Synthesis and Characterization of Poly(aryl ether sulfone) PolyHIPE Materials

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ABSTRACT: The preparation and characterization of poly(aryl ether sulfone) (PES) PolyHIPE (polymerized high internal phase emulsion) materials is described. A maleimide-terminated aryl ether sulfone macromonomer was copolymerized with styrene, divinylbenzene (DVB), or a bis(vinyl ether) species, in the continuous phase of a HIPE. Furthermore, a novel, nonaqueous HIPE methodology was employed, since only dipolar aprotic solvents were able to cosolubilize the polymeric precursor and surfactant. HIPEs of petroleum ether, dispersed in a dipolar aprotic solution of maleimide-terminated PES, PEO−PPO−PEO block copolymer surfactants, comonomer, and AIBN, were successfully prepared and polymerized. The cellular structures and porosities of the resulting materials were characterized by SEM, solvent imbibition, mercury porosimetry, and a Brunauer-Emmett-Teller (BET) treatment of nitrogen adsorption results. All were shown to possess an open-cellular morphology and a secondary pore structure within the polymer walls. Thermogravimetric analysis (TGA) of the materials indicated that critical degradation occurred at higher temperatures than in poly(styrene/DVB) PolyHIPE but lower than the PES macromonomer precursor.

Introduction

Highly porous crosslinked polymer materials are conveniently prepared by polymerization of the monomeric continuous phase of a high internal phase emulsion (HIPE). The generic term PolyHIPE was coined by Unilever researchers to describe these polymeric foams,[1] although similar materials had been described previously, most notably by Bartl and von Bonin.[2,3]

The monomer system which has received the most attention in PolyHIPE studies is styrene/divinylbenzene (DVB). A considerable amount of effort was invested by Williams and co-workers to determine the factors which affect the cellular structure[4] and cell size[5] of the resulting porous polymers, and Sherrington *et al.* have described the production of PolyHIPE materials with high internal surface areas, employing methodologies similar to those used in porous polymer bead preparation.[6] The foamlike morphology of open-cellular PolyHIPE materials can be clearly seen by scanning electron microscopy (SEM) (Figure 1).

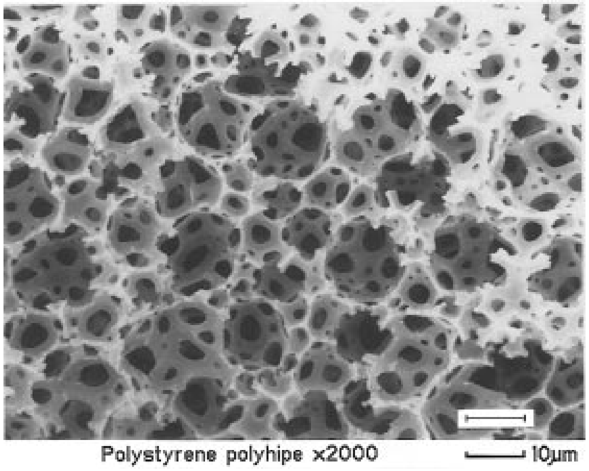

Figure 1. Scanning electron micrograph (SEM) of poly(styrene/DVB) PolyHIPE (bar = 10 μm).

The open-cell polymers are characterized by an extremely low dry bulk density, typically less than 0.1 g cm^{-3}, which is due to complete interconnection between all neighboring cells. Their mechanical properties are similar to conventional gas-blown polystyrene foams, although the smaller cell sizes (in most cases) and higher degree of cellular spherical symmetry of the emulsion-derived foams produces higher compressive strengths. The synthesis, properties, and applications of PolyHIPE materials have been described in a recent review.[7]

Due to the inherent brittleness of polystyrene, however, and the characteristic low density of PolyHIPE polymers, monolithic materials derived from styrene/DVB tend to fragment into particles rather easily under mechanical stress. In addition, they possess low thermooxidative stability. For this reason, investigations into the production of a more thermally stable material, involving a high-performance polymer such as a rigid rod aromatic polyamide, were planned. However, it quickly became apparent that such a polymer would be difficult to prepare from its monomers in a HIPE system, since the usual polycondensation procedures are incompatible with HIPEs involving large quantities of water or aqueous solution.

It was envisaged that this problem might be overcome by preparing linear polycondensation oligomers with an addition-polymerizable group at each chain end. These groups could then be homo- or copolymerized by radical addition methods. This approach seemed compatible with a HIPE format.

Experimental Section

Materials and Instrumentation. *N,N′*-Dimethylacetamide (DMAc) (Aldrich, HPLC grade), *N,N′*-dimethylformamide (DMF) (Aldrich, HPLC grade), dichloromethane (DCM) (BDH), acetic anhydride (BDH), divinylbenzene (DVB) (Aldrich, technical grade), sodium hydroxide (Fisons SLR), and sodium acetate (Fisons SLR) were used as received. 2,2′-Azobis(isobutyronitrile) (AIBN) (BDH) was recrystallized from diethyl ether, 4,4′-isopropylidene diphenol (Bisphenol A) (Aldrich) was recrystallized from acetic acid/water (1:1), tetrabutylammonium bromide (Aldrich) was dried *in vacuo* at 80

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Table 1. Structural and Surface Activity Data on ABA Triblock Copolymers of Poly(ethylene oxide) (PEO) (A) and Poly(propylene oxide) (PPO) (B)

	code		
	L92	F127	F88
appearance	liquid	flake	flake
molec wt PPO segment	2750	4000	2250
wt % EO	20	70	80
molec wt EO each segment	350	4250	4275
total mol wt	3450	12500	10800
HLB no.	5.5	22.0	28.0
cloud point, °C[a]	16	>100	>100
surface tension,[b] dyn/cm, 25 °C	35.9	40.6	48.5
interfacial tension,[c] dyn/cm, 25 °C	3.5	7.0	20.5

[a] 10% aqueous solution. [b] 0.1% aqueous solution. [c] 0.1% aqueous solution versus mineral oil.

°C and stored over anhydrous calcium chloride, and maleic anhydride (Fisons SLR) was recrystallized from chloroform. Dimethyl sulfoxide (DMSO) (Aldrich) and *N*-methyl-2-pyrrolidone (NMP) (Lancaster) were purified by fractional distillation *in vacuo* from 4-Å molecular sieves, following water removal by azeotropic distillation with toluene. Styrene (Fisons) was washed with 1 M sodium hydroxide solution and dried with anhydrous sodium sulfate. 2-Chloroethyl vinyl ether (Aldrich) was fractionally distilled under nitrogen. Amino- and nadimide-terminated poly(aryl ether sulfone)s were obtained as gifts from ICI Materials Research Centre and were used as received. Both had approximate number average molecular weights of 10 000 g mol^{-1}. Poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) triblock copolymer surfactants (Synperonic range, ICI), sorbitan monooleate (Span 80), and all other solvents were used as received. Structural and surface activity data of the block copolymer surfactants are given in Table 1.[8]

Infrared spectra were recorded on a Mattson 1000 FTIR spectrometer. Elemental microanalyses were carried out simultaneously with a Perkin-Elmer 2400 analyser; halogen and sulfur contents were determined by titration methods. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Bruker WM250 spectrometer, referenced internally to the solvent. Scanning electron microscopy (SEM) was performed on a Cambridge Instruments S360 electron microscope. Samples were fractured and coated in gold before examination. Melting points (uncorrected) were recorded on a Gallenkamp digital melting point apparatus, supported with a Hg thermometer. Thermogravimetric analysis (TGA) was performed employing a Stanton Redcroft TG-570 analysis unit, under a static atmosphere of air and at a heating rate of 10 °C/min.

Porosity data were determined by using a Micromeritics Autopore II 9220 mercury porosimeter. Surface areas were obtained with a Micromeritics AccuSorb 2100E unit employing the Brunauer-Emmett-Teller (BET) method.[9] Solvent imbibition studies were performed at ambient temperatures according to the following procedure:[10] approximately 0.1 g of polymer was weighed accurately into each of two preweighed glass sinter sticks. These were then immersed in the required solvent, along with a preweighed empty sinter stick, for 24 h. The samples were then removed, centrifuged at 1000 rpm for 2 min to remove excess solvent, and weighed accurately. The sinter sticks were then reimmersed in the solvent for a further hour, removed, centrifuged, and reweighed. The quantity of solvent absorbed per gram of polymer was determined from these results, by subtracting the weight of dry polymer, empty sinter stick, and solvent absorbed by the blank from the final weight of each sample.

Monomer and Macromonomer Synthesis. Maleimide-Terminated Poly(aryl ether sulfone). Amino-terminated poly(aryl ether sulfone) (H_2N-PES, 50.1 g, ∼10 mmol of NH_2 groups) was placed in a 500-mL three-necked round-bottomed flask, fitted with a condenser, and was dissolved in cyclopentanone (250 mL) with magnetic stirring and heating at 80 °C for 1 h. The solution was then cooled to 5 °C in an ice-water bath, and maleic anhydride (5.12 g, 0.05 mol) in cyclopentanone (30 mL) was added dropwise, with constant mechanical stirring and cooling. Once addition was complete, the solution was warmed to room temperature and stirred for 2 h. Acetic anhydride (26.0 g, 0.25 mol) and sodium acetate (4.10 g, 0.05 mol) were added separately, and the solution was heated at 75−80 °C for 13 h. The reaction mixture was then cooled to room temperature and poured into methanol (1.5 L), causing precipitation of the polymer. This was collected by suction filtration and was washed with hot water, cold methanol, and finally cold diethyl ether. Mass of product = 59.0 g. *Microanalysis.* Calculated: 62.0% H, 3.4% H, 0.3% N, 13.8% S. Found: 63.9% C, 3.7% H, <0.3% N, 10.3% S. *FTIR (KBr disc),* ν/cm^{-1}: 3097, 3075, 1723 (imide C═O), 1585, 1240 (aryl C—O str.), 1151 (S═O str), 868, 836. *^{1}H NMR ($CDCl_3$, 250 MHz)/δ*: 6.9 (s, CH═CH), 7.1 (t, aryl H), 7.9 (t, aryl H). *^{13}C{^{1}H} NMR (jmod, $CDCl_3$, 63 MHz)/ppm*: 117.9, 119.8, 122.2, 130.0, 130.2 (aryl CH); 134.5 (C═C); 135.9, 137.3, 137.8 (aryl C); 151.8, 151.9 (aryl C—SO_2); 159.7, 159.9 (aryl C—O); 160.0, 162.0, 162.2 (C═O).

Bis(4,4′-isopropylidenediphenoxyethyl) Vinyl Ether (BVE, 3). 4,4′-Isopropylidenediphenol (Bisphenol A) (2.30 g, 10.1 mmol), 2-chloroethyl vinyl ether (4.19 g, 39.3 mmol), and toluene (6 mL) were placed in a 100 mL three-necked round-bottomed flask. The mixture was stirred for 5 min under a flow of N_2 gas, after which sodium hydroxide pellets (1.03 g, 25.8 mmol) were added. The mixture was heated at 80 °C for 1 h; subsequently, tetrabutylammonium bromide (0.22 g, 0.7 mmol) dissolved in 2-chloroethyl vinyl ether (1.05 g, 9.9 mmol) was added, along with toluene washings (2 mL). The temperature was increased to 95 °C and maintained for 3 h. A small sample was analyzed by TLC, relative to Bisphenol A, giving a single spot of higher R_f value than the starting material. Upon cooling the reaction flask to room temperature, water (15 mL) was added and the layers were separated. The organic layer was washed with water (4 × 50 mL), dried over anhydrous sodium sulfate and gravity filtered. The solvent and residual 2-chloroethyl vinyl ether were removed from the filtrate by rotary evaporation, leaving a yellow oil. The flask was evacuated at room temperature for 6 h, then cooled in an ice bath, causing the product to crystallize. The crude material was recrystallized from *n*-heptane to give 2.84 g (76%; lit. 91%[11]) of product, melting point = 53−55 °C (lit. 54−55 °C[11]). *TLC (silica, EtOAc:petroleum ether* (40−60 °C) (1:1)): R_f = 0.77, Bisphenol A R_f = 0.51. *Microanalysis*: 75.2% C, 7.8% H; calculated ($C_{23}H_{28}O_4$) 75.0% C, 7.7% H. *FTIR (nujol),* ν/cm^{-1}: 3039, 1618, 1254 (C—O str), 1075 (C—O str). *^{1}H NMR ($CDCl_3$, 250 MHz)/δ*: 1.7 (s, 6 H; CH_3), 4.0−4.3 (m, 12 H; OCH_2CH_2, H_2C═), 6.5 (dd, 2 H; ═CH (J_{trans} = 15 Hz, J_{cis} = 6 Hz)), 6.9 (d, 4 H; aryl H (J_{HH} = 9 Hz)), 7.2 (d, 4 H; aryl H (J_{HH} = 9 Hz)). *^{13}C{^{1}H} NMR (jmod, $CDCl_3$, 63 MHz)/ppm*: 31.7 (CH_3), 41.8 (*C*(CH_3)$_2$), 66.4 (*C*H_2OPh), 66.5 (*C*H_2OCH═CH_2), 87.1 (H_2*C*═CH), 114.1 & 127.9 (aryl CH), 143.6 (aryl *C*C(CH_3)$_2$), 151.8 (H_2C═*C*H), 156.5 (aryl CO).

Solution Polymerizations. Styrene/Maleimide Copolymerization. Styrene (4.1 g, 40.0 mmol) and maleimide (0.50 g, 5.2 mmol) were added to a 25-mL round-bottomed flask, and 2,2′-azobis(isobutyronitrile) (AIBN) (2.5 mg, 0.02 mmol) in toluene (1 mL) was added. The resulting solution was further diluted with toluene (4 mL), and the flask was purged with N_2 gas and sealed. The reaction mixture was heated at 65−70 °C for 24 h; a white precipitate formed after approx. 1.5 h. The flask was then cooled, and the contents were poured into methanol (200 mL). The resulting precipitate was filtered and dried under reduced pressure to give 3.99 g (87%) of polymer. *FTIR (KBr disc),* ν/cm^{-1}:- 3250 (imide -NH), 3062, 3028, 2921, 2848, 1725 (C═O), 1607, 755, 700. *^{1}H NMR (d_8-THF, 250 MHz)/δ*:- 1.5 (s), 1.7 (s), 1.9 (s), 2.6 (s) (-CH, -CH_2); 6.5 (s), 6.6 (s), 7.0 (d) (aryl -H); 9.9 (s, -NH). *^{13}C{^{1}H} NMR (d_8-THF, 63 MHz)/ppm*:- 41.5 (-CH); 126.5, 128.8, 129.7 (aryl -CH); 146.3 (aryl -C), 161.0 (C═O).

Styrene/Maleimide-Terminated Poly(aryl ether sulfone) Copolymerization. Maleimide-terminated poly(aryl ether sulfone) (mal-PES, 1.0 g, ∼0.2 mmol of maleimide groups) was placed in a 25-mL round-bottomed flask, along with cyclopentanone (3 mL). The mixture was stirred magnetically, at room temperature, to dissolve the polymer. AIBN (2 mg, 0.01 mmol) in cyclopentanone (0.5 mL) and styrene (0.2 g, 2.2 mmol) were then added to the flask, which was purged with N_2 gas and sealed. The solution was heated at 80−90 °C for 20 h, after which a gel had formed in the flask. No free liquid was in evidence. The gel was removed and immersed in cold methanol (300 mL) for approximately 30 min, causing it to become tough and rubberlike. A small piece of the material was removed and reimmersed in cyclopentanone (50 mL); the polymer swelled and became gellike once more, but did not dissolve. This was taken as an indication of copolymerization and cross-linking between styrene and the bismaleimide-containing material. Mass of product = 0.94 g (78%). *Microanalysis.* Calculated: 67.0% C, 4.1% H, 0.2% N, 11.5% S. Found: 64.7% C, 3.8% H, <0.3% N, 10.6% S. *FTIR (KBr disc),* ν/cm^{-1}: 3097, 3070, 2971 (aliph CH str), 2935 (aliph CH str), 1729 (C=O), 1593, 1252 (aryl C−O str), 1167 (S=O str), 877, 843.

Bis(vinyl ether)/Maleimide-Terminated Poly(aryl ether sulfone) Copolymerization. Mal-PES (1.0 g, ~0.2 mmol of maleimide groups), bis(4,4′-isopropylidenediphenoxyethyl) vinyl ether (BVE) (0.08 g, 0.2 mmol), AIBN (3mg, 0.02 mmol), and DMAc (2 mL) were placed in a 50-mL round-bottomed flask fitted with a vacuum outlet. The reaction mixture was carefully degassed via a freeze−pump−thaw method. This cycle was repeated at least three times, and the flask finally flushed with N_2 gas and sealed. The sealed flask was then heated at 80 °C, with magnetic stirring, for 48 h. After approximately 3.5 h it was noticed that the solution had gelled. After cooling the flask to room temperature, DCM (30 mL) was added, and the product was allowed to swell for ~2 h. It was then removed from the flask and immersed in methanol (300 mL), causing the material to shrink and become tough. Subsequently, the product was reimmersed in DCM (100 mL) for 48 h followed by methanol (100 mL) for 3−4 h and finally dried *in vacuo* at 70 °C for 8 h. Mass of product = 0.53 g (49%). *Microanalysis:* Calculated: 63.0% C, 3.7% H, 0.3% N, 12.8% S. Found: 63.2% C, 3.5% H, <0.3% N, 10.4% S. *FTIR (KBr disc),* ν/cm^{-1}: 3101, 3076, 2922 (aliph CH str), 2870 (aliph CH str), 1721 (C=O), 1583, 1239 (aryl C−O str), 1147 (S=O str), 871, 837.

Nonaqueous HIPE Preparation. Initial Miscibility Studies. Both maleimide- and nadimide-terminated poly(aryl ether sulfone)s (mal-PES and nad-PES, respectively) were tested for their solubilities in mixtures of cyclopentanone, cyclohexanone, or chloroform (solvents) with either toluene or styrene (nonsolvents). A general procedure is as follows: the polymer (0.5 g) was placed in a test tube, and solvent (1.5 mL) was added. Sonication and/or heating were employed, as required, to ensure complete dissolution of the polymer. Nonsolvent (0.5 mL) was added, and the test tube was shaken to mix the two liquids. The appearance of the final mixture (i.e., homogeneous or two-phase) was noted.

Solvent/Nonsolvent/Surfactant Systems. The solubility of nad-PES in solvent (cyclopentanone, DCM, NMP, or DMAc)/toluene/surfactant mixtures, with varying proportions of each component, was examined. Polymer was placed in a conical flask, and a mixture of solvent and toluene was added. Mild heating was employed to fully dissolve the polymer. The solution was then cooled to room temperature, and surfactant (2.0 g) was added. The resulting mixture was vigorously shaken, and the appearance of the solution was noted.

Preparation of Nonaqueous HIPEs Containing Poly(aryl ether sulfone) in the Continuous Phase. Nonaqueous concentrated emulsions of petroleum ether (100−120 °C) in a DMAc/toluene solution of nad-PES, stabilized with block copolymer surfactants, were prepared. The following procedure is typical: nad-PES (3.0 g) and surfactants F127 and F88 (total of 3.0 g) were placed in a 180-mL wide-necked glass bottle. DMAc and toluene (total of 10 mL) were added, and the polymer and surfactants were dissolved with the aid of gentle heating. The resulting viscous solution was allowed to cool to room temperature and was subsequently stirred with a glass stirring rod fitted with a D-shaped PTFE paddle, attached to an overhead stirrer motor, at approximately 200 rpm (Note: conventional rapid mechanical stirring with a small impeller inhibits HIPE formation.) Petroleum ether (90 mL) was added dropwise, with constant stirring, and a viscous, opaque emulsion started to form. Addition was continued until traces of nonemulsified petrol were visible on the surface of the emulsion. At this point, addition was stopped and the system was stirred for several minutes in an attempt to emulsify the excess petrol. If successful, addition of petrol was recommenced; if excess petrol remained, stirring was also ceased. This process was repeated until traces of nonemulsified petrol remained permanently. The volume of petrol added was noted.

Optimization of Emulsion System for Nonaqueous HIPEs Containing Poly(aryl ether sulfone). Nonaqueous HIPEs containing nad-PES and employing a variety of polar aprotic solvents (DMF, DMAc, DMSO, NMP) with surfactants of different hydrophilic−lipophilic balance (HLB) values were prepared, in order to establish the conditions giving optimum HIPE stability. The procedure was similar to that given above: nad-PES (1.75 g) and surfactants F88 and F127 (total of 1.75 g) were dissolved in solvent (5 mL) in a 180-mL wide-necked glass bottle, with the aid of heating. Once the solution had cooled to room temperature, the HIPE was prepared as above, by dropwise addition of petroleum ether (100−120 °C), with constant mechanical stirring. The volume of petrol which could be emulsified was noted and, thus, the internal phase volume ratio was calculated.

PolyHIPE Preparation. A range of PolyHIPE materials containing poly(aryl ether sulfone) has been prepared by copolymerization of mal-PES with styrene, DVB or the bis(vinyl ether) monomer mentioned above (BVE), in a nonaqueous, highly concentrated emulsion system. Both DMF and DMAc were used as solvents in the polar organic phase, and petroleum ether (100−120°) was used as the dispersed phase. Block copolymer surfactants with HLB values from 24 to 28 were employed to stabilise the HIPEs. A general procedure is given here.

HIPE Preparation. The solvent (DMF or DMAc) was degassed by the freeze-pump-thaw method, and purged with argon. Mal-PES (1.75 g, ~0.4 mmol maleimide groups), surfactants F88 and F127 (total of 1.75 g) and solvent (4.6 mL) were placed in a 180 mL wide-necked glass bottle, under a steady flow of argon. The mixture was stirred as described previously, and the polymer and surfactants were dissolved with the aid of mild heating. Once the solution had cooled to room temperature, AIBN (0.02 g, 0.1 mmol) and styrene (0.36 g, 3.5 mmol) were added, and the solution was stirred as before for 5 min petroleum ether (100−120 °C) (45 mL), previously degassed by sonication for 15 min, was added dropwise to the glass bottle with constant mechanical stirring, under argon, to form the HIPE. As before, addition was ceased when traces of nonemulsified petrol were visible on the emulsion surface. The volume of added petrol at this point was noted.

Polymerization of the HIPE. The nonaqueous HIPE was transferred to a 60-mL polyethylene bottle, which was purged with argon and sealed. This was subsequently immersed in a water bath at 65 °C for 72 h to cause polymerization of the concentrated emulsion. The resulting polymer material was removed from the bottle and extracted in a Soxhlet apparatus with ethanol for 20 h and methanol for 48 h. It was dried *in vacuo* at 70 °C for 8 h.

The other PolyHIPE materials were prepared by replacing the styrene with either DVB or BVE and adjusting the stoichiometry accordingly. A total continuous phase volume of 5 mL was employed throughout.

Results and Discussion

Macromonomer Synthesis and Solution Copolymerizations. Our strategy for the synthesis of poly(aryl ether sulfone) (PES) PolyHIPE materials required a terminally reactive PES prepolymer. Poly(aryl ether sulfone)s are a class of commercially available polymer with high thermal stability and good flame-retardant properties.[12] A popular synthetic route to these involves reaction of the disodium salt of a bisphenol with 4,4′-

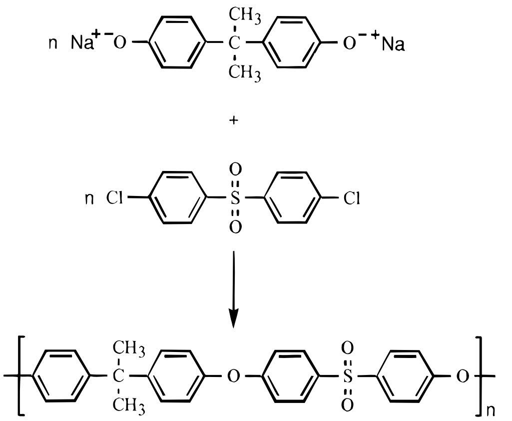

Figure 2. Synthesis of poly(aryl ether sulfone)s.

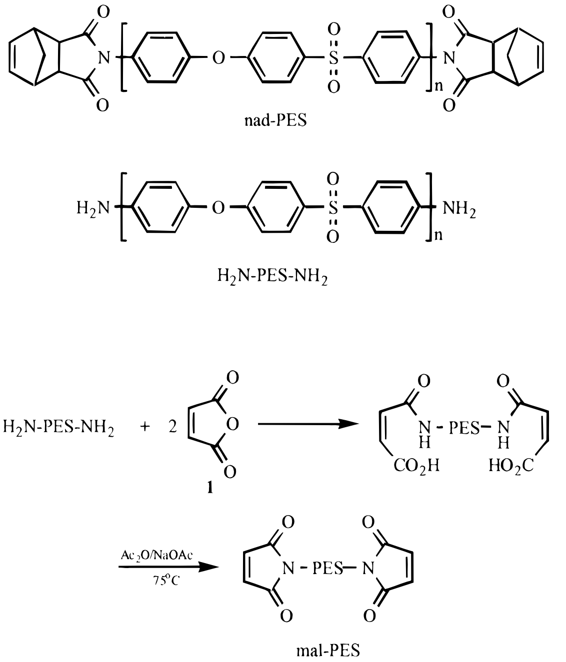

Figure 3. Structures of amino- and nadimide-terminated poly(aryl ether sulfone) materials and synthesis of maleimide-terminated poly(aryl ether sulfone) material.

dichlorodiphenylsulfone (Figure 2). Fortunately, appropriately functionalized polymers are available from ICI, as shown in Figure 3. The nadimide-terminated material was not employed in the preparation of PolyHIPE materials since the nadimide groups cure at high temperatures (250 °C), via the maleimide intermediate produced following a retro-Diels−Alder reaction and elimination of cyclopentadiene.[13] Such high temperatures were unlikely to be compatible with HIPE systems. Furthermore, model solution copolymerizations with styrene at 65 °C showed that even with free radical initiator the nadimide-terminated species reacted too slowly to allow use in PolyHIPE synthesis.

Maleimide end-capped monomers and oligomers are used industrially as thermosets, in the production of advanced composite materials.[14] They are usually cured thermally, at temperatures in excess of 250 °C, which induces cross-linking via the reactive end groups. However, maleimide-containing materials can also be cured by copolymerization of the maleimide double bond with a number of vinyl monomers, and this can be achieved at much lower temperatures, in the presence of a radical initiator. Since maleimide is an electron-poor species, comonomers used should possess electron-rich double bonds. Styrene and vinyl ethers are examples of such monomers, and have been successfully copolymerized with maleimide.[15] Both maleimide[16] and *N*-phenylmaleimide (NPMI)[17] give almost exactly alternating copolymers with styrene. The reactivity ratios for the copolymerization of styrene with NPMI are reported to be $r_1 = 0.047$ and $r_2 = 0.012$ (NPMI is monomer 1)[17].

The end groups of the amino-terminated poly(aryl ether sulfone) material can easily be converted into maleimide groups via reaction with maleic anhydride (**1**), followed by cyclodehydration[18,19] (Figure 3). The synthesis of the maleimide-terminated macromonomer proceeded without difficulties, following a procedure developed at ICI.[20] However, characterization of the product proved more awkward. Since the polymer has a molecular weight[20] of approximately 10 000 g mol^{-1}, the concentration of maleimide groups in the product, even after quantitative reaction, is extremely low, about 2%. Nevertheless, significant differences in the FTIR and NMR spectra of the starting material and product were noticed. For instance, there is a reasonably strong peak at 1723 cm^{-1} in the FTIR spectrum of the polymer product which was not present prior to reaction; this signal is due to the carbonyl groups of maleimide. Also, the ^{1}H NMR spectrum of the product shows a very weak signal at δ 6.9, which is thought to be from CH=CH protons, and the ^{13}C NMR spectrum has a small peak at 134.5 ppm, also resulting from carbon−carbon double bonds. The amino proton signals in the ^{1}H NMR spectrum of the product were severely diminished relative to the spectrum of the starting material. No attempt was made to remove unreacted amino-terminated PES, however.

Having prepared a large quantity of maleimide-terminated poly(ether sulfone) material, its solution copolymerization with styrene was investigated. However, a feed ratio of approximately 1:2 maleimide to styrene units did not result in copolymerization. The reaction was modelled by replacing the PES material with maleimide monomer itself. As maleimide is an electron-deficient species and styrene is electron-rich, copolymerization occurs readily, reportedly giving 1:1 alternating copolymers. The reactivity ratios are given as $r_1 = r_2 = 0.1$.[16]

The formation of a charge-transfer complex between styrene and maleimide was said to be the reason for this alternating copolymerization behavior.[16] A similar mechanism has also been proposed, supported by UV and NMR evidence, for the production of 1:1 alternating copolymers from styrene and maleic anhydride.[21] However, attempts to find evidence of such a complex in the styrene/*N*-phenyl maleimide system, which also gives 1:1 alternating copolymers, were unsuccessful.[17]

In reporting the copolymerization of styrene with *N*-alkylmaleimides, Coleman and co-worker[15] employed a feed ratio of 1 maleimide to 10 styrene units. An approximate feed ratio of 1 maleimide:8 styrene units was used in the model copolymerization in the present work, yielding 87% of copolymer. The composition of the product was found to be 1 maleimide:7 styrene repeat units from the ^{1}H NMR spectrum. The high monomer conversion produces a copolymer which may initially have an alternating structure but which changes to one containing increasing concentrations of styrene units as maleimide is depleted.

The solution copolymerization of styrene and maleimide-terminated PES was subsequently attempted

Table 2. Solubilities of Poly(aryl ether sulfone)s in Solvent and Solvent/Nonsolvent Systems[a]

solvent system	Mal-PES	Nad-PES
Cp	soluble	soluble
Ch	soluble	soluble
CHCl$_3$	insoluble	−
Cp/St	soluble	soluble
Cp/Tol	−	soluble
Ch/Tol	−	soluble[b]

[a] Cp, cyclopentanone; Ch, cyclohexanone; St, styrene; Tol, toluene; − indicates system not investigated.
[b] Soluble on heating.

once more with a monomer feed ratio of 1:11 maleimide groups to styrene. This did indeed produce a copolymer product, as evidenced by the transition of the viscous linear polymer solution to an insoluble gel. The gel product was found to become tough and rigid on immersion in methanol, a nonsolvent for linear PES, whereas it swelled once more, without dissolving, when placed in cyclopentanone, a good solvent for linear PES.

Preparation of HIPEs Containing Poly(aryl ether sulfone)s. The conditions which would lead to the preparation of a concentrated emulsion containing high levels of poly(aryl ether sulfone) (PES) and, ultimately, a highly porous PES material were investigated. The nature of the HIPE employed would be determined by the range of good solvents available for linear PES; this is limited to DCM, cyclopentanone, cyclohexanone, DMF, DMAc, DMSO, and NMP. Thus, it is apparent that there are two HIPE routes potentially available: (i) an aqueous, water-in-oil (w/o) HIPE route, in which a solution of PES in a nonpolar solvent comprises the continuous phase, with an aqueous dispersed phase; and (ii) a nonaqueous HIPE route, involving one of the polar aprotic solvents as the continuous phase liquid and a nonpolar organic liquid as the dispersed phase. We have previously shown that it is possible to prepare nonaqueous HIPEs of two immiscible organic liquids stabilized with PEO−PPO−PEO block copolymer surfactants.[22]

Initial attentions focused on the aqueous route, since these systems are inherently more stable and considerably better known than their nonaqueous counterparts. The first stage was to model the continuous phase solution, which would contain high concentrations of PES and surfactant, as well as a quantity of comonomer such as styrene, a nonsolvent for PES. Toluene was envisaged as a substitute for styrene, and the nadimide-terminated PES (nad-PES) as a model for the maleimide-containing material (mal-PES), in the initial miscibility studies. However, their suitabilities as models had to be determined. The solubilities of both polymers in various solvent and solvent/nonsolvent systems are shown in Table 2.

The results indicate that the polymers have similar solubilities and that styrene and toluene are more or less equivalent. Therefore, toluene and the nadimide-terminated polymer were deemed suitable models.

The surfactant now had to be incorporated into the model solution at sufficiently high concentrations to facilitate HIPE formation. To this end, the solubility of nadimide-terminated PES in solvent/nonsolvent/surfactant mixtures was investigated. The results in Table 3 indicate that a homogeneous solution of nad-PES, surfactant, toluene, and nonpolar organic solvent (cyclopentanone or DCM) could not be obtained. Invariably, a two-phase system of solvated polymer and liquid surfactant was produced, regardless of concentrations of nad-PES and surfactant. Therefore, it was concluded that the preparation of aqueous HIPEs containing any appreciable quantity of nad-PES in the continuous phase would be impossible. However, it can be seen from Table 3 that complete miscibility can be achieved if the solvent is changed to NMP, a polar aprotic solvent. Similarly, the use of DMAc also resulted in homogeneity (although, of course, such solvents preclude the use of water as the HIPE internal phase).

Table 3. Solubility of Nad-PES in Solvent/Toluene/Surfactant Systems

polymer (P) mass, g	solvent (S), mL	toluene (T), mL	ratio P/S/T	surfactant conc, %	result[h]
3.3	6.7[a]	3.3	1/2/1	20[e]	I
2.5	7.5[a]	2.5	1/3/1	20[e]	I
2.5	9.4[a]	0.6	1/3.7/0.3	20[e]	I
1.2	3.8[a]	1.2	1/3/1	20[f]	I
1.0	9.0[a]	1.0	1/9/1	20[f]	I
1.0	9.0[a]	1.0	1/9/1	10[f]	I
0.5	4.5[b]	0.5	1/9/1	10[f]	I
0.5	4.5[c]	0.5	1/9/1	10[g]	H
0.5	4.5[d]	1.0	1/9/2	9[g]	H
0.5	4.0[d]	1.0	1/8/2	20[g]	H
1.0	4.0[d]	1.0	1/4/1	20[g]	H
1.2	3.8[d]	1.2	1/3/1	30[g]	H

[a] Cyclopentanone. [b] DCM. [c] NMP. [d] DMAc. [e] Span 80 (HLB = 4.3). [f] L92 (HLB = 5.5). [g] F127 (HLB = 22). I, inhomogeneous; H, homogeneous.

Table 4. Nonaqueous HIPEs Containing Nad-PES

polymer mass, g	DMAc, mL	toluene, mL	surfactant mass, g	HLB	petrol added, mL	phase ratio (ϕ)
3.0	9.2	0.8	3.0	24[a]	40	0.80
2.5	9.4	0.6	3.5	24[a]	40	0.80
3.0	9.2	0.8	3.0	28[b]	40	0.80

[a] F88/F127 blend (1/2). [b] F88.

Significantly, the continuous phase components are entirely miscible in DMAc on increasing the concentration of both nad-PES and block copolymer surfactant. Therefore, it appeared that a nonaqueous methodology was potentially the best route toward HIPEs containing significant quantities of nad-PES and, consequently, the synthesis of a mal-PES PolyHIPE material.

Nonaqueous HIPEs, consisting of petroleum ether (100−120°) dispersed in a DMAc solution of nad-PES, surfactant, and toluene, were prepared as detailed in the Experimental Section. The continuous phase and HIPE compositions are given in Table 4.

The quantities of polymer, solvent, toluene, and surfactant were varied, giving systems with slightly different nad-PES and surfactant concentrations, and one example where a surfactant HLB of 28 was employed. In each case the continuous phase volume was kept constant at 10 mL. Each system resulted in a HIPE of internal phase volume ratio of 0.8. The concentrated emulsions were highly viscous, notably more so than styrene/DVB HIPEs.

The internal phase volume ratios (ϕ) obtainable under the conditions detailed in Table 4 were moderate, at 0.8. However, it was hoped that this value could be increased, and so the polar solvent and surfactant HLB value were varied to determine the continuous phase components which would lead to a maximum value of (ϕ). The results are shown in Table 5.

Variation of the solvent, at a surfactant HLB of 24, indicated that DMF was slightly better than DMAc and DMSO, and considerably better than NMP, at preparing concentrated emulsion systems. Increasing the HLB number with DMF as solvent produced HIPEs with

Table 5. Optimization of Continuous Phase Composition for the Preparation of Nonaqueous HIPEs Containing Nad-PES[a]

solvent	surfactant HLB	petrol added, mL	phase ratio (ϕ)
DMAc	24[a]	20	0.80
DMF	24[a]	26	0.84
DMSO	24[a]	20	0.80
NMP	24[a]	5	0.50
DMF	26[b]	34	0.87
DMF	28[c]	40	0.89

[a] Continuous phase composition: 1.75 g of nad-PES, 1.75 g of surfactant, 5 mL of solvent. [b] F88/F127 blend (1/2). [c] F88/F127 blend (2/1). [d] F88.

Table 6. Physical Properties of Dipolar Aprotic Solvents[a]

solvent	μ, D	η, cP	n
NMP	4.09	1.67	1.468
DMF	3.86	0.845	1.428
DMAc	4.60	2.141	1.436
DMSO	3.90	2.470	1.476[b]

[a] μ = dipole moment; η = viscosity; n = refractive index. [b] Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 74th ed.; CRC Press: Boca Raton, FL, 1993.

increasing quantities of emulsified petrol. At an HLB number of 28, a HIPE with an internal phase volume ratio of almost 0.9 was obtained. This latter system is truly a high internal phase emulsion and would conceivably lead to the production of a poly(aryl ether sulfone) material of considerable porosity.

It is evident that the nature of the solvent profoundly affects its ability to form concentrated emulsions at a given surfactant HLB value. The differences in properties of each solvent are presumably due to differences in solvation ability for both the polymeric surfactant and nad-PES. NMP does not differ greatly from the other solvents (Table 6[23]) in properties such as dipole moment, viscosity, or refractive index. Therefore, these properties cannot be invoked to explain the poor performance of NMP in the preparation of nonaqueous HIPEs.

The results in Table 5 contrast with those previously described for the stability of nonaqueous HIPEs of petroleum ether in polar solvents, in the absence of nad-PES.[22] Previously,[22] it proved impossible to form a petrol/DMAc HIPE of (ϕ) = 0.9 at any HLB value, whereas with a high concentration of nad-PES dissolved in the DMAc solution, concentrated emulsions were readily formed, albeit at a lower internal phase ratio of 0.8. Similarly, DMF was previously found to form HIPEs only over a narrow surfactant HLB range,[22] giving highly unstable systems. However, addition of nad-PES to the DMF continuous phase results in the successful preparation of emulsions over a wider HLB range and with enhanced stability. This seems to suggest that the properties of the solvents alone are not responsible for the differences in HIPE-forming ability and stabilization observed, in the presence of nad-PES material.

The high viscosities of the continuous phase solutions containing poly(ether sulfone) may be the factor giving rise to enhanced HIPE stability. A viscous continuous phase is one of the factors which can contribute to emulsion (and HIPE) stability by providing a kinetic barrier to droplet coalescence.[24] This could also explain the lower maximum phase volume ratios obtainable in these systems; a highly viscous continuous phase solution inhibits efficient mixing of the phases.[25] It was previously observed, during the preparation of nonaqueous HIPEs without PES material in the continuous phase, that those which did not form at an internal phase volume ratio of 0.9 would generally phase separate completely. However, with dissolved nad-PES, a point was reached where further petroleum ether could not be dispersed in the highly viscous HIPE. Despite this, the emulsion already formed did not collapse.

Another difference caused by the addition of nad-PES material to the continuous phase is the shift in optimum surfactant HLB number to higher values than previously observed.[22] The high concentration of polymer material decreases the polarity of the continuous phase; therefore, more hydrophilic surfactants are required to achieve stable, highly concentrated emulsions.

Poly(aryl ether sulfone) PolyHIPE Preparation. Having established the conditions required for the solution copolymerization of the PES precursor with styrene, and the preparation of stable nonaqueous HIPEs containing high concentrations of mal-PES material, the next step, therefore, was the preparation of a PolyHIPE material.

The HIPEs were formed according to a procedure similar to that previously employed. To prevent unwanted prepolymerization, the initiator and comonomer were added to the continuous phase solution after dissolution of the mal-PES starting material and surfactant and once the solution had cooled to room temperature. All liquids used were degassed, and the entire procedure was performed under argon. Petroleum ether (100−120 °C) was added dropwise until the maximum amount had been incorporated into the emulsion. The HIPEs were polymerized at 65 °C for 72 h, in sealed polyethylene bottles under argon. Subsequently, the polymerized HIPEs were extracted with ethanol and methanol in a Soxhlet apparatus and dried.

To increase the range of porous PES materials which could potentially be produced, the solution copolymerization of a vinyl ether monomer with the maleimide-terminated PES precursor was investigated. Vinyl ethers, being electron-rich vinyl monomers, also produce alternating copolymers with maleimide monomers.[15,26,27] Again, charge-transfer propagation mechanisms have been invoked to explain this phenomenon. The comonomer chosen was bis(4,4′-isopropylidenediphenoxyethyl) vinyl ether (BVE, **3**), which in fact contains two vinyl ether groups. This species has previously been employed in the preparation of bismaleimide/bis(vinyl ether) thermosetting resins,[28] which cure easily at relatively low temperatures to give hard, stable materials. In addition, this monomer is a solid at room temperature. Since styrene and DVB are liquids which are miscible with both phases of the nonaqueous HIPEs, considerable destabilization occurs. A solid comonomer soluble in only the continuous phase would eliminate this problem and potentially enhance emulsion stability. BVE is easily prepared in high yield from Bisphenol A (**2**) and chloroethyl vinyl ether, in the presence of base under phase transfer conditions[11] (Figure 4). Significantly, solubility tests showed this species to be soluble in the dipolar aprotic solvents employed in this study and insoluble in petroleum ether.

The solution copolymerization of BVE with maleimide-terminated PES proceeded at 80 °C in DMAc, under a nitrogen atmosphere. In contrast to the styrene copolymerization, a 1:2 ratio of maleimide to vinyl ether groups was employed. The yield in this reaction was only 49%, which may reflect the increased steric hin-

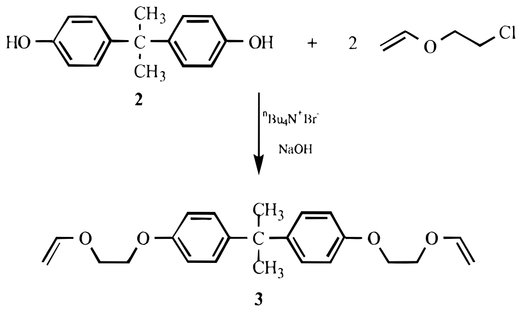

Figure 4. Synthesis of bis(4,4′-isopropylidene diphenoxyethyl) vinyl ether (BVE).

Table 7. Poly(aryl ether sulfone) PolyHIPE Materials Prepared from Nonaqueous HIPEs

comonomer	solvent	HLB no.	phase ratio (ϕ)
styrene[a]	DMF	24[d]	0.82
styrene[a]	DMF	28[e]	0.88
styrene[a]	DMAc	24[d]	0.78
styrene[a]	DMAc	28[e]	0.81
DVB[b]	DMF	24[d]	0.85
DVB[b]	DMF	28[e]	0.87
DVB[b]	DMAc	24[d]	0.73
DVB[b]	DMAc	28[e]	0.80
BVE[c]	DMF	28[e]	0.88

[a] Styrene/maleimide groups, 9/1. [b] DVB/maleimide groups, 5/1. [c] BVE/maleimide groups, 1/1. [d] F88/F127 blend (1/2). [e] F88.

drance between PES chains on copolymerization of the second vinyl group of BVE. However, it was clearly established that copolymerization had occurred to a certain extent.

A range of mal-PES-containing PolyHIPE materials was prepared with either styrene, DVB, or BVE as comonomer. In addition, the physical chemistry of the HIPEs was investigated by employing both DMF and DMAc as solvents and emulsifiers with HLB values of either 24 or 28. The results are shown in Table 7.

The internal phase volume ratios indicate that a number of factors affect the formation of nonaqueous HIPEs of high (ϕ) values. There is a solvent effect, in that HIPEs prepared with DMF are always of higher (ϕ) than those prepared with DMAc. There is also a surfactant effect; increasing the surfactant HLB value increases the volume of petrol which can be incorporated into the emulsion. These results are in keeping with those shown in Table 5 and have been explained in the previous section.

However, more surprisingly, the nature of the comonomer also plays an important role in determining the maximum value of (ϕ). In almost every case, HIPEs prepared with DVB are less stable than equivalent systems containing styrene. The increased hydrophobicity of DVB compared to styrene may increase emulsion destabilization due to its higher compatibility with the petroleum ether dispersed phase.

The solid bis(vinyl ether) comonomer was expected to produce HIPEs with increased internal phase volume ratios and stabilities, compared to those containing styrene or DVB. Internal phase volume ratios obtained were indeed high. However, an improvement in the maximum value of (ϕ), using BVE under optimum conditions, was not observed (Table 7, last entry). This would tend to suggest that an absolute maximum of internal phase volume ratio had been achieved and that the high viscosity of the emulsion was preventing this value from being further increased.

Characterization. Attempts to characterize the chemical structure of the poly(aryl ether sulfone) PolyHIPE materials did not yield any useful information. Microanalytical data were very similar to those of the maleimide-terminated precursor, as were FTIR spectra. The extremely low concentration of comonomer repeat units in the products, coupled with the absence of either different heteroatoms or moieties with distinctive IR absorptions, were the reasons for this. Therefore, no microanalytical or FTIR data are reported here.

Instead, attention has focused on determination of the cellular structure, morphology, porosity, and thermal stability of the materials. A number of techniques were employed; SEM, thermogravimetric analysis (TGA), solvent imbibition, mercury porosimetry, and surface area analysis by nitrogen adsorption.

Scanning electron micrographs of PES PolyHIPE samples are shown in Figure 5 (internal phase volume ratios (ϕ) of emulsion precursors: PES/styrene, $\phi = 0.82$; PES/DVB, $\phi = 0.85$; PES/BVE, $\phi = 0.81$). Each polymer has an open-cellular structure which truly resembles that of conventional PolyHIPE materials. Cell sizes are generally quite large, in the range 10−200 μm. This reflects the higher degree of coalescence which occurs in nonaqueous HIPEs due to their inherent lower stability, compared to their aqueous counterparts.

Another feature which can be seen from Figure 5 is the presence of wall porosity in each material, shown at the points of polymer fracture. This is produced by the polar solvent in the continuous phase, which acts as a porogen. Since the solvent also causes swelling of the cross-linked product, a microporous structure would be expected, with pore sizes in the range 50−100 nm.[6] This can clearly be seen at higher magnification, Figure 6.

The characteristics of the porous structure of the PES PolyHIPE polymers were investigated by nitrogen adsorption, mercury porosimetry, and solvent imbibition. The results are shown in Table 8.

The surface area results, as determined by BET analysis, are lower than would be expected for PolyHIPE preparation in the presence of a porogenic solvent in the continuous phase (typical surface areas 50−350 m^2 g^{-1}).[6] This suggests that the porous structure is not entirely accessible to nitrogen. The reason for this is unknown, but may be due to the formation of a nonporous "skin" on the PolyHIPE internal surfaces, similar to that reported by Hainey *et al.*[6] However, surface areas are higher than those displayed by poly(styrene/DVB) PolyHIPE polymers of intermediate crosslink density, in the absence of a porogenic solvent.[6]

The pore volumes as determined by mercury intrusion are given in Table 8. PES/DVB and PES/BVE polymers show similar values, which are also reasonably close to the theoretical pore volumes based on the internal phase volume ratios of the HIPE precursors (3.7 mL g^{-1} for PES/DVB, 5.3 mL g^{-1} for PES/BVE). However, the styrene-containing copolymer has a much lower pore volume of 1.4 mL g^{-1}, compared to the theoretical value (5.3 mL g^{-1}), which could be caused by collapse of the PolyHIPE structure under high pressure (up to 60 000 psi is used in Hg porosimetry). DVB and BVE are both divinyl comonomers, so polymers prepared from them should be more highly cross-linked than those prepared with styrene. This may lend extra mechanical strength to PES/DVB and PES/BVE PolyHIPE materials.

The pore size distributions were also determined by mercury porosimetry, and are shown in Figure 7. The data are similar for each porous material. All have large numbers of pores between 1 and 100 μm, which

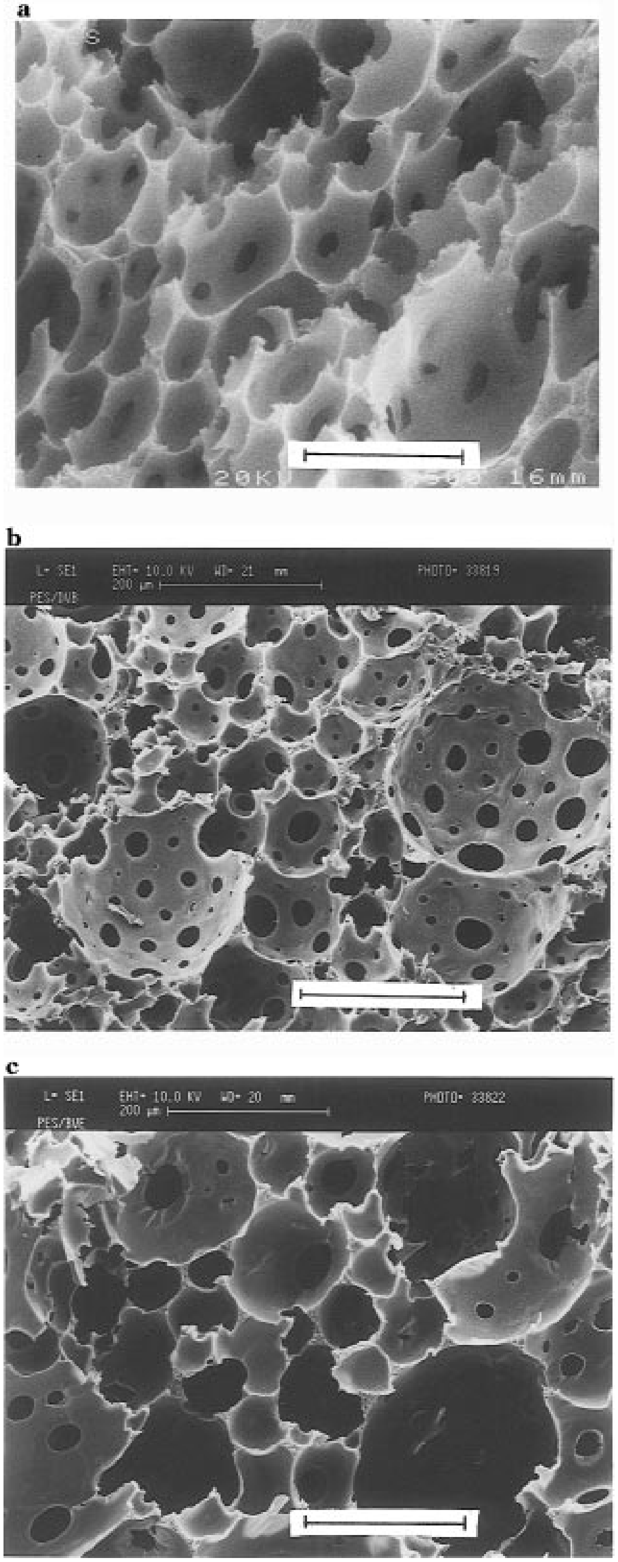

Figure 5. SEMs of PES PolyHIPE materials. (a) PES/styrene (bar = 100 μm). (b) PES/DVB (bar = 200 μm). (c) PES/BVE (bar = 200 μm). For internal phase volume ratios of emulsion precursors, see text.

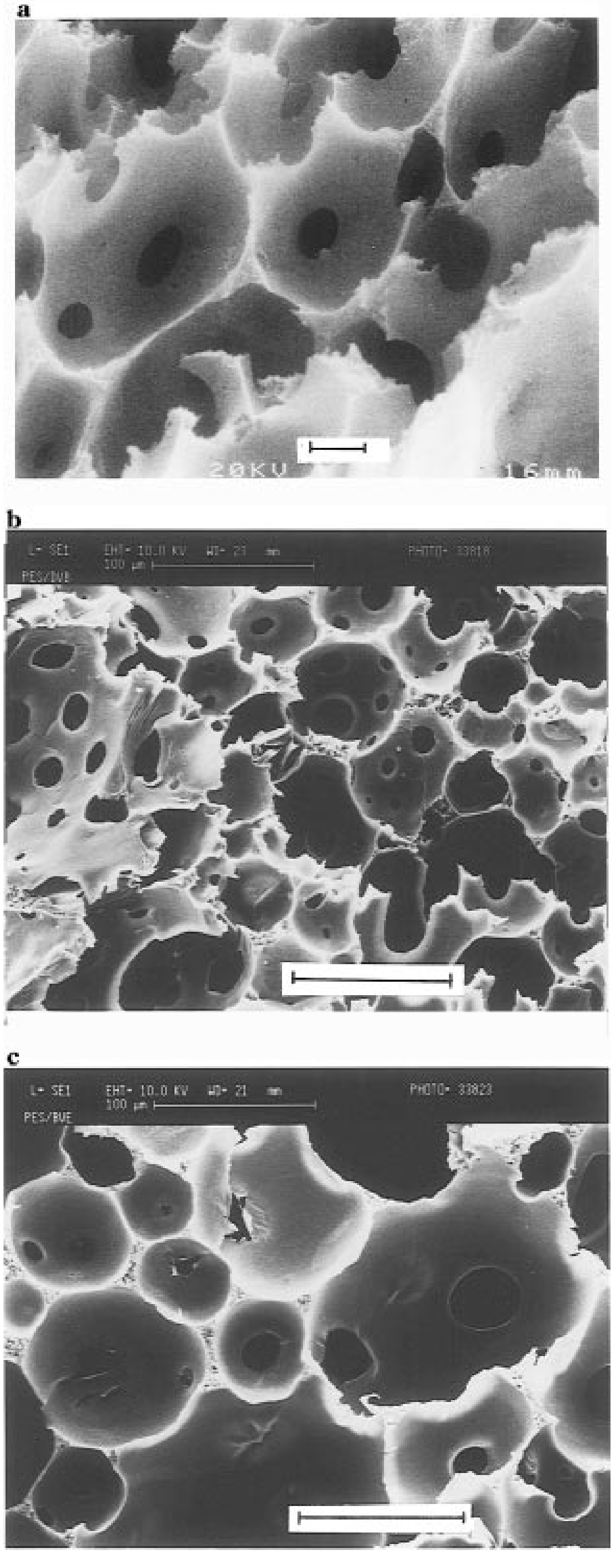

Figure 6. SEMs of PES PolyHIPE materials at higher magnification, showing porous structure within PolyHIPE walls. (a) PES/styrene (bar = 10 μm). (b) PES/DVB (bar = 100 μm). (c) PES/BVE (bar = 100 μm). For internal phase volume ratios of emulsion precursors, see text.

account for almost all of the pore volume. These results correlate with the electron micrographs shown above (Figures 5 and 6). The PES/BVE copolymer, however, has very few pores between 1 and 10 μm, which might be due to an increase in coalescence of dispersed phase droplets on heating of the HIPE.

All three materials also show porosity below 1 μm which is due to the secondary porous structure in the walls of the polymers. The PES/styrene copolymer, however, shows considerably less porosity than the others, which could also be due to collapse of the cellular structure under high pressure.

Solvent imbibition results are also given in Table 8. The polymers all absorb ethanol to more or less the same extent, whereas less toluene is absorbed by the DVB- and BVE-containing materials than PES/styrene.

Table 8. Porosities and Surface Areas of PES PolyHIPE Polymers

polymer	phase ratio (ϕ) of HIPE	surface area, $\mathrm{m^2\,g^{-1}}$	pore volume, $\mathrm{mL\,g^{-1}}$			
			Hg intrusion	EtOH imbibition	toluene imbibition	$\mathrm{CHCl_3}$ imbibition
PES/St	0.82	8.2	1.4	4.2	4.7	6.2
PES/DVB	0.73	7.7	3.0	4.9	2.7	6.2
PES/BVE	0.81	29.0	3.5	4.2	2.8	8.3

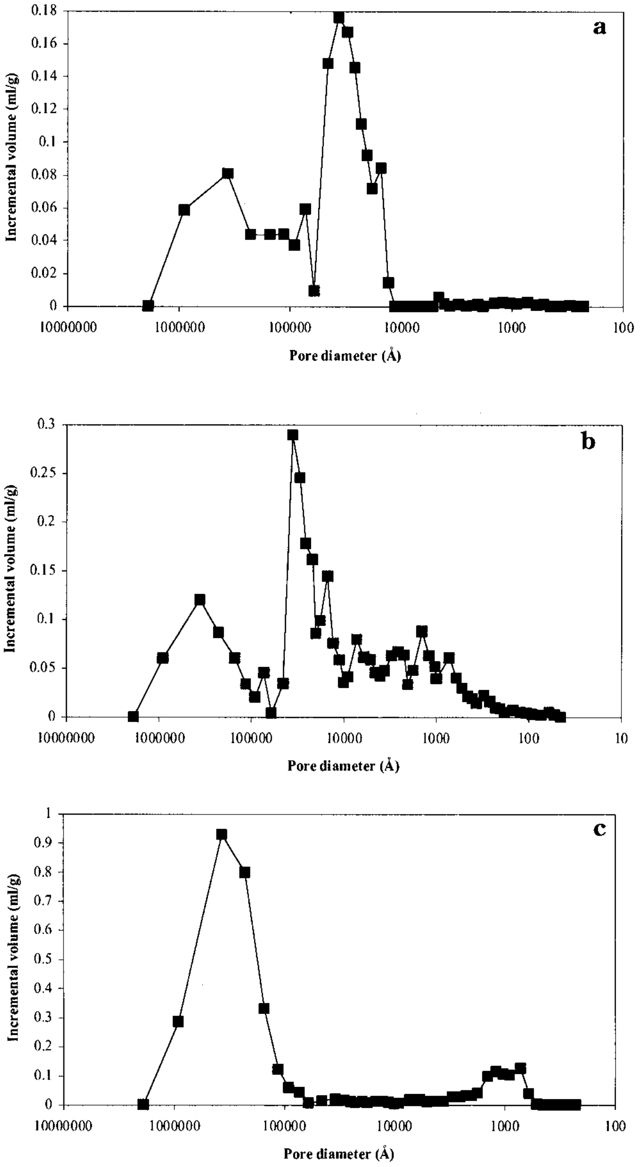

Figure 7. Pore size distributions of PES PolyHIPE materials. (a) PES/styrene. (b) PES/DVB. (c) PES/BVE. Lines are a guide for the eye only. For internal phase volume ratios of emulsion precursors, see text.

The lower absorption of toluene by PES/DVB and PES/BVE may be due to the increased cross-link density of these samples. A more polar solvent can perhaps penetrate the less accessible regions in the more densely cross-linked materials, explaining why the above trend was not displayed with ethanol. As expected, chloroform is absorbed to a greater degree than either ethanol or toluene, as it causes extensive swelling of the polymers. Thus, even the smallest and most remote pores are filled during chloroform imbibition.

The thermooxidative stability of the PES-containing PolyHIPE materials was investigated by thermogravimetric analysis (TGA), under a static atmosphere of air.

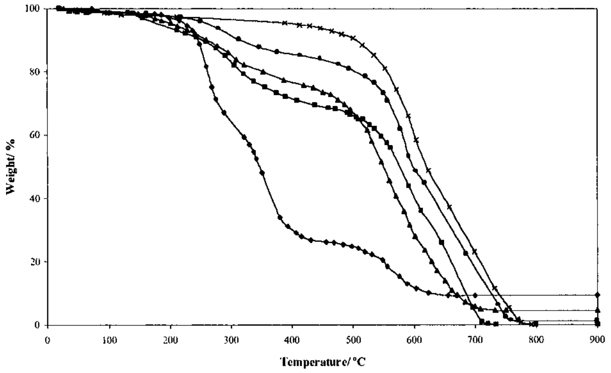

Figure 8. TGA traces of PolyHIPE materials and linear PES precursor: (a) squares, PES/styrene PolyHIPE; (b) triangles, PES/DVB PolyHIPE; (c) circles, PES/BVE PolyHIPE; (d) diamonds, poly(styrene/DVB) PolyHIPE; (e) crosses, mal-PES macromonomer. Lines are a guide for the eye only. For internal phase volume ratios of emulsion precursors, see text.

In addition, TGA was carried out on a 5% cross-linked poly(styrene/DVB) PolyHIPE polymer and on the maleimide-terminated precursor. The decomposition traces are shown in Figure 8.

The traces for PES/styrene (Figure 8a), PES/DVB (Figure 8b) and PES/BVE (Figure 8c) are quite similar. After initial loss of water, up to 100 °C, slight decomposition occurs below 200−250 °C, above which weight loss becomes more drastic. Here, differences can be noticed between the graphs of PES/styrene and DVB, and that of PES/BVE. The former two materials show a greater rate of decomposition than the BVE-containing polymer above about 250 °C. Examining the trace for poly(styrene/DVB) PolyHIPE (Figure 8d), the reason for this difference becomes clear. Critical weight loss occurs at around 250 °C and the cross-linked polystyrene PolyHIPE material undergoes serious degradation. Therefore, the higher instability of the PES/styrene and PES/DVB materials is due to fission at lower temperatures of the weaker copolymer linkages between maleimide units and either styrene or DVB residues.

The DVB-containing copolymer appears to degrade slightly more slowly between 200 and 500 °C than the PES/styrene material. This is probably due to the increased cross-link density of the former copolymer, lending it extra thermal stability. Although degradation of the PES-containing porous polymers and the poly(styrene/DVB) PolyHIPE material starts at around the same temperature, weight loss is far greater in the conventional PolyHIPE, the weight of which levels off at ∼25% at 400 °C. In comparison, poly(aryl ether sulfone) copolymers still retain over 60% of their original mass at ∼550 °C. This shows the much higher thermooxidative stability of the PES-containing PolyHIPE polymers, compared to conventional poly(styrene/DVB) systems.

The PES copolymers start to degrade critically at around 550 °C (Figure 8e). It can be concluded that this is due to the thermal degradation of the poly(aryl ether sulfone) moieties, since the linear maleimide-terminated material starts to lose weight drastically near this temperature.

Conclusions

Nonaqueous HIPEs, comprising two immiscible organic liquids, have been used to prepare PolyHIPE materials from aryl ether sulfone oligomers. These are copolymerized, via reactive maleimide end groups, with styrene, DVB, or a bis(vinyl ether) monomer (BVE), in a nonaqueous HIPE system, by thermally-initiated radical addition. HIPEs of an internal phase volume ratio of almost 0.9 were obtained under optimized conditions. The open-cell morphology of the PES PolyHIPE materials was confirmed by SEM, which also showed the presence of a porous structure within the polymer walls.

Surface areas of the PES PolyHIPE polymers, as determined by a BET treatment of N_2 adsorption results, were moderate for the materials copolymerized with either styrene or DVB and higher for the PES/BVE material. Pore size distributions were investigated by mercury porosimetry. The results seemed to confirm the cell sizes observed by SEM, which were in the range 10−200 mm, and also the presence of smaller pores within the polymer walls. Additionally, the thermooxidative properties of the materials were investigated by TGA. The PES-containing porous polymers possessed higher thermooxidative stabilities than conventional poly(styrene/DVB) PolyHIPE materials, although somewhat lower than that of the poly(aryl ether sulfone) precursor.

The preparation of poly(aryl ether sulfone) PolyHIPE polymers by copolymerization of a reactive oligomer precursor with a number of vinyl monomers, under nonaqueous HIPE conditions, is considered to be a potentially important development in PolyHIPE research as it involves the synthesis of novel, cross-linked, highly porous polymer materials, with improved thermal properties, via a novel, nonaqueous emulsion route.

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