High performance polymer particles for composite matrices: poly(arylene ether ether sulfide)s*

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A method has been developed for the synthesis of semicrystalline poly(arylene ether ether sulfide) materials by first preparing a soluble, amorphous sulfoxide containing precursor, then rapidly reducing the sulfoxide moiety to sulfide. The sulfoxide polymers are synthesized using conventional nucleophilic aromatic substitution reactions between difluorodiphenyl sulfoxide and diphenols. Reduction of the poly(ether ether sulfoxide)s with oxalyl chloride in conjunction with an iodide salt provides quantitative conversion of sulfoxide to sulfide within seconds, and the insoluble, semicrystalline poly(arylene ether ether sulfide) precipitates in the form of fine particles. Using this soluble precursor approach for preparing semicrystalline material allows there to be good control of molecular weight and endgroup structure.

(Keywords: high performance polymers; particle; composite)

INTRODUCTION

Both the preparation and processing of semicrystalline, high molecular weight polymers which have high melting points often pose special problems. Synthesis temperatures either near or above the melting points of the final materials, in conjunction with either specialized high boiling solvents or elevated pressures, are normally essential to obtain high molecular weight materials. Melt processing is difficult due to decomposition associated with the elevated temperatures required, and because of the high melt viscosities of high molecular weight, rigid materials. Insolubility of these polymers limits their use in solution processing operations.

One way to circumvent the need for such specialized synthetic conditions is through the preparation of soluble precursor polymers which can be converted quantitatively to the crystallizable structures in post polymerization reactions. McGrath et al.[1,2] developed a method for preparing poly(arylene ether ether ketone)s by first making an amorphous ketimine derivative of these polymers, then converting them to the corresponding semicrystalline poly(ether ether ketone)s via acid hydrolysis. Upon conversion of poly(arylene ether ether ketimine) to the semicrystalline ketone material (PEEK), these workers noted that fine particles precipitated from the hydrolysis solution. Recently, Wang and Zhang[3] and

Risse and Sogah[4] have also synthesized poly(arylene ether)s using similar precursor strategies.

A potential alternative to melt or solution processing methods is powder processing. However, grinding polymers into the necessary powder sizes is time and energy consuming and small powders (a few micrometres and smaller) cannot be practicably prepared in this manner. Workers in our laboratory studied the hydrolysis/precipitation process of poly(arylene ether ether ketimine)s to PEEK to gain an understanding of how to control the size and size distribution of the resultant particulates[5,6]. We found that when hydrolysis to the ketone was extremely rapid, smaller particles (20–50 nm in diameter) and narrower size distributions resulted. This is probably due to the formation of PEEK (in solution) so rapidly that its concentration significantly exceeds the critical supersaturation point in the solution. Hence, the nucleation rate in this metastable solution is extremely rapid, many stable nuclei form, and relatively little polymer mass remains in solution to adsorb onto these nuclei[6]. The development of fibre reinforced composites via aqueous suspension prepregging methods using the small PEEK powders is currently under investigation[7,8].

We were interested to learn whether very fine powders could be precipitated from similar metastable solutions using other rapid chemical conversions of soluble precursor polymers to crystalline materials. Thus, the original impetus behind development of the poly(arylene ether ether sulfide) materials discussed in this paper was to answer this question. However, these polymers also represent a new class of semicrystalline, high performance

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polymers and a new post polymerization reaction has been introduced. This paper describes the chemistry used to prepare these new materials and demonstrates the formation of submicrometre particulates in controlled precipitation processes.

Previous syntheses of poly(arylene ether ether sulfoxide)s have been described by Johnson et al.[9], but properties of the materials were not discussed. Some authors have also attempted to develop methods for the synthesis of poly(arylene ether sulfide)s[10,11], but the limited solubility of these materials precluded the attainment of high molecular weight. Fujisawa et al.[12] also converted these arylene ether sulfides to the corresponding sulfoxides by oxidation with hydrogen peroxide.

EXPERIMENTAL

Materials

N-methylpyrrolidone (NMP) was dried and distilled over P_2O_5 under vacuum, then stored in septum capped brown bottles under nitrogen until used. Hydroquinone (99.9%), oxalyl chloride, and tetrabutylammonium iodide (Aldrich) were used as received. 4,4'-Biphenol and 4-t-butylphenol were sublimed under vacuum prior to use. 1,1,2,2-Tetrachloroethane (Aldrich) was distilled over P_2O_5 prior to use. Toluene (Fisher) was first washed with concentrated H_2SO_4 followed by a saturated solution of sodium bicarbonate and water. It was then dried over anhydrous sodium sulfate followed by P_2O_5 and finally over sodium, then distilled under nitrogen. Potassium carbonate (Aldrich) was dried in the vacuum oven at $\sim 100°C$ overnight prior to use. Fluorobenzene was distilled over P_2O_5 prior to use. Chlorobenzene was washed first with concentrated H_2SO_4 followed by a saturated solution of sodium bicarbonate and water. After drying over anhydrous sodium sulfate and P_2O_5, it was distilled over CaH_2.

G.p.c.

G.p.c. was performed using a Waters 150-C chromatograph operating at 60°C with a μStyragel column set comprised of 500 Å and 10^3 Å columns. H.p.l.c. grade NMP containing 0.5% w/w LiBr was used as the mobile phase at a rate of 1 ml min^{-1}. Dual concentration and viscosity detectors were employed, and a universal calibration method calibrated with polystyrene standards was used to calculate absolute molecular weights.

Thermal analysis

Thermal measurements were run using a Perkin–Elmer DSC-7 instrument. D.s.c. was carried out under an atmosphere of He in sealed pans. T.g.a. was carried out with a heating rate of 10°C min^{-1} in an atmosphere of either air or N_2 as specified.

Synthesis of 4,4'-difluorodiphenyl sulfoxide

The procedure of Leonard and Sutton[13], a Friedel–Crafts acylation of fluorobenzene with thionyl chloride, was used to prepare this compound. It was purified by crystallizing from petroleum ether twice (m.p. 51–51.5°C).

Synthesis of 4,4'-dichlorodiphenyl sulfoxide

The procedure described above was carried out except chlorobenzene was used instead of fluorobenzene and the product was purified by crystallizing twice from toluene (m.p. 145–146°C).

Typical example of synthesis of controlled molecular weight poly(arylene ether ether sulfoxide)s: from difluorodiphenyl sulfoxide and hydroquinone [M_n (theory) = 20 000 g mol^{-1}]

To a dry, four-necked round bottomed flask fitted with a mechanical stirrer, Dean–Stark trap, and nitrogen inlet and outlet, difluorodiphenyl sulfoxide (9.53 g, 0.04 mol) and hydroquinone (4.3379 g, 0.0394 mol) followed by 4-t-butylphenol (0.1815 g, 1.208 × 10^{-3} mol) were transferred quantitatively under nitrogen flow, and dissolved in dry NMP (93 ml, 15% solids). Dry K_2CO_3 was added to the mixture (8.3 g, 0.06 mol) followed by toluene (60 ml) as the azeotroping agent. A slow stream of nitrogen was passed through the reaction mixture during the reaction. The reaction mixture was first heated at 145°C (bath temperature) with stirring for 6–12 h while the toluene/water azeotrope was removed to dehydrate the system. Then the temperature was raised to 185°C (bath temperature, 163°C reaction temperature) and the remaining toluene was removed from the reaction mixture by distillation. After 36 h at this temperature, the reaction mixture was cooled and coagulated by pouring into a rapidly stirred 2:1 v/v mixture of methanol and water. The polymer was dried at 100°C in a vacuum oven to a constant weight.

Reduction of poly(arylene ether ether sulfoxide)s to the corresponding poly(arylene ether ether sulfide)s

A poly(arylene ether ether sulfoxide) based on hydroquinone ($M_n = 20 000$ g mol^{-1}, 11 g, 0.036 mol) was placed in a dry four-necked 1 l round bottomed flask fitted with a mechanical stirrer, and nitrogen inlet and outlet. The polymer was dissolved in dry tetrachloroethane (220 ml) under a slow stream of nitrogen at 50°C, then a solution of tetrabutylammonium iodide (33.24 g, 0.09 mol, 99.7 ml from a stock solution of 35 g in 105 ml tetrachloroethane) was transferred into the reaction flask. Oxalyl chloride (5.5 g, 3.8 ml, 0.043 mol) was then added rapidly via syringe to the rapidly stirring polymer solution. Immediately upon introduction of the oxalyl chloride, iodine was liberated, carbon monoxide and carbon dioxide gas evolved, and the corresponding sulfide polymer precipitated in the form of fine particles. The reaction mixture was stirred at the 50°C reaction temperature for 5 min, then poured into methanol (600 ml) and filtered. The polymer particles were washed several times with MeOH, and transferred to a beaker containing a 5% solution of sodium thiosulfate (500 ml). After stirring for ~ 1 h, the particles were again collected and washed several times with water (2 l) followed by MeOH (1 l). The polymer was dried in a vacuum oven at 40°C for 10 days.

Proton n.m.r.

Proton n.m.r. was used to establish conditions whereby quantitative conversion of poly(arylene ether ether sulfoxide)s to poly(arylene ether ether sulfide)s was achieved. Poly(arylene ether ether sulfide)s based on hydroquinone were used for this purpose. Approximately 100 mg of the sulfide polymer was suspended in dry NMP (5 ml) in a 25 ml round bottomed flask containing a magnetic stir bar and capped with a rubber septum. Air in the flask was replaced with dry N_2 and the mixture was heated in an oil bath (to $\sim 160–170°C$) and held at that temperature until the polymer dissolved. The solution was quickly transferred to an n.m.r. tube and the ^{1}H
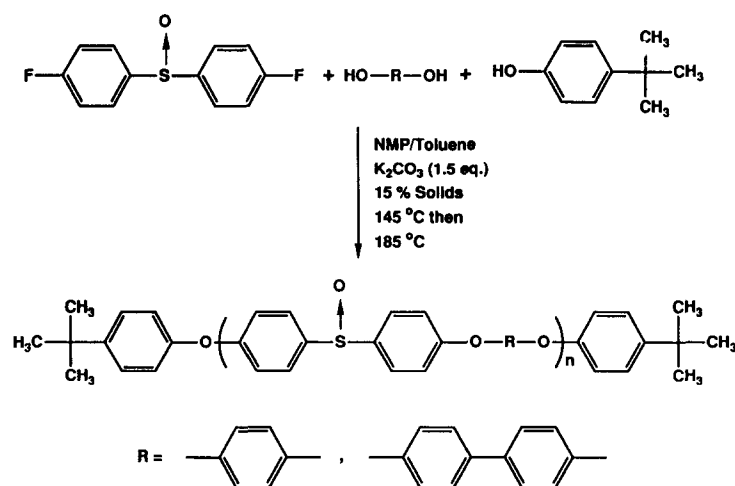
Figure 1 Synthesis of poly(arylene ether ether sulfoxide)s

n.m.r. spectrum was collected at a probe temperature of 130°C in a Varian Unity 400 NMR operating at 400 MHz. The ^{1}H n.m.r. of the precursor sulfoxide polymer was also obtained under the same conditions. In those cases, these sulfoxide polymers were dissolved in NMP at room temperature.

Particle size analysis

The procedure used to stabilize and measure the particle size of the poly(arylene ether ether sulfide)s is essentially the same as that of Brink et al.[14]. The poly(arylene ether ether sulfide) 'particles' based on 4,4'-biphenol and difluorodiphenyl sulfoxide obtained from the above described reduction process were suspended in NMP and stirred with 10% w/w of a poly(pyridine ether-co-ether ether ketimine) (30 mol% pyridine) copolymer for 24 h at room temperature. Afterwards, the mixture was sonicated for 1 min and stirred for 24 h. During this process, the pyridine containing copolymer adsorbs onto the surfaces of the polysulfide particles. Upon acid hydrolysis of this material, the ketimine converts to ketone, the pyridine units become protonated, and the pyridine containing polymer collapses onto the particle surface and crystallizes. Acid hydrolysis of this mixture was done at 80°C using dilute HCl. The particles were then washed with water several times to ensure removal of ionic impurities from the system. The polymer particles were then suspended in water, sonicated for 1 min, and particle size analysis was run using a Shimadzu particle size analyzer (model no. SA CP3). A median particle diameter of 1.1 μm was obtained in this case.

RESULTS AND DISCUSSION

High molecular weight poly(arylene ether ether sulfoxide)s can be prepared using nucleophilic aromatic substitution reactions employing the use of sulfoxide activating groups on the dihalide monomers (*Figure 1*). Both difluorodiphenyl sulfoxide and its chlorine analogue can be prepared with good yields, and in one step, using Friedel–Crafts reactions between thionyl chloride and the appropriate halobenzene[13]. However, the increased reactivity of the fluorine containing monomer was found to be necessary for the attainment of high molecular

Table 1 Molecular weight analysis of controlled molecular weight poly(arylene ether ether sulfoxide)s based on hydroquinone and 4,4'-biphenol[a]

M_n (theory)	M_n (exp.)	M_w/M_n	η (dl g^{-1})[b]
Hydroquinone			
8000	8600	2.08	0.19
20000	21000	2.11	0.35
40000	36000	1.94	0.43
Uncontrolled	139000	2.08	2.28
4,4'-Biphenol			
8000	8200	1.98	0.27
15000	15000	2.00	0.35
30000	20000	1.99	0.44
Uncontrolled	42000	2.00	0.80

[a] By g.p.c.
[b] Intrinsic viscosity by g.p.c.

weight materials. Both hydroquinone and 4,4'-biphenol have been explored as comonomers in this study.

In order to control rheological parameters such as melt viscosity for polymeric materials, it is important to control molecular weight. This is particularly critical for fully formed thermoplastics because of the relatively high viscosities encountered. Moreover, materials such as these relatively rigid poly(arylene ether ether sulfide)s which have high upper transition temperatures must undergo processing operations at elevated temperatures, and, thus, non-reactive end groups could contribute substantially to increased stability during these steps. Using 4-t-butylphenol as a non-reactive endcapping reagent for the soluble poly(arylene ether ether sulfoxide) precursor polymers, we have used g.p.c. to establish relatively good agreement between targeted and experimental molecular weights (*Table 1*). Following conversion of the sulfoxide moiety to sulfide, the materials have semicrystalline morphologies and, hence, become insoluble in g.p.c. solvents. To ensure that the reduction reaction does not significantly affect molecular weight, a poly(arylene ether ether sulfoxide) was prepared using bisphenol-A as the comonomer. The corresponding poly(arylene ether ether sulfide) from this precursor polymer is amorphous and molecular weights of the precursor and the reduced material could be compared using chromatographic
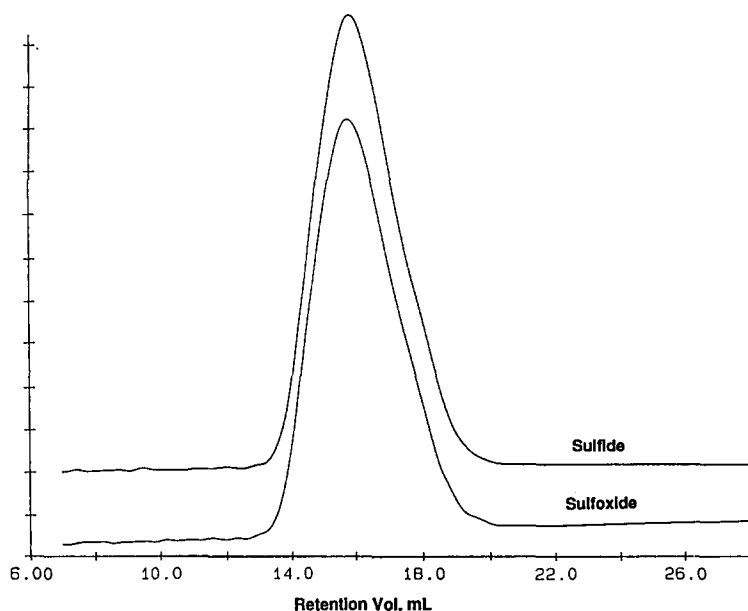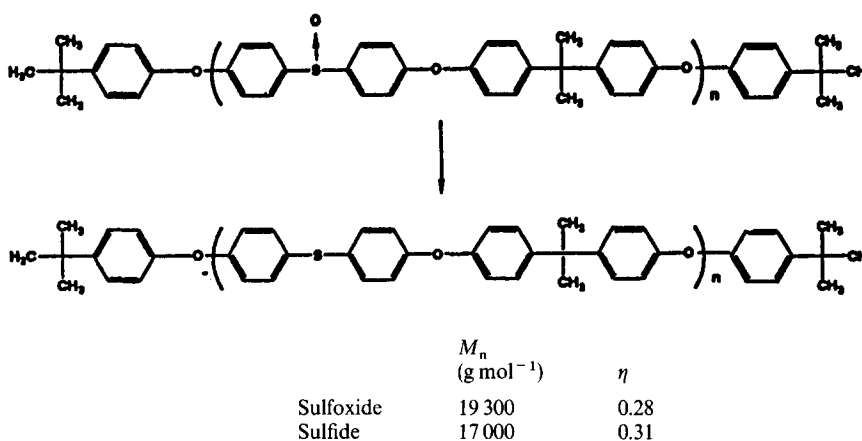
Figure 2 Demonstration of retention of molecular weight upon reduction:

	M_n (g mol^{-1})	η
Sulfoxide	19 300	0.28
Sulfide	17 000	0.31

measurements. This analysis indicated no change (within the g.p.c.'s experimental error of ~10%) in molecular weight upon chemical conversion to the sulfide (*Figure 2*).

A variety of reagents for reduction of sulfoxide to sulfide are reported in the literature[15]. As described earlier, we were interested in generating fine polymer particles upon reducing this particular set of polymers. Our previous work on particle formation[5,6] had indicated that smaller particles and narrower particle size distributions should result when the chemical conversion reaction was rapid enough to achieve near quantitative conversion prior to particle nucleation. Hence, a major consideration in identifying a suitable method for reduction was to find a process which would be quantitative within, at most, a few seconds. A stoichiometric amount of oxalyl chloride in conjunction with a minimum of two molar equivalents of tetrabutylammonium iodide, using 1,1,2,2-tetrachloroethane as the solvent (*Figure 3*) produced quantitative results essentially immediately upon reagent addition. This was a modification of a method originally used by Olah et al.[16], who employed sodium iodide in acetonitrile. The organic iodide salt was preferred for this work because of its solubility in the polymer solvent (1,1,2,2-tetrachloroethane).

Although the mechanism of this reduction has not been studied, possible reaction pathways are depicted in
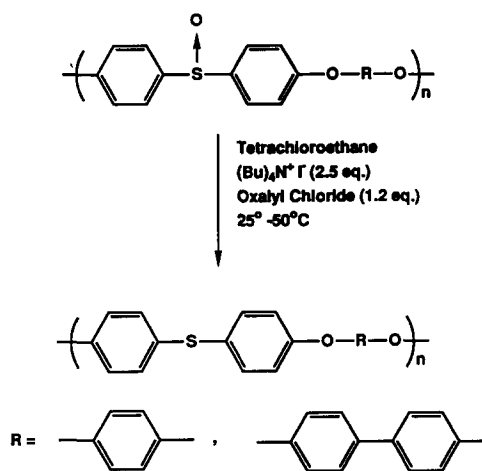

Figure 3 Conversion of poly(arylene ether ether sulfoxide)s to poly(arylene ether ether sulfide)s

Figure 4. The first step probably involves the somewhat nucleophilic sulfoxide oxygen displacing a chloride from oxalyl chloride to produce an unstable intermediate complex. Then iodide attacks either at the sulfur or at the remaining chloride. Attack at either position causes the evolution of carbon monoxide and carbon dioxide,

and the sulfur is rapidly reduced. ^{1}H n.m.r. was used to establish quantitative conversion of the polysulfoxides to polysulfides under the conditions described in the Experimental section. For this purpose, poly(arylene ether ether sulfide) based on hydroquinone was used since it was soluble in NMP at high temperatures ($\sim 130°$C). Unfortunately, we have not been successful in finding a solvent for the poly(arylene ether ether sulfide) based on 4,4'-biphenol. *Figure 5* depicts the aromatic regions of the solution spectra of a poly(arylene ether ether sulfoxide) and corresponding poly(arylene ether ether

Figure 4 Possible pathways for reduction of sulfoxides to sulfides

sulfide) based on hydroquinone collected in NMP at 130°C. Note that the protons *ortho* to the sulfoxide ring at ~ 7.8 ppm in the spectrum of the precursor material have shifted quantitatively upfield after reduction.

Table 2 shows thermal transitions of the poly(arylene ether ether sulfoxide)s and corresponding poly(arylene ether ether sulfide)s. The sulfoxide polymers are amorphous displaying only glass transitions, whereas the corresponding sulfides are semicrystalline, exhibiting both glass transition and melting transitions. Note that the chemical structure of the poly(arylene ether ether sulfide) based on hydroquinone is analogous to poly(phenylene sulfide) wherein oxygen has been substituted for sulfur at regular points along the backbone. Thus, it appears reasonable that the thermal transitions of these two materials are close [$T_g = 85°$C and $T_m = 285°$C for poly(phenylene sulfide) and $T_g = 102°$C and $T_m = 251°$C for poly(arylene ether ether sulfide) from hydroquinone]. As expected, substitution of biphenol for hydroquinone increases rigidity and the thermal transitions are higher.

Table 3 summarizes t.g.a. measurements of these materials. The polysulfoxides undergo a sharp weight loss corresponding to $\sim 5\%$ around 400°C in both N_2 and air (*Figure 6*). Although this behaviour needs further investigation, t.g.a.–mass spectrum analysis suggests that sulfur dioxide may be evolved at this temperature. As indicated in *Table 3*, the semicrystalline poly(arylene ether ether sulfide)s are relatively thermally stable materials.

As previously mentioned, one major objective in developing both the soluble poly(arylene ether ether sulfoxide)s and the corresponding semicrystalline polysulfides was to assess whether the general process of using a rapid chemical conversion to the semicrystalline material, with resultant crystallization from solution,
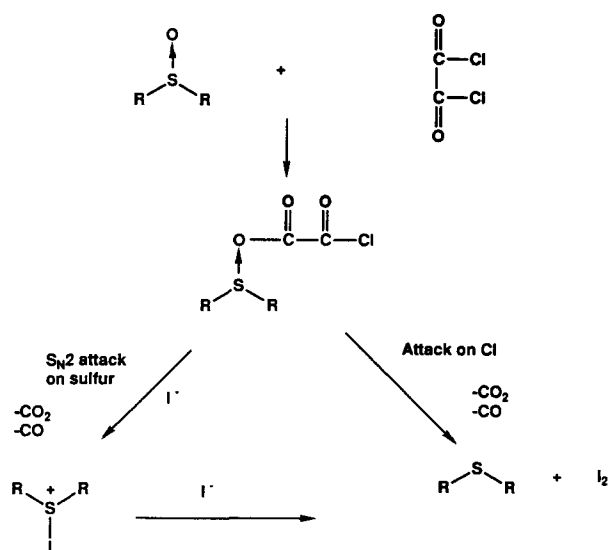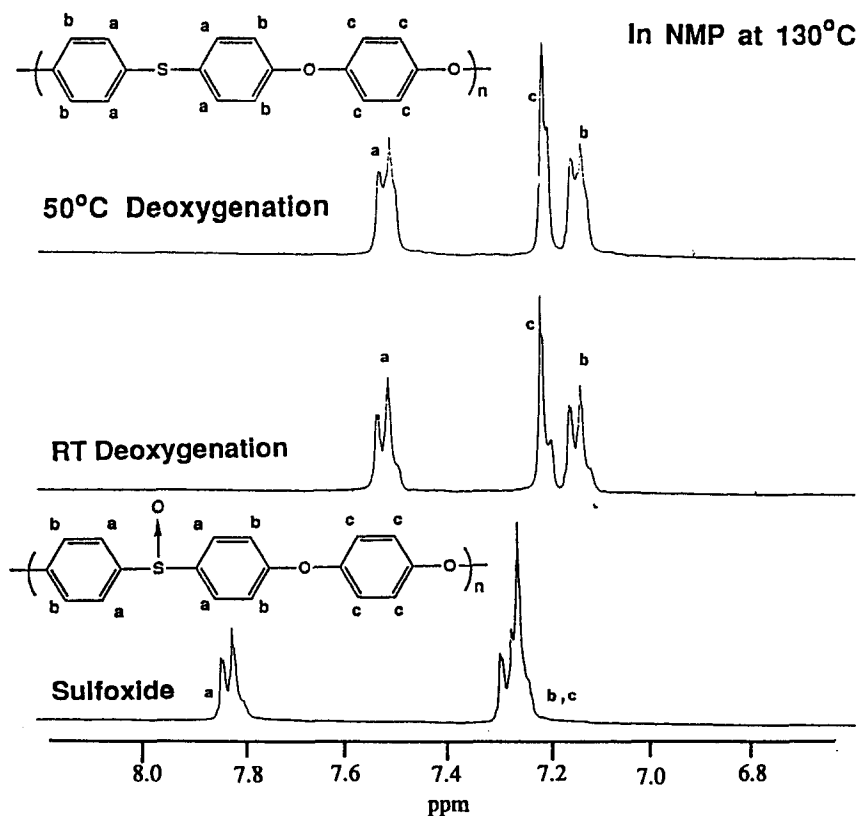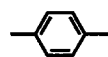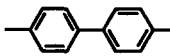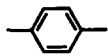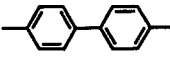

Figure 5 Demonstration of quantitative conversion of poly(arylene ether ether sulfoxide)s to the sulfides by ^{1}H n.m.r.

produces extremely fine particulates. Recent work in our laboratories has demonstrated the formation of very fine particles using this general method for preparing poly(ether ether ketone)s[5,6]. Thus, aqueous suspensions of the polysulfide particles were prepared using an electrostatic stabilizer previously developed in our laboratories[14], and particle size and size distribution were measured using a centrifugal method in conjunction with a light scattering detector. The suspensions were prepared
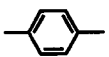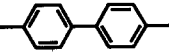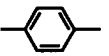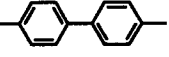
(*Figure 7*) by first stirring the poly(arylene ether ether sulfide) particles, along with ~10 wt% poly(pyridine ether-*co*-ether ether ketimine)[14], in NMP. This allowed sufficient time for the stabilizer (which was dissolved in the solvent) to adsorb onto the particle surfaces. The soluble ketimine/pyridine stabilizer was then hydrolysed to the ketone using dilute HCl, with concurrent protonation of the pyridine units. This hydrolysis process yields a semicrystalline aromatic stabilizer. Thus, the

Table 2 D.s.c. of poly(arylene ether ether sulfoxide)s and sulfides

R	T_g (°C)[a]	T_m (°C)[b]
Sulfoxide		
—⟨benzene⟩—	178	–
—⟨biphenyl⟩—	216	–
Sulfide		
—⟨benzene⟩—	102	251
—⟨biphenyl⟩—	148	311

[a] Glass transition temperature
[b] Melting temperature

Table 3 T.g.a. weight loss of poly(arylene ether ether sulfoxide)s and sulfides

R	N_2 (°C)	Air (°C)
Sulfoxide (initial weight loss)		
—⟨benzene⟩—	420	408
—⟨biphenyl⟩—	429	420
Sulfide (5% weight loss)		
—⟨benzene⟩—	532	522
—⟨biphenyl⟩—	525	520
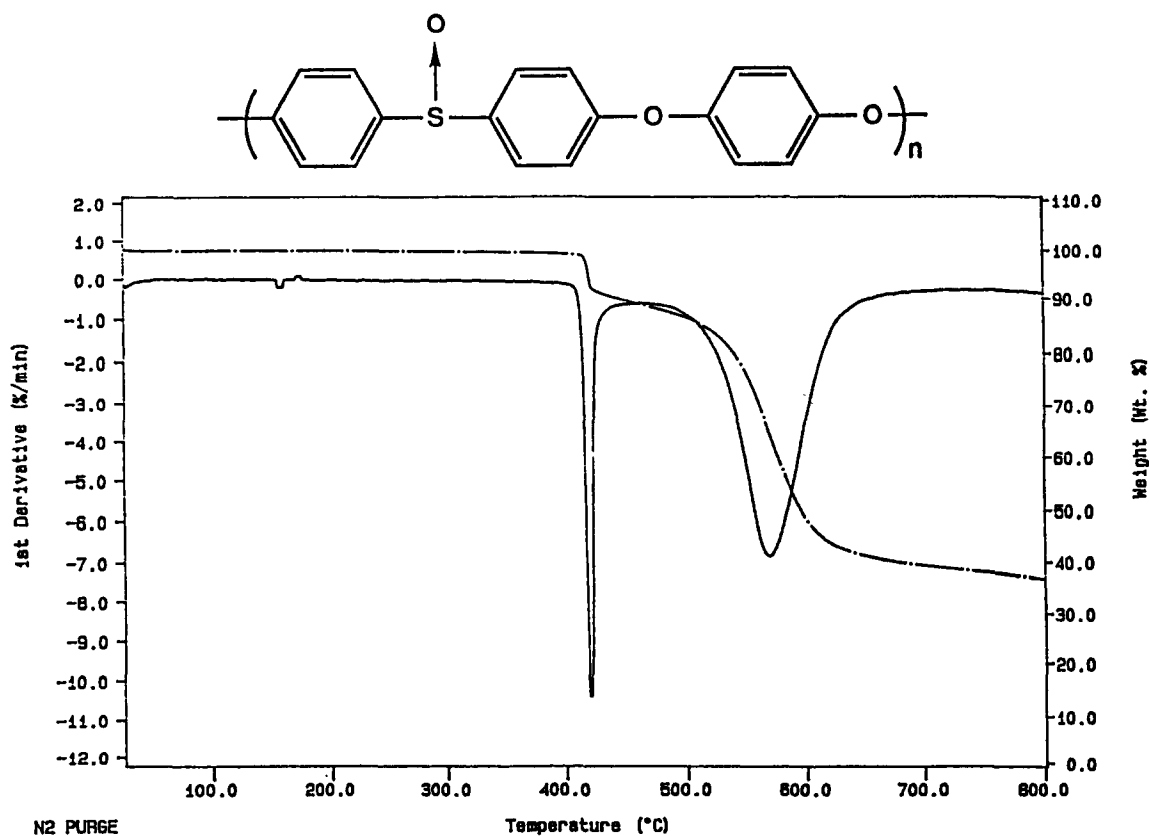
Figure 6 Typical t.g.a. trace of poly(arylene ether ether sulfoxide)s in nitrogen atmosphere

"aggregated particles"

10 w/w%

1. Sonicate 1 min and stir 24h
2. Hydrolyse with dil. HCl
3. Filter, wash
4. Suspend in H₂O and sonicate 1 min.
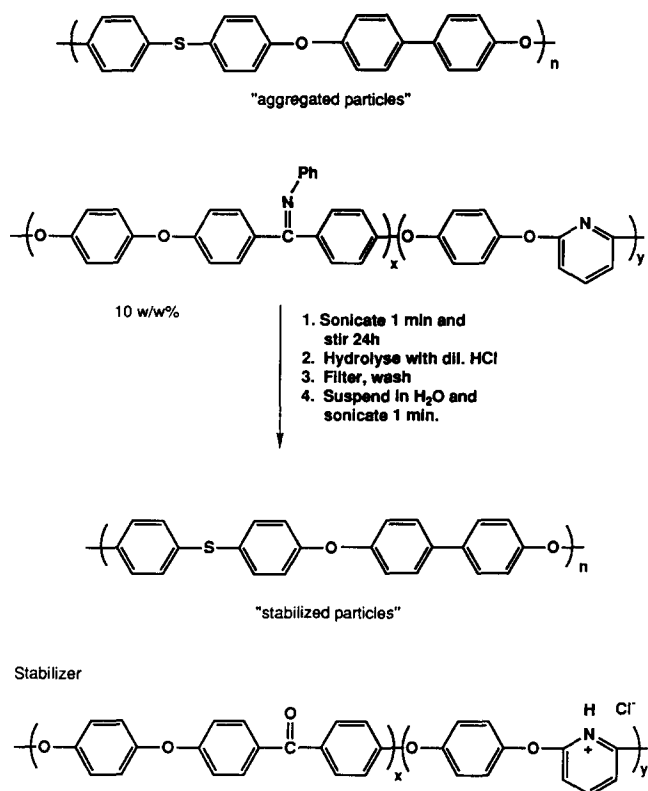

"stabilized particles"

Stabilizer

Figure 7 Poly(pyridine ether-*co*-ether ether ketone) stabilizer for poly(arylene ether ether sulfide) particles in water

stabilizer collapses onto the particle surface and forms a charged particle surface. The particles were filtered from NMP, resuspended in water, and the particle size was measured. The instrument used for these measurements analyses the turbidity of the sedimenting suspension and utilizes Stokes' law to correlate the sedimentation rate to particle size. The solvent density and viscosity as well as the density of the particle are required[17]. The solvent used was water ($\rho = 0.998 \, \text{g ml}^{-1}$, $\eta = 0.938 \, \text{cP}$) and the density of the particles was approximated as $1.3 \, \text{g ml}^{-1}$. The median particle size obtained using this method was in the range of $1 \, \mu\text{m}$.

Upon rapid reduction of the soluble sulfoxide to the corresponding insoluble sulfide, it is believed that at first a supersaturated solution of the sulfide is formed. The semicrystalline poly(arylene ether ether sulfide) crystallizes from solution by nucleation and then growth. If all the sulfoxide is quantitatively reduced to the sulfide well before nucleation begins, many nuclei are formed in a very short time and very small particles of narrow size distribution result. If reduction is not sufficiently fast, stable nuclei begin to form under conditions where the nucleation rate is slower. The density of nuclei is lower and fewer particles with larger sizes result.

CONCLUSIONS

A new class of poly(arylene ether ether sulfide) materials have been prepared by first making soluble sulfoxide derivatives, then by rapidly converting these amorphous materials to semicrystalline polymers. In this manner, good control can be exercised over molecular weight, and end groups can be stabilized with non-functional capping reagents. Moreover, by controlling the sulfoxide to sulfide reduction process, the materials can be prepared in the form of micrometre size particulates. The properties of fine polymer particles and the construction of composite materials using fine powders are under investigation in our laboratories. Future collaborative work will also focus on studying the crystallization and morphology of these materials along with a comparison of the properties of poly(arylene ether ether sulfide)s with materials of related chemical and morphological structures such as poly(phenylene sulfide)s and poly(arylene ether ketone)s.

ACKNOWLEDGEMENTS

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