Dithioacetalisation of PEEK: a general technique for the solubilisation and characterisation of semi-crystalline aromatic polyketones†

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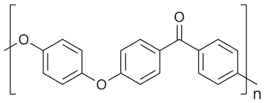
The family of semi-crystalline, aromatic, high-temperature thermoplastics known as poly(ether-ketone)s are insoluble in conventional organic solvents, but undergo completely general and quantitatively reversible reactions with alkanedithiols in strong acid media, to give soluble poly(dithioacetal)s, which are readily characterisable by GPC and light scattering techniques.

Aromatic poly(ether-ketone)s, such as PEEK (**1**), PEK (**2**) and PEKEKK (**3**), are important engineering polymers for applications requiring durability under extreme operating conditions.[1] At the molecular level, they possess inherent thermo-oxidative and hydrolytic stability, and their semi-crystalline morphologies (with melting points typically in the range 340–380 °C) afford excellent thermomechanical stability and resistance to solvent attack.[2]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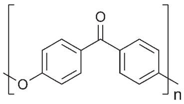
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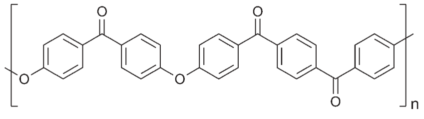
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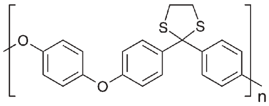
Such materials are completely insoluble in conventional organic solvents at temperatures below *ca.* 300 °C. At ambient temperatures they can be dissolved only in strong acid–solvent mixtures, such as trifluoroacetic acid–dichloromethane, which protonate the carbonyl groups.[3] Although this degree of solvent-resistance is extremely valuable for many industrial applications of poly(ether-ketone)s, it can make their detailed characterisation by techniques such as NMR spectroscopy, gel permeation chromatography (GPC) or light scattering very difficult. For example, currently-optimised conditions for GPC analysis of PEEK involve column temperatures well above 100 °C and a mixture of phenol and trichlorobenzene as eluent.[4]

A possible solution to the difficulties of characterisation would be to convert the crystalline poly(ether-ketone) (without degradation, cross-linking or chain-extension) to a more soluble, non-crystalline derivative. We have, for example, shown that reduction of aromatic poly(ether-ketone)s with alkyl silanes in strong acid solution leads to copolymers containing both ketone and methylene linkages. However, solubility is achievable here in only a very narrow copolymer composition range, as aromatic polyketones and polymethylenes both adopt crystalline morphologies.[5] Since the extent of reduction is often difficult to control, this solubilisation method is of only limited application. Sulfonation of PEEK in 98% sulfuric acid has also been used to produce amorphous and therefore more soluble ionomers for GPC analysis,[6] but again it is difficult to control the extent of reaction, and this approach is limited to poly(ether-ketone)s containing readily sulfonated sub-units (*e.g.* hydroquinone or 4,4′-biphenol residues); polymers such as PEK (**2**) and PEKEKK (**3**) are inert to concentrated sulfuric acid.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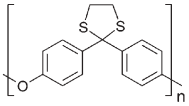
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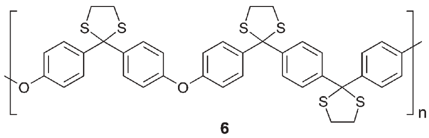
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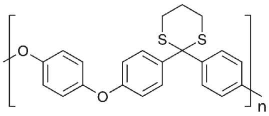
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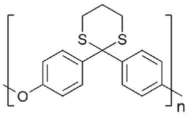
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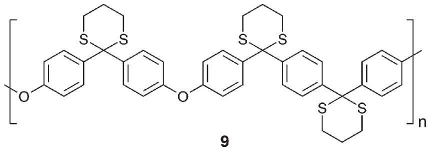
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In this communication we report that *dithioacetalisation* (well-established as a protection strategy for carbonyl groups in small molecules)[7] provides an extremely simple, quantitative, reversible and non-degradative approach to the solubilisation and characterisation of crystalline aromatic polyketones. Thus, reaction of excess ethane-1,2-dithiol with a commercial sample of high-MW PEEK (T_g = 144 °C, T_m = 334 °C, η_{inh} = 0.82 dL g^{-1}) in a mixture of trifluoroacetic acid, boron trifluoride and dichloromethane gave, after 18 h at room temperature, a quantitative yield of the poly(ether-dithioacetal) **4**. This novel polymer proved readily soluble in THF and in chloroform, and analysis by ^{1}H and ^{13}C NMR spectroscopy confirmed that essentially quantitative dithioacetalisation of the carbonyl groups had been achieved.

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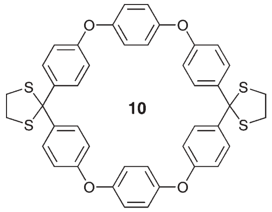
Analogous reactions were achieved for polyketones **2** and **3**, affording poly(thioacetal)s **5** and **6**. The three commercial poly(ether-ketone)s (**1**–**3**) were also quantitatively derivatisable by propane-1,3-dithiol, yielding polymers **7**, **8** and **9** respectively.

Model reactions on the cyclic dimer[8] and trimer[9] of PEEK gave the tricyclic and tetracyclic poly(dithioacetal)s **10** and **12**, and **11** and **13** respectively in high yields. The single crystal X-ray structure of macrocycle **10** is shown in Fig. 1, confirming the tricyclic dithioacetal formulation.‡ No by-products from ring-opening side-reactions of the ether-ketone macrocycles, or from ring–ring linking reactions, could be detected in reactions of these cyclic systems, strongly suggesting that dithioacetalisation should not affect the degree of polymerisation of analogous poly(ether-ketone)s.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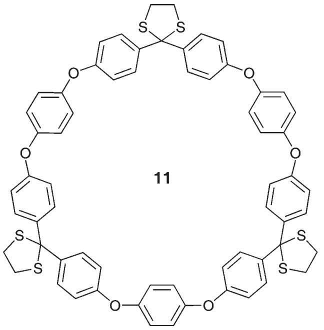
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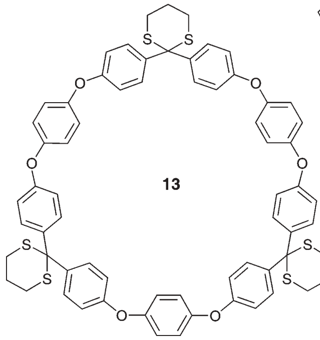
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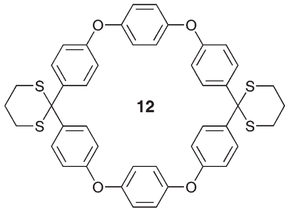
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However, to confirm that dithioacetalisation does indeed offer a genuinely non-degradative approach to the solubilisation of poly(ether-ketone)s, a commercial sample of PEEK (**1**) was first analysed by high-temperature GPC (phenol–1,2,4-trichlorobenzene, 115 °C), then derivatised quantitatively with propane-1,3-dithiol, and finally deprotected by refluxing in chloroform with a mixture of 2-iodo-2-methylpropane and DMSO.[10] The regenerated sample of PEEK (99% recovery, $T_g = 143$ °C, $T_m = 334$ °C, $\eta_{inh} = 0.83$ dL g^{-1}) was then re-analysed by GPC under the same conditions as above. Chromatograms of the starting and regenerated samples of PEEK (**1**) are shown in Fig. 2, indicating that no significant change occurs in the MW distribution of this polyketone as a result of dithioacetalisation.

The amorphous character and consequent solubility of the linear poly(dithioacetals) **4**–**9** enabled them to be readily analysed by GPC at ambient temperature in conventional solvents such as chloroform and THF, using both refractive index (RI) and light scattering (LS) detection. The importance of light scattering detection in characterising materials of this type is shown in Fig. 3, where two samples of poly(dithioacetal) **4** that appear almost identical under RI detection are found to differ very substantially under LS detection, by virtue of the enhanced sensitivity of light scattering to molecules of high molar mass. The significance of this result is that even trace amounts of very high MW material can markedly affect the flow-characteristics of molten polymers, so that two samples that appear identical from melt-viscosity measurements can in fact have very different MW distributions and, as a consequence, entirely different mechanical properties. This is especially significant for thermoplastics with MWs near the tough–brittle transition—as is generally the case with matrix polymers for long-fibre composite materials where a compromise is always necessary between toughness (increasing with MW) and processability (decreasing with increasing MW as a result of increasing melt-viscosity). The dithioacetalisation–GPC–light scattering technique reported here, now enables MW distributions of crystalline, aromatic poly(ether-ketone)s to be analysed at the same level of detail as more conventionally-soluble amorphous polymers. The new methodology thus represents a key advance in the development and understanding of high-toughness thermoplastic matrices for aerospace and automotive composites.

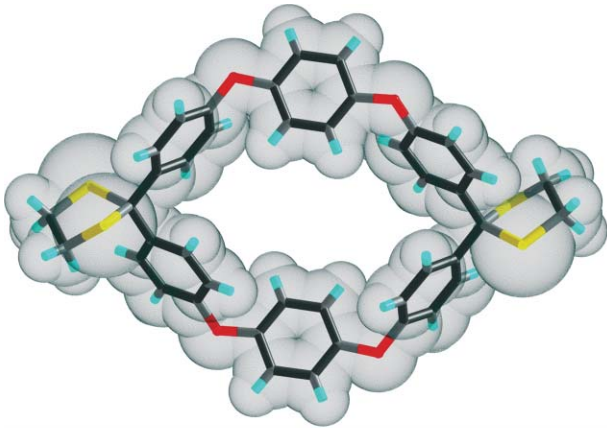

Fig. 1 Single crystal X-ray structure of the tricyclic bis(dithioacetal) **10**, derived from the cyclic dimer of PEEK. The molecule lies about a crystallographic inversion centre.

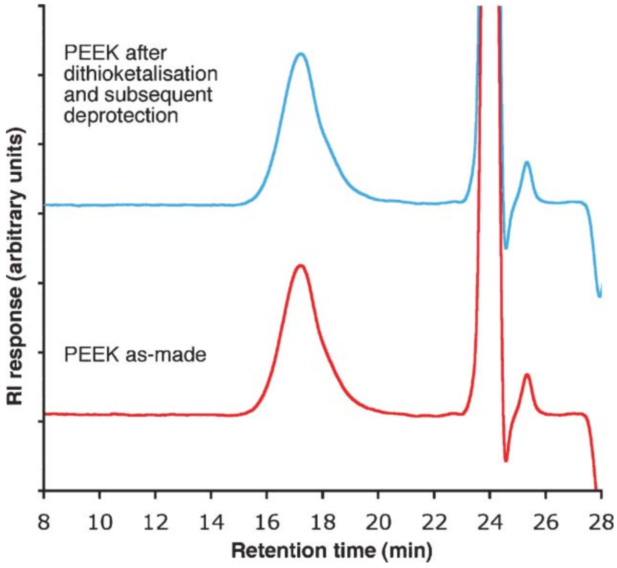

Fig. 2 GPC analyses of PEEK (**1**) before dithioacetalisation (red line, M_w = 78 000; M_n = 31 000), and after the dithioacetalisation/deprotection (blue line M_w = 78 000; M_n = 31 000) (phenol–1,2,4-trichlorobenzene as eluent at 115 °C; RI detection; polystyrenes as standards).

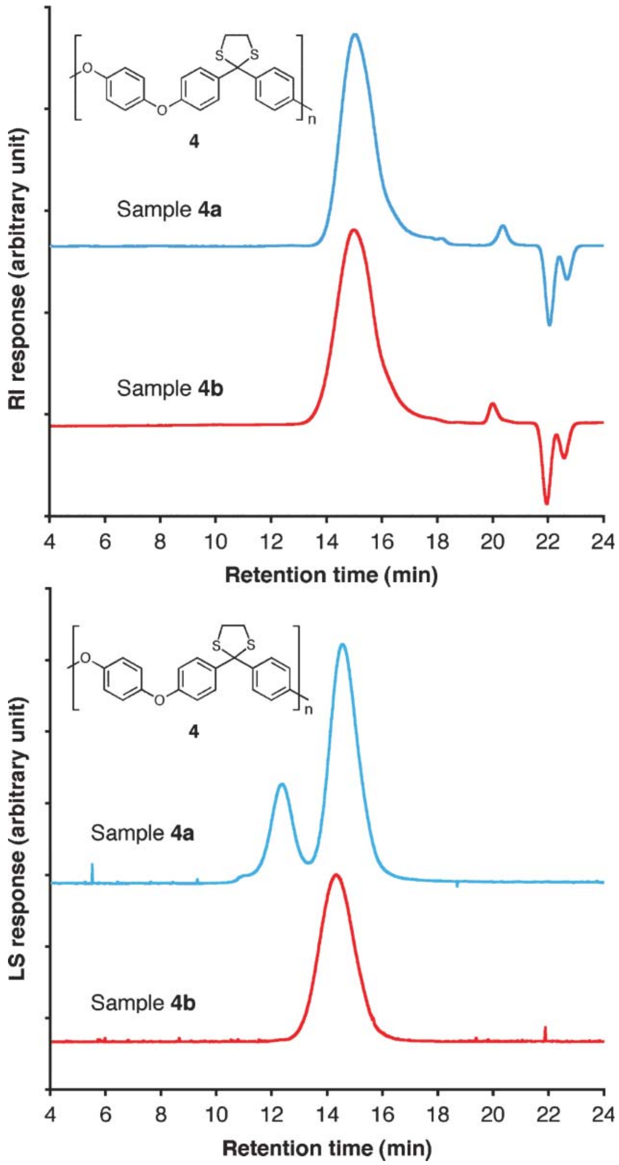

Fig. 3 GPC chromatograms for two samples of the PEEK-derived poly(dithioacetal) **4**, using (a) refractive index detection (above) or (b) light scattering detection (below). A high molar mass component, which is present in polymer **4a** but virtually absent from polymer **4b**, is clearly identified by the new dithioacetalisation–GPC–LS technique.

In conclusion, we have shown that dithioacetalisation offers a simple but completely general and non-degradative method for the solubilisation of semi-crystalline aromatic poly(ether-ketone)s, a class of high temperature engineering thermoplastics that is growing rapidly in importance but whose insolubility in conventional solvents has, until now, been a serious obstacle to their detailed characterisation at the molecular level.

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Notes and references

‡ *Crystal data* for **10**: crystals from dichloromethane–methanol. $C_{42}H_{32}O_4S_2$, M = 728.92, orthorhombic, a = 32.218(6), b = 11.257(2), c = 8.895(2) Å, U = 3246.5(10) Å^3, T = 150 K, space group *Pbca*, Z = 4, μ(Mo-Kα) = 0.32 cm^{-1}, 5074 independent reflections measured, R_1 = 0.0931, wR_2 = 0.2383 for 2168 reflections with $I > 2\sigma(I)$. CCDC 649151. For full crystallographic data in CIF format see DOI: 10.1039/b708116b

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