hg intrusion was carried out by using a Micromeritics Autopore 9220 instrument, and the volumes of water, methanol, and toluene imbibed were determined by a simple centrifugation method previously reported.[19] Again, each sample was in the form of small particles as above.

Electron Microscopic Investigations. In order to obtain a more direct insight into the ultrastructure of the Polyhipe materials, both scanning and transmission electron micrographs (SEM and TEM) were obtained. Specimen preparations were as follows.

Polyhipe polymer extracted and dried as above was carefully broken into pieces (~1 mm × 2 mm × 10 mm), which were mounted on stubs with a fresh face uppermost in each case. It is important not to use a face that has been cut or sawed since this distorts and damages the cellular structure. Samples were sputter-coated from a gold/palladium electrode, and micrographs were taken by using 6 kV on a Philips 500 SEM at 800× and 6400× magnification.

Samples were prepared for TEM by embedding in a support resin (Lowicryl K4M; Chemische Werke Lowi; a proprietary methacrylate-based resin containing 4.8% cross-linker), which was cured by using reflected UV light at room temperature. Light gold to silver interference-colored sections with a nominal thickness of 70 nm were cut by using a diamond knife on a Reichert Ultracut E ultramicrotome at room temperature and mounted onto 700-hexagonal-mesh copper grids. Micrographs were recorded at 7000× and 50 000× magnification on a Zeiss 902 analytical transmission electron microscopy operating at 80 kV. Enhanced contrast was produced by zero-loss electron imaging using the integral electron spectrometer and was used to reveal the fine structural details of the matrix and porous structure *without the use of heavy metal stains.*

Results and Discussion

Polymerizations. The polymerization of a wide range of styrene–divinylbenzene based HIPE formulations has been completed, and of relevance to the present report are the representative examples cited in Table I. Each of these involved an internal aqueous phase of ~90 vol %, and polymerization of each yielded a stable monolithic polymeric block fully incorporating the aqueous phase. This is consistent with the literature to date.[15,17] Exhaustive extraction of the Polyhipe polymers with hot ethanol, followed by vacuum drying, led to essentially complete removal of the aqueous phase. The residual monoliths consists of fully interconnected open-cell Polyhipe polymers, each with an overall low bulk density. Scanning electron micrographs, parts a–f of Figure 1 (magnification 800×), confirm the expected structure. (For publication purposes, Figures 1–4 have been reduced by 95%.)

X5PV90 (Table I) can be regarded as a basic Polyhipe polymer and corresponds to the materials claimed in the original Unilever patent.[15] The surface area of this is 3.8 m^2 g^{-1} (Table I). By analogy with conventional suspension polymerization of styrene–divinylbenzene mixtures to yield resin beads,[20,21] the walls of X5PV90 can be regarded as equivalent to the matrix, a "gel-type" resin. As such these would be expected to be glassy and rigid and to be essentially devoid of any porous structure. Continuing the analogy further, it can be predicted that the surface area of a Polyhipe polymer might be increased by generating porosity within the walls by using a porogen or diluent in the organic phase of the HIPE.[20-22] The porogen might be a solvent capable of solvating the resulting cross-linked polystyrene matrix,[23] or it might be one that induces precipitation of the polymer as it forms (as in macroreticular resins).[24] Indeed, X55PV90(0.5T), X55PV90(1T), and X80PV90(1T) are examples of Polyhipe polymers where toluene has been used successfully as a solvating porogen. X20PV90(0.5PE) is an example where petroleum ether has been used as a precipitating porogen, similar to the use of dodecane, recently described by Williams.[25] Other solvents that have been used as precipitant porogens in conventional styrene–divinylbenzene resins are higher alcohols and carboxylic acids. However, these are not suitable in the case of Polyhipe polymers because they are sufficiently surface active to prevent formation of the HIPE in the first instance or to cause inversion of the HIPE structure when heated to induce polymerization. The overall physical stability of the porogen-modified Polyhipe polymers is a little lower than the basic material and in particular X20PV90(0.5PE) and X55PV90(1T) tend to powder rather easily. However, by adjusting other parameters in the HIPE, e.g., by reducing the aqueous-phase volume a little, the increased fragility can be compensated to some extent.

Surface Area and Porosity Characteristics. The data for the various Polyhipe polymers (Table I) show that when the cross-link ratio is increased to 20% and petroleum ether is used as a precipitant porogen, X20PV90(0.5PE), almost a 10-fold increase in the surface area available to N_2 is observed. This change is consistent with the behavior of conventional styrene–divinylbenzene resin beads, where such porogens are known to induce the formation of a family of relative large pores (up to ~10 000 Å in diameter).[21] The very detailed work reported by Williams,[25] who used dodecane as an organic-phase diluent, focused on the hole formation in Polyhipe polymers. This represents an important contribution to the understanding of these systems, but the major effect of aliphatic hydrocarbon diluents is undoubtedly the induction of polymer phase separation within the walls of the Polyhipe polymer.

Perhaps more surprising, however, is the increase in surface area with X20PV90, within which the only change is an increase in cross-link ratio from 5 to 20%. This suggests that some porosity is generated within the walls of this polymer as well, and as we shall see later this is indeed the case. One possibility here is that Span 80 itself functions as a precipitant porogen, at least when high cross-linking and chain entanglement occurs with a 20% divinylbenzene content. The use of toluene as a solvating porogen with high levels of divinylbenzene yields Polyhipe polymers X55PV90(0.5T), X55PV90(1T), and X80PV90(1T) with substantially increased surface areas, up to ~100-fold. Again, this is totally consistent with conventional styrene–divinylbenzene resins, where such polymerization compositions are known to yield resins with a large family of pores of very small diameter, leading to high surface areas.[21] The trend in surface area within these three toluene-modified polymers is also exactly as expected with the levels of cross-linker and porogen used in each case.

The measurement of the total pore volume of the Polyhipe polymers presents a problem. The data from Hg-intrusion experiments clearly refer to the dry state in each case. However, the very high pressure involved in this type of measurement always raises the potential problem of collapse of the sample. Certainly, in the case of X5PV90 this seems to occur in practice. This is the most flexible of all the samples, and the Hg-intrusion volume of 0.8 mL g^{-1} suggests that the structure simply contracts on application of pressure. The other samples, however, were robust under the same conditions, even X55PV90(IT) and X20PV90(0.5PE), which under shear are rather powdery. The Hg-intrusion volumes of all of these seem more reasonable, with those for the toluene-modified species starting to approach the level that might be expected based on the original HIPE composition (90% water and 10% oil). In these cases shrinkage during polymerization and subsequent cleaning and drying is clearly rather minimal. The pore-size distribution curves for all the samples except X5PV90 generated from the Hg-intrusion data are very similar and give little information about the porosity of the walls. A typical curve is shown in Figure 5, where the dominant maxima in the range 1–10 μm clearly correspond to the large Polyhipe polymer cells shown in the scanning electron micrographs (parts a–f of Figure 1).

The values for the amount of water imbibed into each polymer are also not particularly useful because they are distorted by wettability problems, especially in the case of the toluene-modified species. The high degree of hydrophobicity of these is very obvious, even to the naked eye. Wettability is considerably improved in the case of methanol, but strangely no correlation is apparent with the Hg-intrusion data. Methanol, of course, is a nonsolvent for polystyrene, and so the polymer matrix itself would not be expected to swell. There may remain, therefore, penetration problems, and the low values for the toluene-modified species may reflect that methanol fails to enter all of the small pores. This cannot be the case, however, with toluene, which readily dissolves polystyrene and swells its cross-linked counterpart. Overall, the levels of toluene imbibed are indeed much higher, but the values for X55PV90(0.5T) and X80P90(1T) are somewhate low, as indeed is that for X55PV90(1T), bearing in mind the Hg-intrusion data. The much increased imbibition values for the first three polymers simply reflect their overall ability to swell in toluene, and this is obvious to the naked eye. The last three toluene-modified species in contrast are very heavily cross-linked, and gross swelling is inhibited. What is not clear, however, is why the volume available to Hg apparently is not utilized by toluene. Possibly internal expansion of the polymer matrix into the small pores actually causes a net reduction in the space available for solvent.

Ultrastructure of Polyhipe Polymers. The remarkable set of electron micrographs of these Polyhipe polymers provide very visual evidence for many of the conclusions drawn above. As far as we are aware the transmission electron micrographs of these materials are the first to enter the public domain. We believe that these offer the most informative picture of the ultrastructure of these polymers and, coupled with the N_2 adsorption data, represent as near as possible the unperturbed structures of the dry materials.

The scanning electron micrographs (800×) in parts a–f of Figure 1 show the overall similar interconnected cellular macrostructure of the materials. Any variations here are not significant (e.g., Figure 1e), and corresponding features have been found in other Polyhipe polymers. The large pore volumes result directly from the large internal volumes of water used originally in the HIPES, and the large average cell size undoubtedly corresponds to the size of the water droplets in the HIPES. This is quite different from the "water pools" incorporated into cross-linked polystyrenes reported recently by Menger and his coworkers,[26] where the "pools" are typically <10 nm in radius and the phase volume of water is only 10–20 vol %. At magnification 6400, parts 1–f of Figure 2, details of the wall structures start to appear, and important differences are now manifest. The surface of X5PV90 (Figure 2a) appears flat, and the roughness seems to increase in the sequence X5PV90 < X20PV90 < X20PV90(0.5PE) < X55PV90(0.5T) ≈ X55PV90(1T) ≈ X80PV90(1T). In addition, at the points where the intersections of walls are discontinuous, there is clear evidence for secondary pore

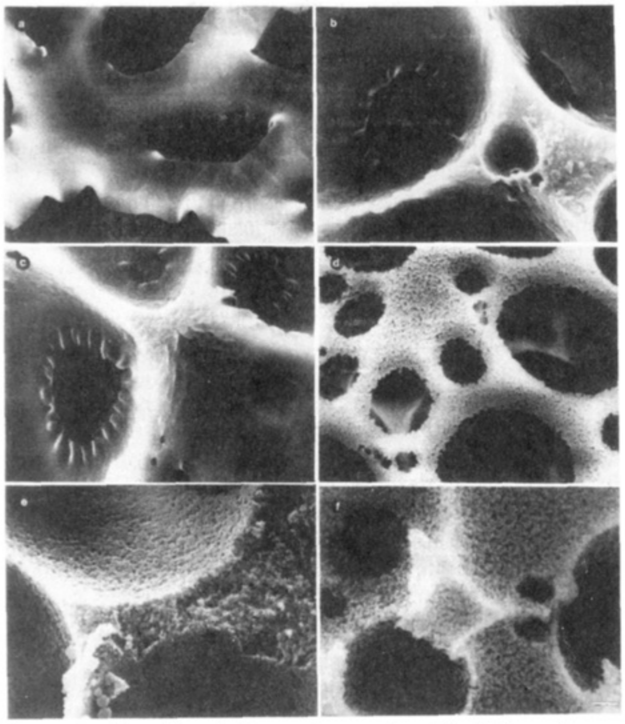

Figure 2. Scanning electron micrographs of Polyhipe polymers, scale bar 1.5 μm: (a) X5PV90; (b) X20PV90(0.5PE); (c) X20PV90; (d) X55PV90(0.5T); (e) X55PV90(1T); (f) X80PV90(1T).

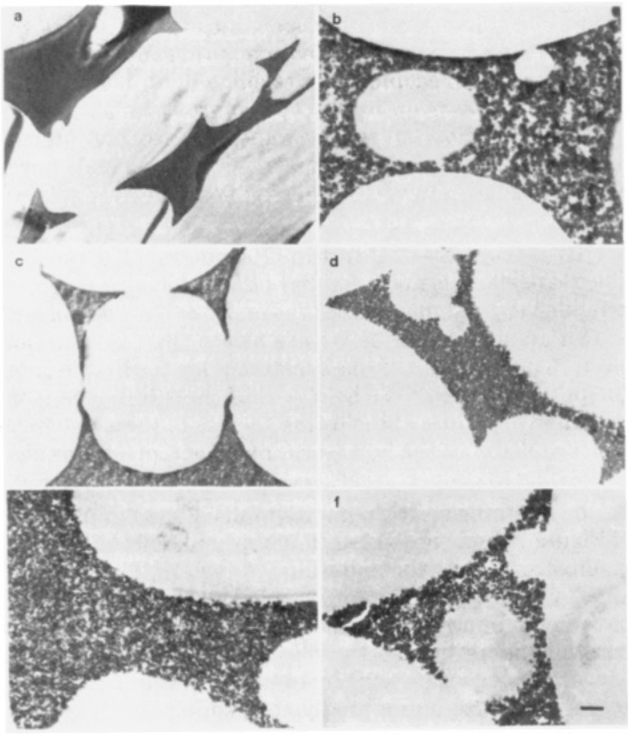

Figure 3. Transmission electron micrographs of Polyhipe polymers, scale bar 1.5 μm: (a) X5PV90; (b) X20PV90(0.5PE); (c) X20PV90 (arrow indicates thick polymer layer on cell walls); (d) X55PV90(0.5T); (e) X55PV90(1T); (f) X80PV90(1T).

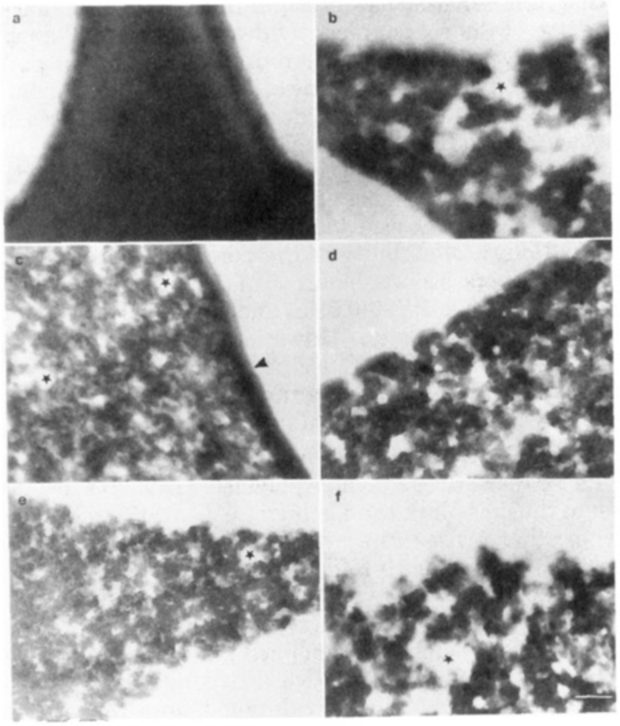

Figure 4. Transmission electron micrographs of Polyhipe polymers, Scale bar 200 μm: (a) X5PV90; (b) X20PV90(0.5PE); (c) X20PV90; (d) X55PV90(0.5T); (e) X55PV90(1T); (f) X80PV90(1T). The asterisk indicates a secondary pore structure, which contributes to overall surface area of the polymer.

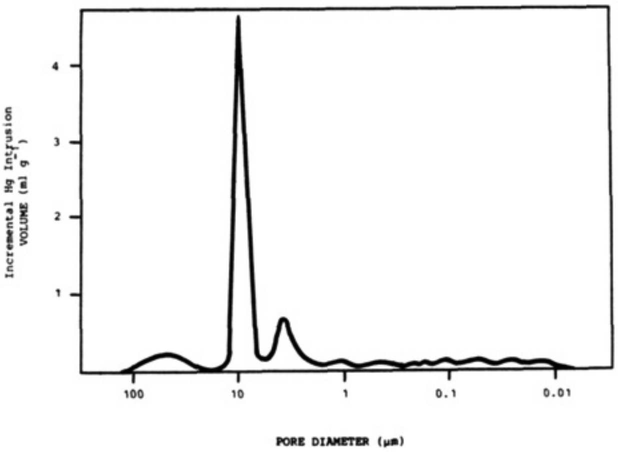

Figure 5. Pore size distribution of X80PV90(1T) from Hg intrusion data.

structures. This is confirmed in the transmission electron micrographs, where, in addition, differences in the secondary pore structures become clear. At magnifications 7000 and 50 000 (Figures 3a and 4a), X5PV90 shows no pore structure in the walls and is apparently a glassy polymer presumably with only molecular dimensions between chains. A definite pore structure, however, is generated in X20PV90 (Figures 3c and 4c, asterisks), but access to these pores seems severely limited by a continuous thick polymer layer on the surface of the cell walls (arrow). Nevertheless the total surface area does increase from 3.8 to 22 m^2 g^{-1}, and so N_2 gas must penetrate to some extent. A more clearly defined pore structure is evident in X20PV90(0.5PE) (Figures 3b and 4b) with a relatively small number of large pores (asterisks). This result is consistent with the known behavior of precipitant porogens, like aliphatic hydrocarbons, and the wall structure essentially corresponds to the morphology of conventional macroreticular styrene–divinylbenzene resin beads.[24] There is good visual evidence for significant access to these pores, and the surface area of 33 m^2 g^{-1} seems to correlate with this picture. The three remaining Polyhipe polymers prepared with toluene as a solvating porogen show equally clear porous structures within their walls with excellent accessibility (Figures 3d–f and 4d–f). On average the pore size is much smaller, and again this is in agreement with the behavior found in conventional resins.[23] The structures also correlate very well with the measured surface areas.

It is important to note that the transmission micrographs reported here were generated employing an enhanced contrast technique and no heavy metal staining has been used. The resulting data is therefore characteristic of the native polymers, and we are currently applying sophisticated image analysis techniques to product quantitative data on pore structure. In principle, transmission micrograph pore profile diameter should relate directly to pore diameters, pore profile perimeters to pore surface areas, and pore profile areas to pore volumes. The results of such analysis of conventional resins are now available and will be published in due course. Analyses of the present micrographs are now underway.

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Registry No. (Styrene)(divinylbenzene) (copolymer), 9003-70-7; toluene, 108-88-3.