Photochemical recycling of polyarylene sulfide

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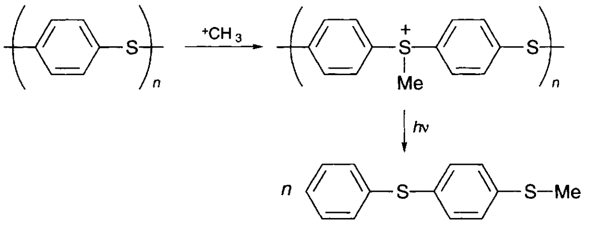
The selective degradation of polyarylene sulfide *via* soluble polysulfonium salts was employed to give the monomer.

High performance engineering plastics possess characteristics such as thermal and chemical stability in use; however, such properties also make them difficult to dispose of as waste. This difficulty can be overcome by making use of a soluble photoactive precursor system. Polyarylene sulfide, noted as the sixth general-purpose engineering plastic,[1,2] is a crystalline polymer and is not soluble in any solvent,[3] which makes its decomposition difficult. However, given the favourable valence exchange of the sulfur atom from a thioether to a sulfonium group,[4–8] the formation of a sulfonium moiety should result in a red shift of the electric absorption band and a decrease in the binding energy,[9,10] which should allow selective photo-cleavage of the chain. On the basis of this idea, process *via* soluble polysulfonium salts might be employed to selectively degrade polyarylene sulfide to the monomer (Scheme 1).

Poly[methyl(4-phenylthiophenyl)sulfonium trifluoromethanesulfonate], a representative polysulfonium salt is noted as a soluble photoactive precursor which has a regular structure of alternating thiophenylene and phenyl alkyl sulfonium units, and is synthesized by the sulfoxide–acid reaction.‡ The resulting polysulfonium salts are soluble in methanol and acetonitrile. It was confirmed that poly(*p*-phenylene sulfide) with $M_w = 1.65 \times 10^4$ can be directly alkylated at the sulfur atom by reaction with methyl trifluoromethane sulfonate in methanesulfonic acid at room temperature. A typical procedure is as follows. A 25 ml, round-bottom flask equipped with a Teflon-covered magnetic stirring bar was charged with poly(*p*-phenylene sulfide) (1 g, 9.25 mmol monomer equiv.). Methanesulfonic acid (5 ml) and methyl trifluoromethane sulfonate (3.04 g, 18.5 mmol were added and the mixtured stirred for a period of 10 h. The reaction was then quenched by pouring it into ice-water. The spectroscopic data of the precipitated polymer were similar to that of poly[methyl(4-phenylthiophenyl)sulfonium] salts. The substitution level was determined to be *ca.* 50% by means of the ^{1}H NMR spectrum, showing that poly(*p*-phenylene sulfide) is efficiently converted to the sulfonium salt.

The model compound methyl(phenyl)(4-methylthiophenyl)sulfonium trifluoromethanesulfonate§ (6.3×10^{-5} mol dm^{-3}; λ_{max} 295 nm; ε 1.9×10^4 cm^{-1} dm^3 mol^{-1}) was dissolved in methanol and introduced into a 1 cm quartz cell. UV irradiation of the sulfonium salt was carried out at 365 nm at 25 °C in methanol (4 ml). Both spectra change with two isosbestic points [Fig. 1(*a*)]. Absorption at 294 nm, attributed to methyl 4-phenylthiophenyl sulfide, decreases corresponding to the increase in the absorption at 252 nm, attributed to methyl phenyl sulfide. After the photolysis, methyl phenyl sulfide was isolated as the main product (96%; λ_{max} 252 nm). The sulfonium salt obviously preferentially cleaves to methyl phenyl sulfide. The propyl(phenyl)(4-propylthiophenyl)sulfonium salt is also similarly decomposed by the photolysis. The reaction rate of the propyl salt (1.1×10^{-2} s^{-1}, 25 °C) is greater than that of the methyl salt (4.2×10^{-3} s^{-1}, 25 °C) at the same irradiation wavelength. The higher reactivity of the former salt in the photolysis is caused by its larger extinction coefficient at the irradiation wavelength of 350 nm, as the propyl substituent



Scheme 1

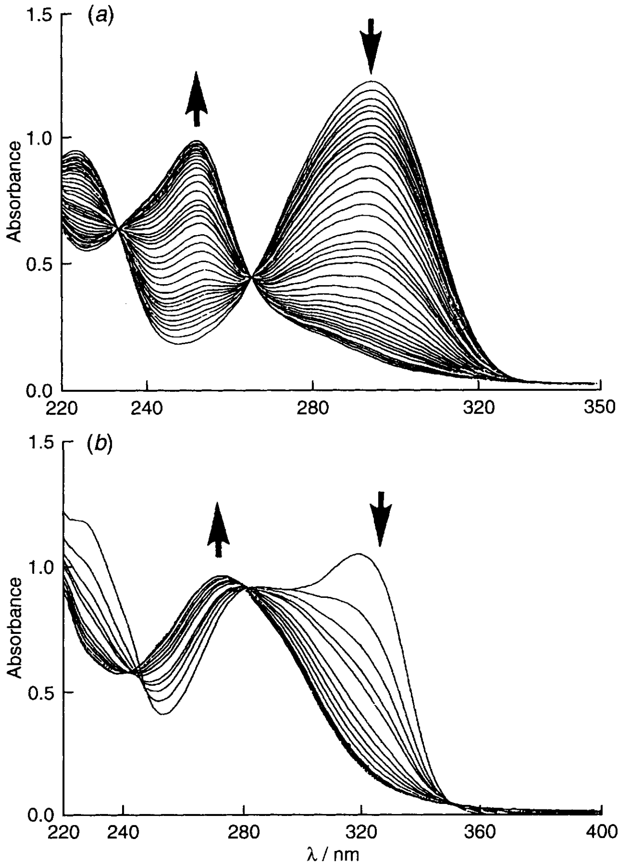


Fig. 1 (*a*) UV spectra changes of methyl(phenyl)(4-methylthiophenyl)sulfonium trifluoromethanesulfonate (6.3×10^{-5} mol dm^{-3}) by photo-irradiation at 365 nm in methanol at 25 °C. The absorption band at 252 nm, attributed to methyl phenyl sulfide, increases with a concomitant decrease in the absorption band at 295 nm during the photolysis. The time interval for the irradiation is 10 s for the first six lines, 20 s for the next four lines, 40 s for the next 8 lines and 80 s for the following 16 lines. (*b*) UV spectra changes of poly[methyl(phenyl)(4-methylthiophenyl)sulfonium trifluoromethanesulfonate] (6.3×10^{-5} mol dm^{-3}) on photo-irradiation at 365 nm of in methanol at 25 °C. The absorption band at 273 nm, attributed to methyl 4-phenylthiophenyl sulfide, increases with a concomitant decrease in the absorption band at 317 nm during the photolysis. The time interval for the irradiation is 10 s for the first six lines, 20 s for the next four lines and 40 s for the following 16 lines.

results in a shift of λ_{max} to a longer wavelength due to the electron-donating effect.

The experimental results reveal the predominant cleavage of the S^+–C bond to the phenyl ring having an electron donor group (methylthio group) in the *para*-position, even though there are three sulfonium–carbon bonds (Ph–S^+, CH_3–S^+ and S^+–$PhSCH_3$) in the sulfonium salts. Upon irradiation at a lower wavelength (250 nm) the electronic spectrum no longer exhibited any isosbestic points. Once formed, methyl phenyl sulfide is decomposed by the higher energy irradiation.

Poly[methyl(4-phenylthiophenyl)sulfonium trifluoromethanesulfonate] (6.3×10^{-5} mol dm^{-3} as a unit structure) in methanol has a λ_{max} at 317 nm (ε 2.05×10^4 cm^{-1} dm^3 mol^{-1}) which is shifted to a longer wavelength (295 nm) due to d–π conjugation. After irradiation at 365 nm, the spectrum of the polysulfonium salt changed with an isosbestic point [Fig. 1(*b*)], with the absorbance at 273 nm increasing more rapidly (<40 s) than that of the monomeric sulfonium salt. The main product of the photolysis, methyl 4-phenylthiophenyl sulfide¶ (λ_{max} at 273 nm, ε 1.78×10^4 cm^{-1} dm^3 mol^{-1}) was identified by gas chromatography and was isolated in over 80% yield. Other by-products, such as diphenyl sulfide and bis(4-methylthiophenyl)sulfide, were present in yields of less than 5%. This suggests that diphenyl sulfide is eliminated once, after which cleavage of methyl 4-phenylthiophenyl sulfide units is repeated continuously. Polysulfonium salts show higher photoreactivity than monomeric salts due to their larger extinction coefficient at 365 nm.

The polysulfonium cation is preferentially degraded to the corresponding monomer by a lower energy photolysis than that for the monomeric sulfonium. These results make possible a selective photo-degradation of poly(arylene sulfide) *via* its polysulfonium salt.

Footnotes

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‡ Poly[methyl(4-phenylthiophenyl)sulfonium trifluoromethanesulfonate] was synthesized as follows. A 100 ml round-bottom flask equipped with a Teflon-covered magnetic stirring bar was charged with methyl(4-phenylthiophenyl)sulfoxide (1 g, 4 mmol). The flask was cooled to 0 °C, and precooled trifluoromethanesulfonic acid (5 ml) was added with stirring. The temperature was increased slowly to room temperature over a period of 0.5–1 h. The reaction solution turned from colourless to pale blue. The reaction are continued for another 20 h at room temperature. The reaction was quenched by pouring it into ice-water and the precipitated polymer was chopped in a blender, washed with water and dried *in vacuo* at room temperature for 20 h. The polymer was isolated in 100% yield (1.53 g). The structure was confirmed by the following spectroscopic data; ν_{max} (KBr)/cm^{-1} 3086, 3023, 2932 (C–H), 1570, 1478, 1422 (C=C) 1258, 638 (C–F), 1161, 1067 (S=O), 816 (C–H); ^{1}H NMR (DCO_2D, Me_4Si) δ: 7.7 and 7.9 (Ar–H, 8 H), 3.8 (CH_3, 3 H); ^{13}C NMR (DCO_2D, Me_4Si) δ: 141.7, 132.3, 130.2 and 124.0 (Ar–C), 27.5 (CH_3).

§ Methyl(phenyl)(4-phenylthiophenyl)sulfonium cation was synthesized by the reaction between thioanisole and methyl phenyl sulfoxide in trifluoromethanesulfonic acid. The methyl(phenyl)(4-phenylthiophenyl)sulfonium cation is isolated as a stable trifluoromethanesulfonate salt. The spectroscopic data are as follows; ν_{max}(KBr)/cm^{-1} 3002, 2922 (C–H), 812 (C–H), 743, 680, 625; ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 14.6 and 28.4 (methyl C), 119.7, 126.4, 127.2, 129.5, 130.2, 131.4, 134.6 and 148.9 (phenyl C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.45 and 3.65 (methyl, 6 H), 7.36, 7.58, 7.63, 7.79 and 7.63 (phenyl, 9 H m).

¶ After the photo-irradiation, methyl 4-phenylthiophenyl sulfide was isolated and the structure confirmed by the following spectroscopic data; υ_{max} (KBr)/cm^{-1} 3056, 2919 (C–H), 1580, 1476, 1437 (C=C), 810 (C–H), 739, 689; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.29–7.01 (phenyl, 9 H, m), 2.28 (methyl, 3 H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 15.6 (methyl C), 126.7, 127.2, 129.1, 130.2, 131.4, 132.2, 136.7 and 138.2 (phenyl C) (Calc. for $C_{13}H_{12}S_2$: C, 67.2; H, 5.21. Found: C, 66.8; H, 5.28%).

References

1 L. C. Lopez and G. L. Winlkes, *J. Macromol. Sci., Rev. Macrol. Chem. Phys.*, 1989, **29** 83.

2 H. W. Hill, Jr., *Ind. Eng. Chem., Prod. Res. Dev.*, 1979, **18**, 252.

3 J. E. Frommer, *Acc. Chem. Res.*, 1986, **19**, 2.

4 *The Chemistry of the Sulfonium Group*, ed. J. M. Stirling, Wiley, New York, 1981.

5 K. Yamamoto, E. Shouji, H. Nishide and E. Tsuchida, *J. Am. Chem. Soc.*, 1993, **15**, 5819.

6 D. M. Roush, E. M. Price, L. K. Templeton and C. H. Hethcock, *J. Am. Chem. Soc.*, 1979, **101**, 2971.

7 R. D. Miller, A. F. Renaldo and H. Ito, *J. Org. Chem.*, 1988, **53**, 5571.

8 B. M. Novak, E. Hagen, S. Hoff and A. Viswanathan, *Macromolecules*, 1994, **27** 1985.

9 W. Chery, N. Epiotin and W. T. Borden, *Acc. Chem. Res.*, 1977, **10**, 167.

10 F. D. Saeva, B. P. Morgan and H. R. Luss, *J. Org. Chem.*, 1985, **50**, 4360.

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