Reversible, Nondegradative Conversion of Crystalline Aromatic Poly(ether ketone)s into Organo-Soluble Poly(ether dithioketal)s

Howard M. Colquhoun,*,[†] Philip Hodge,[§] François P. V. Paoloni,[†] P. Terry McGrail,[‡] and Paul Cross[‡]

Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, U.K., School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, U.K., and Cytec Engineered Materials Ltd., Wilton Centre, Redcar, Teesside TS10 4RF, U.K.

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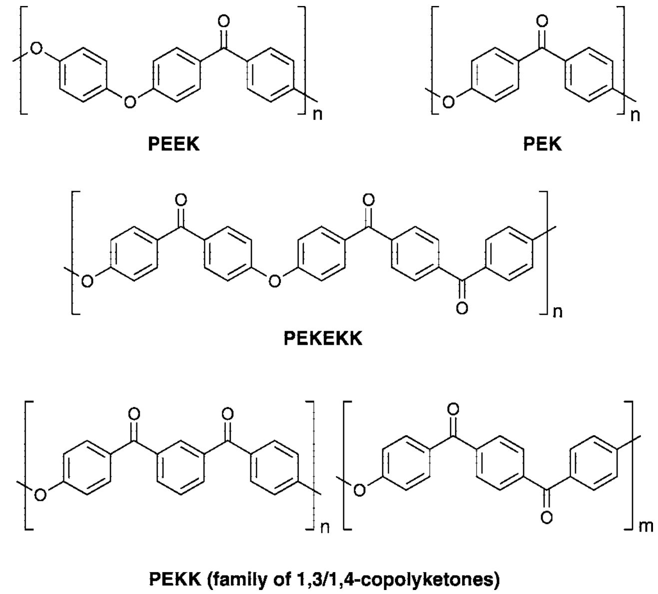
ABSTRACT: Crystalline aromatic poly(ether ketone)s such as PEEK and PEK may be cleanly and reversibly derivatized by dithioketalization of the carbonyl groups with 1,2-ethanedithiol or 1,3-propanedithiol under strong acid conditions. The resulting 1,3-dithiolane and 1,3-dithiane polymers are hydrolytically stable, amorphous, and readily soluble in organic solvents such as chloroform and THF and are thus (unlike their parent polymers) easily characterized by gel permeation chromatography (GPC). GPC analysis of a range of derivatized PEEK samples using light-scattering detection revealed, in some instances, a bimodal molecular weight distribution with a small but potentially significant (and previously undetected) very high-molecular-weight fraction.

Introduction

The semicrystalline aromatic poly(ether ketone)s are an industrially important class of high-performance thermoplastics with outstanding physicochemical properties.[1,2] For example, PEEK (Chart 1) is widely used in situations that require mechanical stability at high temperatures or in aggressive environments, and it also finds increasing application as a matrix in long-fiber composite materials.[2a] As with the amorphous poly(ether sulfone)s, aromatic poly(ether ketone)s exhibit high thermal stability and excellent resistance to oxidation and γ-radiation, but their crystalline character also provides greatly enhanced thermomechanical stability and solvent resistance.[2b] However, the lack of solubility of these materials can be a major obstacle for detailed characterization, so a full understanding of the relationship between their properties and their structure at the molecular level is often very difficult to achieve. Analysis of PEEK and some related poly(ether ketones) by gel permeation chromatography (GPC) may be carried out in a mixture of phenol and 1,2,4-trichlorobenzene,[3–6] but this technique requires a combination of high temperatures (typically >115 °C) and corrosive/hazardous solvents, so relatively specialized GPC systems are required.

There have been several reports describing amorphous (and therefore soluble) precursor polymers of poly(ether ketone)s that can be fully characterized before their final conversion to insoluble, semicrystalline materials. Systems of this type have involved the use of *t*-butyl-substituted monomers,[7,8] or the protection of the carbonyl groups as ketimines[9–14] or ketals,[15] again in the monomer design stage. A number of post-synthesis derivatization reactions of semicrystalline poly(ether ketone)s have also been described, although the insolubility of the latter in conventional solvents precludes the application of many types of chemistry. Nevertheless, PEEK may be sulfonated simply by dissolving in concentrated sulfuric acid, and the resulting polysulfonate ionomers are then soluble in polar aprotic solvents such as *N*,*N*-dimethylformamide or *N*,*N*-dimethylacetamide.[16] Lithium salts of sulfonated PEEK have thus been analyzed by room-temperature GPC in *N*-methylpyrrolidone.[17,18] However, this approach is far from general in that many potentially important poly(ether ketone)s such as PEK, PEKEKK, and PEKK (Chart 1) do not readily undergo sulfonation (because every ring carries at least one deactivating carbonyl group); therefore, they cannot be characterized by this method. A different derivatization approach depends on the reduction of the ketone linkages in poly(aryl ether ketone)s by triethylsilane and strong acids to yield poly(ether methylene)s, but these derivatives often prove to be crystalline across the whole composition range (CO/CH$_2$), so they may be exceptionally characterized only by GPC methods.[19]

Chart 1. Some Industrially Important Poly(ether ketone)s



The protection of carbonyl groups as cyclic dithioketals, a procedure that is well established in organic synthesis,[20] is potentially an extremely attractive approach to the derivatization of aromatic poly(ether ketone)s because dithioketal groups are stable over a wide pH range. Crucially, in the present context, it seemed probable that this type of reaction would not be inhibited by the strong acid cosolvents that are required to solubilize crystalline poly(ether ketone)s in chlorocarbons at

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* Corresponding author. E-mail: h.m.colquhoun@rdg.ac.uk.
[†] University of Reading.
[§] University of Manchester.
[‡] Cytec Engineered Materials, Ltd.

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ambient temperature.[21–23] We now report that dithioketalization in fact provides a completely general solution to the problem of achieving nondegradative derivatization and solubililization of semicrystalline aromatic poly(ether ketone)s and that the derived poly(ether 1,3-dithiolane)s and poly(ether 1,3-dithiane)s are very readily characterized by GPC in conventional organic solvents with both refractive index (RI) and light-scattering (LS) detection. Deprotection of dithioketal derivatives of PEEK is found to regenerate essentially unchanged starting polymer, and dithioketalization studies of fully soluble, amorphous poly(ether ketone)s confirm that these reactions are free of cross-linking or degradative side reactions. Part of this work has been reported in a preliminary communication.[24]

Experimental Section

Instrumentation. Proton and ^{13}C NMR spectra were obtained on a Bruker DPX250 spectrometer at 250 and 62.5 MHz, respectively. Resonances were recorded in δ (ppm) and referenced to residual solvent resonances or tetramethylsilane. Infrared spectra of polymers were obtained from films produced by evaporation of chloroform solutions on KBr plates and were recorded on a Perkin-Elmer FT 1700 instrument. Thermal analyses were carried out by differential scanning calorimetry (DSC) at a heating rate of 10 °C min^{-1} on a Mettler DSC20 system under a nitrogen atmosphere. The system was calibrated using the melting enthalpies and peak positions for indium, zinc, and lead. Glass transitions are quoted as onset values and crystallization and melting temperatures as the position of the corresponding exo- or endotherms. Thermogravimetric analyses (TGA) were performed on a TA-Q50 instrument using ca. 10 mg of material and heating to 500 °C at a rate of 10 °C min^{-1} under a nitrogen atmosphere.

Inherent viscosities (η_{inh}) were determined at 25 °C using filtered 0.1 wt % solutions of polymer in a Schott AVS 470 autoviscometry system and CT52 thermostatted water bath. Crystalline poly(ether ketones) were dissolved in 98% sulfuric acid with stirring for 18 h to ensure complete dissolution and (for PEEK) sulfonation, and the resulting solutions were characterized using an Ubbelohde capillary viscometer (Schott no. 53113). Viscometry of the dithioketal polymers was carried out in chloroform using a narrow-bore capillary viscometer (Schott no. 53103).

GPC was carried out in chloroform at 35 °C on a Polymer Laboratories GPC220 system with two 10 μm mixed-B PL columns (300 × 7.5 mm). Chloroform was used as a general eluent for the GPC of poly(ether dithioketal)s because not all such polymers proved to be fully soluble in tetrahydrofuran. Chloroform solutions of all of these materials were readily obtained at a concentration of ca. 2 mg mL^{-1} after being stirred overnight at room temperature. The RI detector was calibrated with a range of 10 polystyrene standards (Polymer Laboratories Easycal PS2). Light-scattering analyses were carried out with a PD2000 LS detector, and molecular weights included the low mass fraction. The detector constants and the interdetector delay were determined with a single PMMA standard ($M_p = 100\,000$) of known concentration. The increment refractive index (dn/dc) of each sample was calculated from its concentration and the detector constants. The LS response at 15° was used only for molecular weights greater than 10 kDa. X-ray powder diffraction patterns were acquired on a Siemens D5000 diffraction system using Cu-Kα radiation. Polymer samples for X-ray analysis were obtained as fine powders by precipitation from dilute dichloromethane solutions with methanol.

Materials. Commercial-grade samples of PEEK (**a**, **b**, and **c**) and PEKK (**a** and **b**) were donated by Cytec Engineered Materials, and research samples of PEK and PEKEKK were kindly provided by ICI plc. Diphenylsulfone and 4,4′-difluorobenzophenone were purchased from Acros. Boron trifluoride diethyl etherate, 1,2-ethanedithiol (EDT), hydroquinone, 4-fluorobenzophenone, and 1,3-propanedithiol (PDT) were obtained from Aldrich. Trifluoroacetic acid was purchased from Apollo. Chloroform, dichloromethane, methanol, potassium carbonate, and sodium carbonate were obtained from Fisher. Potassium and sodium carbonates were dried at 120 °C under vacuum prior to use. All other chemicals and solvents were used as received unless otherwise stated.

Polymer Synthesis and Derivatization. Representative poly(ether ether ketone) syntheses, dithioketalization reactions, and deprotection procedures are described below. Full synthetic details of the other poly(ether ketone)s and poly(ether dithioketal)s prepared in this work are given in the Supporting Information.

Synthesis of PEEK (d, e). Potassium carbonate (0.352 g, 2.55 mmol), sodium carbonate (5.135 g, 48.45 mmol), hydroquinone (5.505 g, 50.00 mmol), 4,4′-difluorobenzophenone (13.092 g, 60.00 mmol) and diphenylsulfone (61.99 g, 284.0 mmol) were placed in a wide-necked cylindrical reaction vessel fitted with a nitrogen gas inlet and outlet and a mechanical stirrer. The ingredients were mixed and flushed with nitrogen for 30 min. The reaction vessel was then placed in a Wood's metal bath preheated to 180 °C. The reaction mixture was held at 180 °C for 1 h with stirring and then raised to 320 °C over an additional 1 h. After 3 h at this temperature, the now viscous solution was poured onto an aluminum tray and left to cool. The resulting solid was ground in an ultracentrifuge mill and extracted with hot methanol to remove the polymerization solvent. The dried powder was extracted with boiling water, filtered, dried, extracted twice with hot methanol, and finally dried in a vacuum oven at 100 °C to yield the poly(ether ether ketone) PEEK-**d** as a white powder (15.049 g, 91% yield), $T_m = 342$ °C.

A similar polycondensation was carried out using potassium carbonate (0.42 g, 3.06 mmol), sodium carbonate (6.16 g, 58.14 mmol), hydroquinone (6.61 g, 60.00 mmol), 4,4′-difluorobenzophenone (13.09 g, 60.00 mmol), and diphenylsulfone (39.40 g, 180.50 mmol). After 3 h at the final polymerization temperature, 4-fluorobenzophenone (2.00 g, 10.0 mmol) was added, and the reaction was continued for an additional 30 min. The polymeric product was isolated as above and then finally extracted by hot chloroform with a Soxhlet apparatus to give poly(ether ether ketone) PEEK-**e** (15.29 g, 88% yield) as an off-white powder, $T_m = 339$ °C. ^{1}H NMR (250 MHz, CDCl$_3$/TFA 6:1, δ): 7.12 (4 H, AA'XX', Ar), 7.21 (4 H, s, Ar), 7.85 (4 H, AA'XX', Ar). ^{13}C NMR (62.5 MHz, CDCl$_3$/TFA 6:1, δ): 117.4, 122.6, 130.9, 133.9, 152.2, 162.5, 200.1. IR (KBr): $\nu_{C=O}$ 1645 cm^{-1}, ν_{C-C} 1592 cm^{-1}.

Synthesis of Poly(ether ether 1,3-dithiolane)s 1a−c. To a stirred solution of PEEK-**a** (1.153 g) in a mixture of dichloromethane (20 mL) and trifluoroacetic acid (5 mL) was added EDT (0.752 g, 7.99 mmol), followed by boron trifluoride diethyl etherate (0.571 g, 4.02 mmol) under an atmosphere of nitrogen. After 18 h at room temperature, the deep-red solution was diluted with dichloromethane (50 mL) and poured in cold methanol (100 mL). Poly(ether ether 1,3-dithiolane) **1a** (1.456 g, 100% yield) was recovered upon filtration as a fine white powder. Poly(ether ether 1,3-dithiolane) **1b** (0.720 g, 99% yield) was synthesized in the same manner from PEEK-**b** (0.576 g), and poly(ether ether 1,3-dithiolane) **1c** (0.711 g, 97% yield) was synthesized from PEEK-**c** (0.576 g). ^{1}H NMR (250 MHz, CDCl$_3$, δ): 3.40 (4 H, s, CH$_2$), 6.88 (4 H, AA'XX', Ar), 6.99 (4 H, s, Ar), 7.53 (4 H, AA'XX', Ar). ^{13}C NMR (62.5 MHz, CDCl$_3$, δ): 40.6, 76.5, 117.6, 121.2, 130.2, 139.3, 152.8, 157.4. IR (KBr): ν_{C-H} 3039 cm^{-1}, ν_{C-H} 2926 cm^{-1}, ν_{C-C} 1603 cm^{-1}, ν_{C-C} 1490 cm^{-1}, ν_{C-O} 1224 cm^{-1}.

Synthesis of Poly(ether ether 1,3-dithiane)s 2a−e. To a stirred solution of PEEK-**a** (0.576 g) in a mixture of dichloromethane (20 mL) and trifluoroacetic acid (2 mL) was added PDT (0.431 g, 3.98 mmol), followed by boron trifluoride diethyl etherate (0.291 g, 2.05 mmol) under an atmosphere of nitrogen. After 3 days at room temperature, the dark-red solution was poured in methanol (100 mL). Poly(ether ether 1,3-dithiane) **2a** (0.705 g, 93% yield) was recovered upon filtration as a white powder. The same procedure was used for the syntheses of **2b** (97% yield), **2c** (96% yield), **2d** (92% yield), and **2e** (100% yield). ^{1}H NMR (250 MHz, CDCl$_3$, δ): 1.99 (2H, br, CH$_2$), 2.76 (4 H, br, S-CH$_2$), 6.91 (4 H, AA'XX', Ar), 7.02 (4 H, s, Ar), 7.59 (4 H, AA'XX', Ar). ^{13}C NMR (62.5 MHz, CDCl$_3$, δ): 29.9, 62.2, 117.9, 121.4, 131.3, 137.3, 152.8, 157.6. IR (KBr): ν_{C-H} 3039 cm^{-1}, ν_{C-H} 2907 cm^{-1}, ν_{C-C} 1602 cm^{-1}, ν_{C-C} 1490 cm^{-1}, ν_{C-O} 1225 cm^{-1}.

Scheme 1. Synthesis of Poly(ether ether 1,3-dithiolane) (1a−1c, *r* = 0) and Poly(ether ether 1,3-dithiane) (2a−2e, *r* = 1) from PEEK by Reaction with EDT and PDT, Respectively

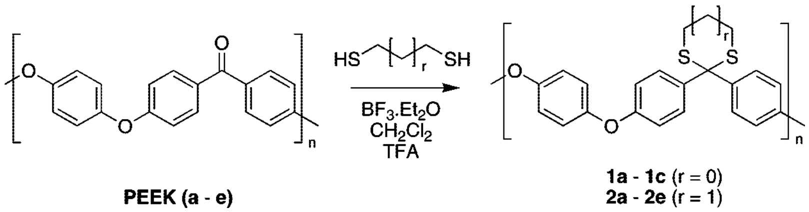


Table 1. Characterization Data for Poly(ether ether 1,3-dithiolane)s 1a−1c (*r* = 0) and Poly(ether ether 1,3-dithiane)s 2a−2e (*r* = 1)

entry	starting polymer	dithiol	product	conversion (%)[a]	η_{inh} (dL g^{-1})[b]	M_n (kDa)[c]	M_w/M_n[c]	T_g (°C)
1	PEEK-**a**	EDT	**1a**	99	0.35	15.8	3.03	157
2	PEEK-**b**	EDT	**1b**	98	0.38	16.2	4.26	160
3	PEEK-**c**	EDT	**1c**	99	0.39	19.4	3.49	182
4	PEEK-**a**	PDT	**2a**	97	0.39	19.2	4.00	179
5	PEEK-**b**	PDT	**2b**	98	0.31	19.3	4.30	182
6	PEEK-**c**	PDT	**2c**	99	0.45	25.2	4.13	185
7	PEEK-**d**	PDT	**2d**	97	0.11	2.4	1.46	141
8	PEEK-**e**	PDT	**2e**	98	0.43	19.8	5.32	186

[a] Calculated from ^{1}H NMR spectra. [b] Measured in chloroform at 25 °C. [c] Measured by GPC in chloroform at 35 °C using a light-scattering detector; M_n and M_w include the oligomeric tail.

Regeneration of PEEK from its Poly(dithioketal) Derivatives. To a solution of **1a** (0.091 g; 0.25 mmol) in chloroform (10 mL) were added rapidly DMSO (0.390 g; 5.00 mmol) and 2-iodomethylpropane (0.460 g; 2.50 mmol). After 2 days at 70 °C, the dark solution was cooled and poured in methanol (100 mL). The precipitate was recovered by filtration and was extensively washed with methanol and finally dried in a vacuum oven at 80 °C. Poly(ether ether ketone) **15** (0.069 g, 96%) was isolated as a gray solid. ^{1}H NMR (250 MHz, CDCl$_3$/TFA 6:1, δ): 7.11 (4 H, AA'XX', Ar), 7.20 (4 H, s, Ar), 7.85 (4 H, AA'XX', Ar). ^{13}C NMR (62.5 MHz, CDCl$_3$/TFA 6:1, δ): 117.4, 122.5, 130.9, 133.9, 152.2, 163.5, 200.0. IR (KBr): $\nu_{C=O}$ 1648 cm^{-1}.

To a solution of **2a** (0.189 g; 0.5 mmol) in chloroform (20 mL) were added rapidly DMSO (0.780 g; 10.00 mmol) and 2-iodo-2-methylpropane (0.930 g; 5.00 mmol). After 3 days at 70 °C, the dark solution was cooled and poured in methanol (100 mL). The brown precipitate was recovered by filtration and extensively washed with methanol and dried in a vacuum oven at 80 °C. Poly(ether ether ketone) **18** (0.135 g, 94%) was isolated as a pale-gray solid. ^{1}H NMR (250 MHz, CDCl$_3$/TFA 6:1, δ): 7.10 (4 H, AA'XX', Ar), 7.19 (4 H, s, Ar), 7.84 (4 H, AA'XX', Ar). ^{13}C NMR (62.5 MHz, CDCl$_3$/TFA 6:1, δ): 117.4, 122.6, 131.0, 133.9, 152.2, 163.5, 200.0. IR (KBr): $\nu_{C=O}$ 1648 cm^{-1}, ν_{C-C} 1599 cm^{-1}.

Results and Discussion

Dithioketalization of Poly(ether ketone)s. When PEEK powder was suspended in a 10:1 (v/v) mixture of dichloromethane and trifluoroacetic acid in the presence of excess EDT or PDT, the polymer particles swelled considerably, but homogeneous solutions were not observed, even after prolonged and vigorous stirring. However, upon the slow addition of boron trifluoride diethyl etherate, the stirred reaction mixture gradually changed over the course of a few hours to a clear, viscous, deep-red solution. Poly(ether dithioketal)s 1 and 2 were recovered in >95% yield from such solutions as a white solid by precipitation in methanol (Scheme 1).

Dithioketalization of semicrystalline poly(ether ketone)s could be achieved only in the presence of trifluoroacetic acid as cosolvent. Therefore, when the reaction of PEEK with EDT was attempted in pure dichloromethane, the starting polymer failed to dissolve, even after 10 days. Also, at least a two-fold excess of dithiol and extended reaction times (ca. 16 h) were required to ensure the complete dithioketalization of the ketone groups. The too rapid addition of the Lewis acid also often led to initial precipitation of the polymer, and it was occasionally observed that this limited the conversion.

Three different samples of PEEK (**a**−**c**) were derivatized by EDT to give the poly(ether ether 1,3-dithiolane)s **1a**, **1b**, and **1c** (Scheme 1 and Table 1, entries 1 to 3). Upon precipitation in methanol, the poly(dithioketal) **1a** was recovered as a fine powder, whereas **1b** and **1c** were isolated as fibrous solids. These novel materials were soluble in dichloromethane, chloroform, and tetrahydrofuran but were insoluble in diethyl ether, acetone, toluene, DMF, or NMP. The same samples of PEEK were also derivatized with PDT to give poly(ether ether 1,3-dithiane)s **2a**, **2b**, and **2c** (Scheme 1 and Table 1, entries 4 to 6). A low-molecular-weight sample of PEEK (**d**, η_{inh} = 0.18 dL g^{-1} in H$_2$SO$_4$) obtained by polycondensation of hydroquinone with a large excess 4,4′-difluorobenzophenone (1.2 mol equiv) in diphenylsulfone was also converted to the poly(ether ether 1,3-dithiane) **2d**. Finally, a very high-molecular-weight sample of PEEK (**e**, η_{inh} = 0.99 dL g^{-1} in H$_2$SO$_4$) was synthesized by polycondensation of hydroquinone and 4,4′-difluorobenzophenone (equimolar ratio), and any remaining phenolic end groups were capped by the addition of 4-fluorobenzophenone to terminate polycondensation. The resulting polymer was converted to the poly(ether ether 1,3-dithiane) **2e**.

The extent of conversion of the carbonyl groups in PEEK was determined by ^{1}H and ^{13}C NMR spectrometry and by FT-IR spectroscopy. Proton NMR spectra for **1a** and **2a** are shown in Figure 1. The structure of poly(ether ether 1,3-dithiolane) **1a** was confirmed by the appearance of a singlet resonance at 3.40 ppm assigned to the methylene protons. The pattern of aromatic resonances is similar to that obtained for the precursor PEEK (recorded in a mixture of CDCl$_3$ and TFA, 6:1 v/v) but the peaks are shifted upfield by ca. 0.2 to 0.3 ppm. An extremely weak signal can just be detected at 7.06 ppm, corresponding to the hydroquinone residue in PEEK, but at less than 1% of the integrated intensity of the corresponding poly(ether ether 1,3-dithiolane) resonance. In the ^{13}C NMR spectrum, no carbonyl resonance could be detected in the 190−200 ppm region, correlating with the appearance of peaks at 76.5 ppm (quaternary carbon) and 40.6 ppm, (methylene carbon). Finally, the absence of a peak at around 1650 cm^{-1} in the IR spectrum of **1a** confirmed essentially complete conversion of carbonyl groups.

In the case of polymer **2a**, the aromatic region of the ^{1}H NMR spectrum was very similar to that of **1a**, but a weak doublet

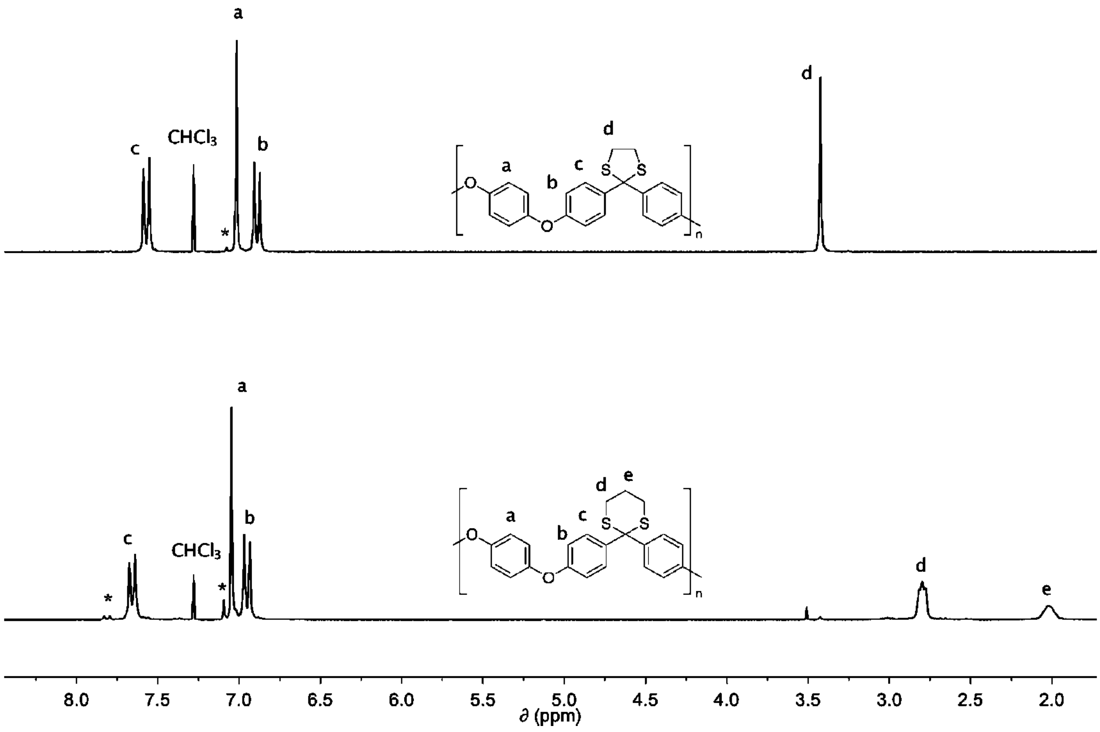
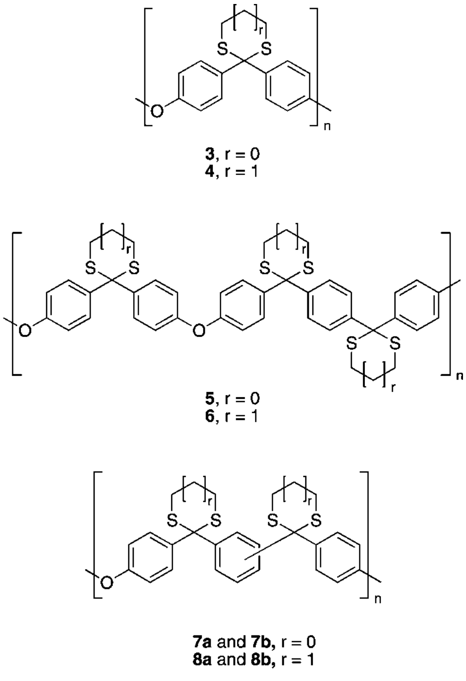


Figure 1. ^1H NMR spectra ($CDCl_3$)of polymers **1a** (upper trace) and **2a** (lower trace). The singlet and doublet resonances marked with a star correspond to unreacted [ether ether ketone] repeat units.

resonance at 7.82 ppm and a singlet at 7.07 ppm were also present, attributable to unreacted, ketone-containing monomer residues. Integration of the spectrum indicated that such residues represented less than 3 mol % of the total polymer. Broad multiplets attributed to the methylene groups at 1.99 and 2.76 ppm integrated as 2 and 4 protons, respectively, per repeat unit. The ^{13}C NMR spectrum of **2a** showed resonances at 24.8, 29.9, and 62.2 ppm corresponding to the methylene and quaternary carbons, respectively. Corresponding NMR analyses of polymers **2b**−**2e** indicated that these were chemically identical to **2a** and again contained less than 3% of residual carbonyl groups. Spectroscopic data for **1b** and **1c** were very similar to those described for **1a**, and conversions were again only marginally less than quantitative, as determined by ^1H NMR analysis (Table 1).

Analogous dithioketalizations of PEK, PEKEKK, and two different compositions of the copolymer PEKK (Chart 1) afforded the poly(ether 1,3-dithiolane)s **3**, **5**, **7a**, and **7b** and the poly(ether 1,3-dithiane)s **4**, **6**, **8a**, and **8b** (Chart 2). These materials were obtained in high yield under conditions identical to those described above for dithioketalization of PEEK. The derivatives of PEKK (**7a**, **7b**, **8a**, and **8b**) were readily soluble in chloroform but only partially soluble in tetrahydrofuran. Spectroscopic analyses of these poly(dithioketal)s showed essentially the same features as the data for **1** and **2**. Conversions, estimated by ^1H NMR spectroscopy, were >97% (Table 2). The methylene resonances were again sharp singlets for the poly(1,3-dithiolane)s, but broad, poorly resolved multiplets for poly(1,3-dithiane)s.

Chart 2. 1,3-Dithiolane (*r* = 0) and 1,3-Dithiane (*r* = 1) Derivatives of PEK, PEKEKK, and PEKK



3, r = 0
4, r = 1

5, r = 0
6, r = 1

7a and **7b**, r = 0
8a and **8b**, r = 1

Dithioketalization of Amorphous Poly(ether ketone)s. A series of highly soluble, amorphous poly(aryl ether ether ketone)s containing the isopropylidene or hexafluoroisopropylidene moiety were synthesized by nucleophilic polycondensation in *N*-methylpyrrolidone in the presence of potassium carbonate. Polymer **9** was prepared from 4,4′-isopropylidenediphenol and 4,4′-difluorobenzophenone, and its structure was confirmed by comparison to previous data.[25] As a result of the presence of the isopropylidene unit, polymer **9** is amorphous ($T_g = 143$ °C). It proved to be readily soluble in tetrahydrofuran, chloroform, and dichloromethane, but had only a rather low degree of polymerization, as indicated by GPC (Table 3, Entry 1). A related poly(aryl ether ketone) **10** ($T_g = 111$ °C) was obtained by polycondensation of 4,4′-(hexafluoroisopropylidene)diphenol with 4,4′-difluorobenzophenone.[26,27] The resulting amorphous polymer was highly soluble in organic solvents and had a much higher molecular weight than **9** (Table 3, entry 2).

As shown in Scheme 2, poly(ether ketone)s **9** and **10** were readily converted to their 1,3-dithiolane derivatives **11** and **13** by reaction with excess EDT in the presence of boron trifluoride.

Table 2. Properties of the Dithioketal Derivatives of PEK, PEKEKK, and PEKK

entry	starting polymer	dithiol	product	conversion (%)[a]	η_{inh} (dL g^{-1})[b]	M_n (kDa)[c]	M_w/M_n[c]	T_g (°C)
1	PEK	EDT	**3**	99	0.31	18.9	3.26	184
2	PEK	PDT	**4**	98	0.37	24.4	4.11	212
3	PEKEKK	EDT	**5**	>99	0.24	26.3	2.36	193
4	PEKEKK	PDT	**6**	98	0.35	28.6	3.09	228
5	PEKK-a	EDT	**7a**	>99	0.17	14.9	2.11	171
6	PEKK-b	EDT	**7b**	>99	0.19	19.0	2.23	181
7	PEKK-a	PDT	**8a**	>99	0.27	18.7	3.73	205
8	PEKK-b	PDT	**8b**	98	0.27	37.4	3.85	215

[a] Calculated from ^{1}H NMR spectra. [b] Measured in chloroform at 25 °C. [c] Measured by GPC in chloroform at 35 °C using a light-scattering detector; M_n and M_w include the oligomeric tail.

Table 3. Properties of Amorphous Poly(ether ether ketone)s 9 and 10 and Their Dithioketal Analogues 11, 12, 13, 14

entry	polymer	M_n (kDa)[a]	M_w/M_n[a]	T_g (°C)
1	**9**	3.90	2.02	143
2	**10**	18.1	3.73	111
3	**11**	5.60	1.86	145
4	**12**	5.30	1.89	160
5	**13**	24.8	3.66	164
8	**14**	27.7	3.06	180

[a] Measured by GPC in chloroform at 35 °C using a light-scattering detector.

Unlike the semicrystalline poly(ether ketone)s described earlier in this study, conversion of **9** and **10** did not require trifluoroacetic acid as cosolvent because the starting polymers were freely soluble in dichloromethane. Similarly, the reaction of **9** and **10** with PDT afforded the poly(ether ether 1,3-dithiane)s **12** and **14**. The poly(dithioketal)s **11**, **12**, **13**, and **14** were recovered in excellent yield after precipitation in methanol.

Dithioketalisation of a Macrocyclic Model Compound. All of the evidence from polymer dithioketalization reactions suggested that they were extremely clean, but to test this conclusion, a model study was carried out using the cyclic dimer of PEEK (**15**).[28] Reaction with ethane-1,2-dithiol under the same conditions as those used for the linear polymer indeed afforded the tricyclic bis-dithioketal (**16**) in 98% isolated yield (Scheme 3). The ^{1}H NMR spectrum of **16** showed no evidence of any other compound. Allowing for mechanical losses on workup, this study confirms that the dithioketalisation of aromatic ether ketones, under the conditions established here, can be quantitative and therefore free of byproduct or degradation reactions.

Properties of Poly(ether dithioketal)s. Poly(ether ether dithioketal)s **1a** and **2a** were stable up to ca. 280 °C under nitrogen, as determined by TGA (Figure 2). Further heating resulted in a sharp downward step in the weight-loss curve (21% for **1a**; 24% for **2a**), and analysis of these polymers by DSC revealed the onset at 280 °C of a correspondingly strong endotherm that was not present in subsequent scans. It seems likely that this process involves specific degradation and loss of the dithioketal moiety, especially because the weight loss closely correlates with the mass of the protecting group. At higher temperatures, there was little further change until ca. 400 °C, when progressive loss of weight began. Decomposition of **1a** was also isothermally analyzed at 300 °C for 30 min under nitrogen, during which time volatile products were evolved. The resulting material was a tough black solid, which we assume to be cross-linked because it proved to be noncrystalline by DSC but insoluble in acetone, chloroform, and chloroform/trifluoroacetic acid mixtures.

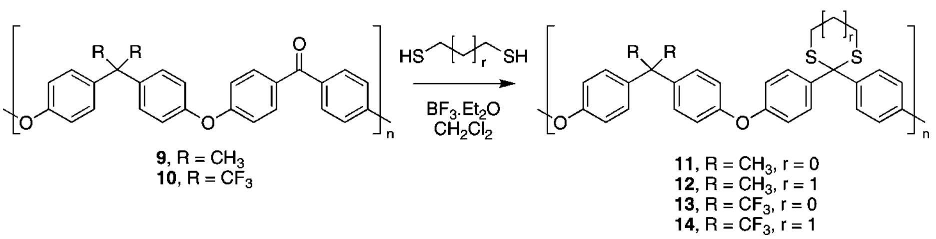
All of the poly(dithioketal)s synthesized in this work were found to be amorphous, as shown by both DSC (glass-transition temperatures are given in Tables 1, 2, and 3) and X-ray diffraction. The T_g values of poly(ether dithioketal)s were systematically greater than those for their parent polyketones, and 1,3-dithiolane polymers showed lower glass-transition temperatures than the corresponding poly(1,3-dithiane)s. Conversion of the carbonyl groups in aromatic poly (ether ketone)s to dithioketal units thus offers a completely general method for inhibiting crystallization. The steric bulk of the cyclic dithioketal group will clearly inhibit polymer chain-packing, and the changes in bond angle and inter-ring torsion angles at the bridging carbon will make it more difficult for the polymer chain to adopt the linear, "zigzag" conformation that allows the parent polyketones to crystallize so readily.[29]

Molecular Weight Distributions. To validate the idea that molecular weight distributions for insoluble, semicrystalline polyketones might be accessible from GPC data for their soluble dithioketal derivatives, the molecular weight distributions of the amorphous poly(ether ketone)s **9** and **10** were compared directly with those of their dithioketal derivatives **11**, **12**, **13**, and **14**. The solubility conferred by the presence of isopropylidene or hexafluoroisopropylidene units allowed both derivatized and underivatized materials to be analyzed by GPC in chloroform under identical conditions. As shown in Figure 3, the shapes of the GPC traces of **9**, **11**, and **12** were essentially identical, but the relative intensity of the oligomer peak was lower for **11** and **12** than for the parent poly(aryl ether ketone) **9**. Integration of the different peaks showed that **9** contained ca. 4.1% of low-molecular-weight oligomers, but the levels of oligomers in **11** and **12** were approximately 2.6 and 2.9%. During the dithioketalization process, derivatized oligomeric (probably cyclic)[30] material would be retained in solution more readily than the polymer at the precipitation stage, so accounting for the lower oligomer content in the final product. GPC traces recorded with a light-scattering detector revealed no additional high-molecular-weight fraction in the derivatized polymers, confirming that dithioketalization does not lead to any significant degree of cross-linking.

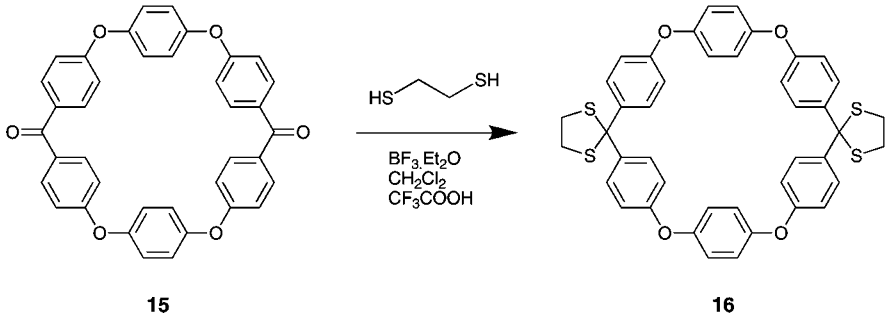
Upon conversion of poly(ether ketone) **9** to poly(ether ether 1,3-dithiolane) **11**, the molar mass of the repeat unit increases by a factor of 1.19 (from 406.5 for **9** to 482.7 for **11**). On this basis, values of $M_n = 4700$ and $M_w = 8700$ can be calculated for the parent polyketone **9** on the basis of the GPC data for its derivative **11** (Table 3). Similarly, conversion of **9** to the 1,3-dithiane polymer **12** increases the mass per repeat unit by a factor of 1.22, giving calculated MW values for **9** of $M_n = 4300$ and $M_w = 8500$. The actual GPC values of M_n and M_w found for the parent polymer are 3900 and 7900, respectively. Whereas these values are in reasonable agreement with the values calculated from derivatized polymer data, they suggest that the derivatization technique results in a slight overestimation of polyketone molecular weight.

Similar results were obtained for the hexafluoroisopropylidene-based polyketone **10** and its derivatives **13** and **14**. Oligomeric material represented ca. 10.2% by weight of **10**, but only 7.8% for **13** and 7.9% for **14** (Figure 4). Such high levels of oligomers accounted for the high PDI of these materials. The molecular weight of **10** could be estimated from the molecular weights of **13** and **14** (Table 3) to yield $M_n =$ 21 600 and $M_w =$ 78 900 and $M_n =$ 23 500 and $M_w =$ 72 100 respectively. The corresponding values for **10** measured directly

Scheme 2. Synthesis of Poly(ether ether 1,3-dithiolane) ($r = 0$) and Poly(ether ether 1,3-dithiane) ($r = 1$) from the Amorphous Polyketones 9 and 10



Scheme 3. Dithioketalization of the Macrocyclic Dimer of PEEK



were $M_n = 18\,100$ and $M_w = 67\,500$. From inspection of Figure 4, it is clear that the slight discrepancies in M_n and M_w for **10**, calculated from the poly(dithioketal) data, are mainly due to loss of oligomer content on dithioketalization. Also, the hydrodynamic volume occupied by a polyketone will certainly be different from that of the corresponding dithioketal derivatives as a result of the different bridging-angle and rigidity of the carbonyl or dithioketal unit.

As shown in Figure 5, there is a good correlation between the inherent viscosities of the poly(1,3-dithiane)s **2a**−**2e** in chloroform and the inherent viscosities of the corresponding samples of PEEK (**a**−**e**), measured in concentrated sulfuric acid. These results are a further indication that the relative order of molecular weights is maintained during dithioketalization of PEEK and that the formation of poly(dithioketal)s takes place without side reactions.

Size-exclusion chromatography with light-scattering detection is a powerful tool for revealing the presence of low concentrations of high-molecular-weight fractions that would go unnoticed if only a refractive index detector were used. This is because the response observed with a light-scattering detector is proportional to the concentration multiplied by the molecular weight, whereas with a refractive index detector, the response is directly proportional to the concentration of polymer. Therefore, although light-scattering can underestimate the importance of low-molecular-weight oligomers, this technique will reveal the presence of even a small fraction of very high-molecular-weight chains,[31] which can be of crucial importance in determining both the rheological and toughness characteristics of linear polymers. These characteristics are of extreme importance in terms of processability and materials performance, especially in the context of long-fiber composites where a key requirement is to achieve high levels of toughness in the matrix polymer without its melt viscosity being so great that fiber penetration and flow during prepregging and fabrication is compromised.

In the present work, Figure 6 shows that the GPC traces for the different PEEK samples **2a**, **2b**, and **2c** are essentially monomodal, as judged with RI detection. However, the light-scattering detector (Figure 7) showed bimodal distributions for **2b** and **2c**, with high-molecular-weight fractions that may result from branching, chain extension, or both caused by side reactions during polymer synthesis.[2b] The high-molecular-weight

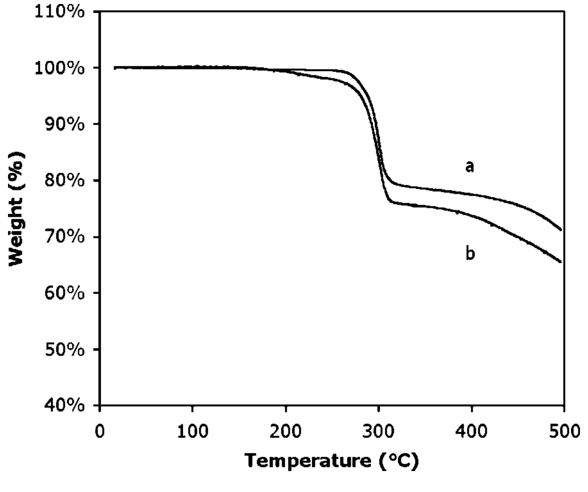


Figure 2. Thermogravimetric analyses of (a) poly(ether ether 1,3-dithiolane) **1a** and (b) poly(ether ether 1,3-dithiane) **2a**.

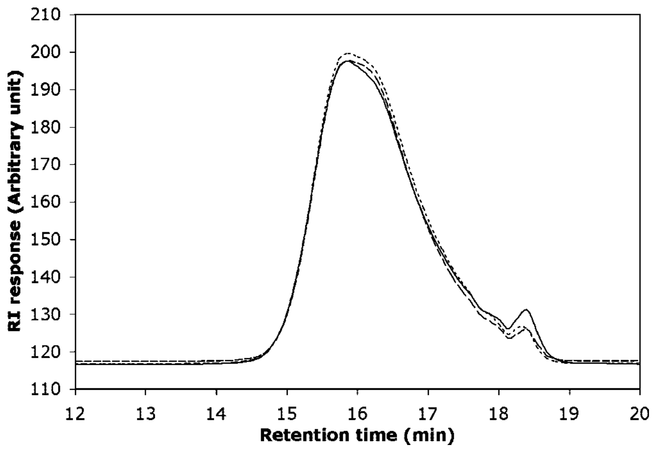


Figure 3. GPC traces of **9** (—), **11** (---) and **12** (•••) in chloroform (RI detection).

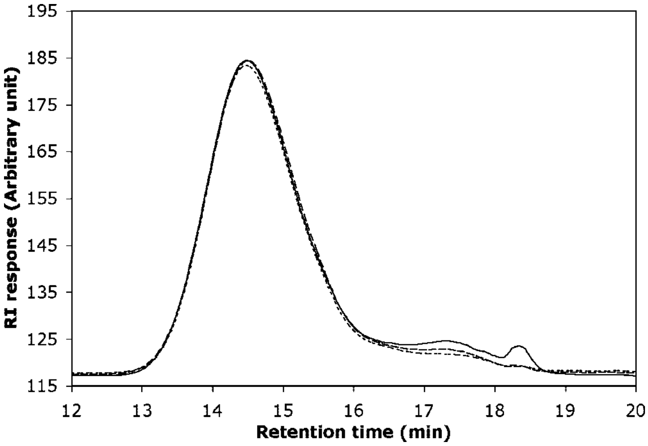


Figure 4. GPC traces of **10** (—), **13** (---) and **14** (•••) in chloroform (RI detection).

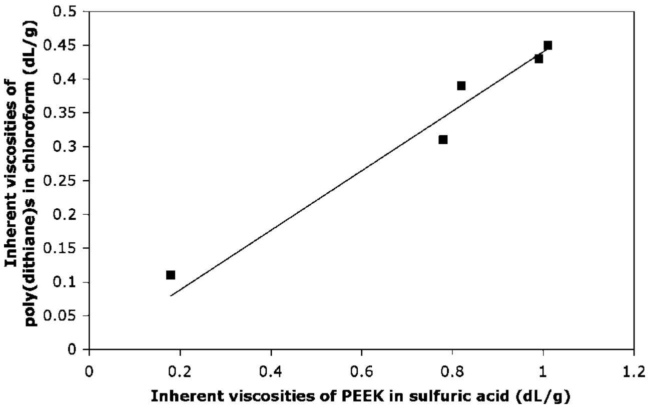


Figure 5. Inherent viscosities of poly(ether ether 1,3-dithiane)s **2a**–**2e**, measured in chloroform, plotted against inherent viscosities of the corresponding PEEK sample recorded in concentrated sulfuric acid.

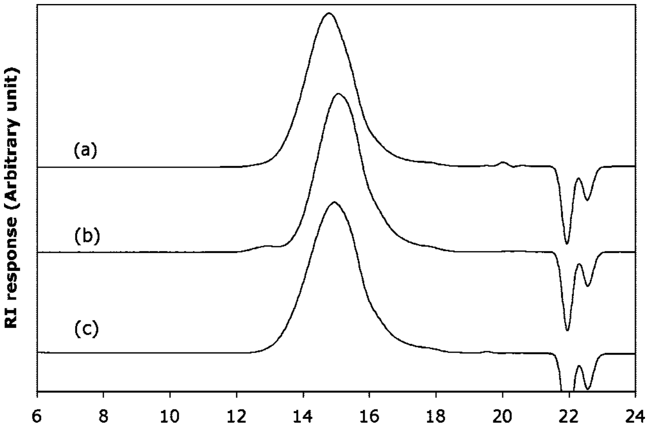


Figure 6. Refractive index GPC traces of the poly(1,3-dithiane) derivatives (a) **2a**, (b) **2b**, and (c) **2c**.

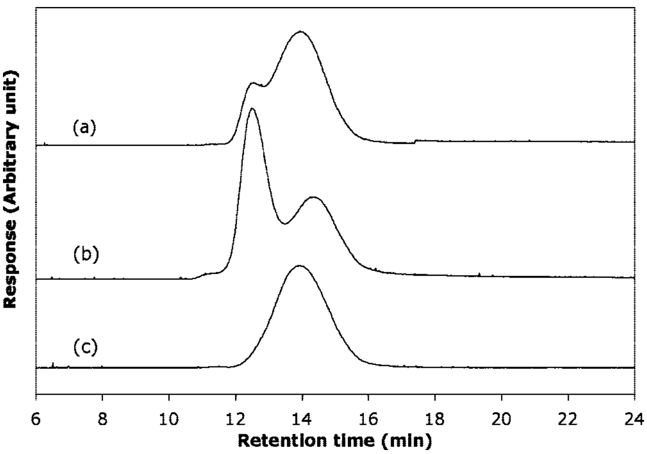


Figure 7. Light-scattering GPC traces of the poly(1,3-dithiane) derivatives (a) **2a**, (b) **2b**, and (c) **2c**.

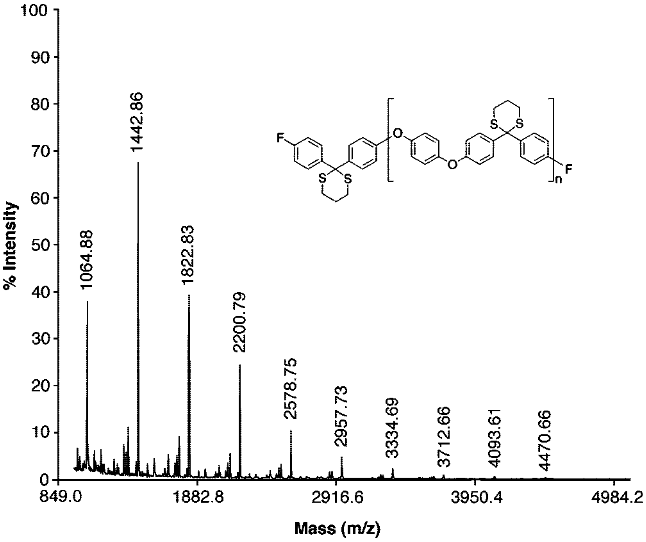


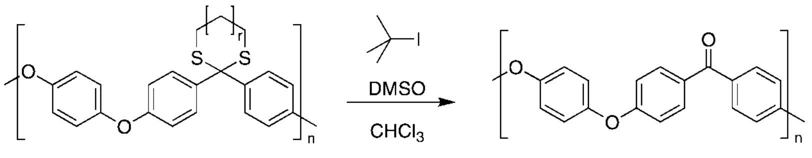
Figure 8. MALDI-TOF mass spectrum (reflectron mode) of **2d**. The inset shows the structure corresponding to the main series of peaks ($n = 2$ to 11, no cationizing agent).

fractions were found to have peak molecular weights M_p of ca. 642 kDa for **2b** and 404 kDa for **2c**, values which are some 10 times higher than those of the main fraction in each case. A high molecular weight fraction was not, however, observed for sample **2a**. Completely analogous traces are observed for **1a**–**c** and **2a**–**c**, confirming that this behavior is not an artifact of the dithioketalization process. Instead, it can be concluded that these genuinely reflect the presence of very high molar mass fractions in PEEK-**b** and PEEK-**c**. Also, this phenomenon was not exclusive to samples derived from PEEK because the dithioketal derivatives **5** and **6** (from PEKEKK) also possessed high-molecular-weight fractions that were not visible by the refractive index detector alone (e.g., $M_p = 800$ kDa for **5**).

The factor of mass increase in the repeat unit of PEEK upon conversion to **1** is 1.26. Therefore, the molecular weight values for **1a** (Table 1) would indicate that PEEK-**a** has $M_n = 12\,500$ and $M_w = 37\,900$. These values are in the same range as those found by Daoust and coworkers using the sulfonation technique.[17] A similar calculation applied to poly(ether ether 1,3-dithiane) **2** (where the mass-increase factor is 1.32) leads to $M_n = 14\,600$ and $M_w = 58\,600$ for PEEK-**a**. Clearly, this method can be applied to PEK, PEKEKK, or PEKK derivatives to obtain information very easily on the molecular weight of these commercially significant polymers (Table 2), and indeed it seems likely that this new technique can be extended to essentially any aromatic poly(ether ketone).

The analysis of poly(ether ether dithane) **2d** by MALDI-TOF mass spectroscopy confirmed that this material was primarily composed of low-molecular-weight oligomers ranging from the dimer up to the decamer (Figure 8). The polymer is end-capped at both chain ends by fluorophenyl groups as a result of the large excess of 4,4′-difluorobenzophenone used during the polymerization of the parent ketone material. This experiment again confirms that the dithioketalization of PEEK is complete

Scheme 4. Deprotection of Poly(ether ether 1,3-dithiolane) (1a, $r = 0$) and Poly(ether ether 1,3-dithiane) (2a, $r = 1$)



1a, r = 0
2a, r = 1

17
18

and free from cross-linking or chain degradation and that the molecular weight calculated by GPC is representative of the materials. There are a few examples of chain-end analysis by MALDI-TOF MS of poly(ether ketone)s, supporting the exclusive formation of cyclic polymers during step-growth polymerization under strict kinetic conditions.[32] However, these studies were limited to amorphous, soluble polyketones, and the indirect characterization of dithioketal derivatives might extend the scope of the materials examined.

Regeneration of PEEK from Poly(dithioketals). Cyclic dithioketals are often used as reversible protecting groups during multistep reactions in organic synthesis, and there is a wide range of methods available for their conversion to aldehydes or ketones,[20] including oxidative hydrolysis with hydrochloric acid and hydrogen peroxide.[33] However, our attempts to deprotect the poly(ether ether 1,3-dithiolane) **1a** using the latter procedure proved to be completely unsuccessful. Reactions with 3-chloroperbenzoic acid and trifluoroacetic acid in dichloromethane[34] were somewhat more successful but still led to only partial deprotection. Quantitative conversion of poly(ether ether 1,3-dithiolane) **1a** back to PEEK (sample **17**) was finally achieved by prolonged reaction with a mixture of 2-iodo-2-methylpropane and dimethyl sulfoxide at high temperature.[35] To ensure that the polymer would be solubilized, at least during the initial stages of the reaction, chloroform was used as a cosolvent (Scheme 4). After 3 days at 70 °C, a pale-gray powder was recovered by precipitation in methanol and filtration. Excess reagents were removed by extensive extraction of the polymeric product with hot methanol. Polymer **2a** was also successfully deprotected, under identical conditions, to afford the poly(ether ether ketone) sample **18**. Complete regeneration of PEEK was confirmed by ^{1}H and ^{13}C NMR spectroscopy carried out in a mixture of deuterated chloroform and trifluoroacetic acid because **17** and **18** were insoluble in chloroform alone. Also, a strong peak at 1650 cm^{-1} in the IR spectrum confirmed that the carbonyl group had been regenerated. No glass transition was detected for **17** during the first DSC scan, suggesting an unusually high level of crystallinity, and, consistent with this, its melting point was also slightly higher than that typically observed for PEEK (342 °C, c.f. 334 °C). However, the inherent viscosities of PEEK-**a** and **17** were essentially identical (0.82 and 0.83 dl g-1, respectively), suggesting that the differences in thermal behavior arise from differences in degree of crystallinity and in crystallite perfection, specifically in a greater lamellar thickness for the regenerated polymer **17**. Polymer **18** possessed both T_g (onset at 144 °C) and T_m (peak temperature 334 °C) identical to the starting sample of PEEK.

As a final test of the reversibility of dithioketalization in aromatic poly(etherketones), GPC data for the regenerated material **18** and its parent polymer PEEK-**a** were obtained at high temperature in phenol/trichlorobenzene as solvent. The two chromatograms and molecular weight values derived from these are shown in Figure 9, providing conclusive evidence of the quantitative reversibility of dithioketal formation in crystalline aromatic poly(ether ketone)s.

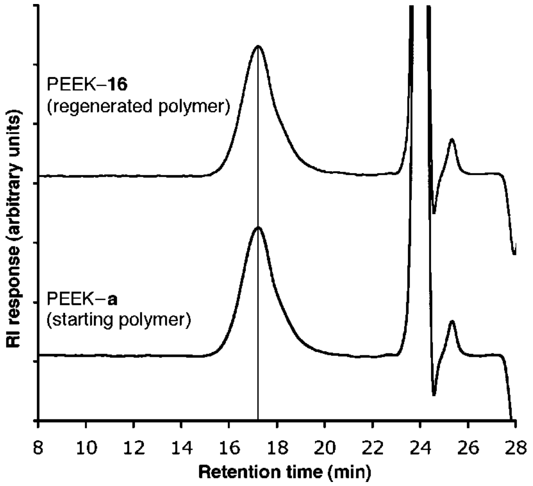


Figure 9. GPC analyses of PEEK (**1**) before dithioketalization (lower trace, M_w = 78 000; M_n = 31 000) and after dithioketalization/deprotection (upper trace M_w = 78 000; M_n = 31 000) (phenol/1,2,4-trichlorobenzene as eluent at 115 °C; RI detection; polystyrenes as standards).

Conclusions

Dithoketalization provides a completely general approach to the derivatization of aromatic poly(ether ketone)s. The resulting poly(dithioketals) are readily soluble in conventional organic solvents such as chloroform or (in some cases) THF and hence are easily characterized by GPC with both refractive index and light-scattering detection. The latter technique can reveal high molar mass fractions that are not detected by RI methods and that can be crucial in determining polymer melt-flow characteristics. Dithioketalization is free of degradative or cross-linking side reactions, and although the derivatized polymers are stable and easily handled, they can be quantitatively deprotected to regenerate the starting poly(etherketone)s without loss of molecular weight.

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Supporting Information Available: Synthetic details and characterization data for poly(ether-dithioketal)s **3**, **4**, **5**, **6**, **7**, and **8**, poly(ether-ketone)s **9** and **10**, poly(ether-dithioketal)s **11**, **12**, **13**, and **14**, and the tricyclic bis(thioketal) **16**. This information is available free of charge via the Internet at http://pubs.acs.org.

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