Polymer Bulletin 33, 29–35 (1994)

Polymer Bulletin

The synthesis and characterisation of poly(paraphenyleneaminosulfone)

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Summary

Poly(*para*phenyleneaminosulphone), which contains alternating electron donating and electron withdrawing functionalities linked by a *para*phenyl group, has been synthesised and characterised. The significant order observed may be due to intermolecular hydrogen bonding.

Introduction

Although potentially conducting polymers have been the subject of considerable research efforts in the past twenty years much of the work has concentrated on poorly characterised materials with complex, and often unknown, structures and morphologies. More recent studies have focused on the synthesis of well defined polymers (1-4) the study of structure-property relationships in these materials (5-8) and the theoretical modelling of such structures (9-11).

As part of our work on the synthesis of new tailored oligomers and polymers for information technology (12) we have undertaken to investigate the synthesis and characterisation of a series of materials containing alternating electron donating (**D**) and electron accepting (**A**) functionalities linked by a conjugated group (figure 1).

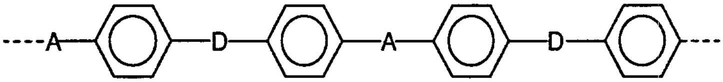

Figure 1. Target structure - general formula.

In this report we describe the synthesis and characterisation of a polymeric material of this type in which the donor function is provided by an amino (**-NH-**) group and the electron acceptor is a sulfone (**-SO$_2$-**) moiety.

Experimental

Synthesis

The polymer was synthesised *via* the reaction between 4,4'-difluorophenylsulfone and 4,4'-diaminophenylsulfone in dimethyl sulfoxide (DMSO) as outlined in figure 2.

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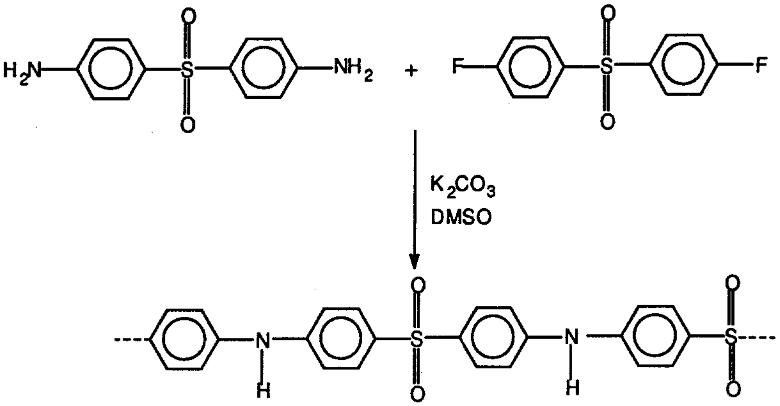


Figure 2. Reaction scheme for the synthesis of poly(paraphenyleneaminosulfone).

A mixture of 4,4'-diaminodiphenylsulfone (2.483g, 0.01mol), 4,4'-difluorodiphenylsulfone (2.542g, 0.01mol) and anhydrous potassium carbonate (2.76g, 0.02mol) in DMSO (100ml) was refluxed with stirring for five hours. The solution was poured into water (100ml) and the product which precipitated was isolated by filtration, washed with acetone (300ml) and dried in the vacuum oven at 100°C for 5hrs. This product was ground up (pestle and mortar) and vacuum dried for a further five hours at 180°C to give the product (4.98g, 99.1%) as an orange/yellow solid. The analytical data obtained from this material are discussed below.

Instrumental

Infrared spectra were recorded as KBr discs using a Perkin-Elmer 1600 FTIR spectrophotometer. Solution (DMSO-d_6) ^{1}H-NMR and ^{13}C-NMR experiments were carried out using either a Varian Gemini or a Varian VXR400S instrument operating respectively at 199.975MHz and 399.952MHz for the proton experiments and at 50.289MHz and 100.577MHz for the carbon experiments. Solid-state ^{13}C-NMR spectra were obtained using a Varian VXR300 spectrometer operating at 75.431MHz. Studies of thermal properties were carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter and a PL Thermal Sciences TG-760 thermogravimetric analyser. Wide-angle X-ray scattering (WAXS) patterns were obtained at room temperature with a Siemens D-5000 diffractometer using powdered samples. Molecular weight determinations were performed in DMSO using a Gonotec Vapour Pressure Osmometer (VPO).

Results and Discussion

The material is polymeric with a number average molecular weight of approximately 38,000 gmol^{-1} as revealed by VPO measurements.

The infrared spectrum of the reaction product is consistent with the anticipated structure and is characterised by the presence of at least two broad absorptions at around 3500cm^{-1} which are attributed to the N-H stretching vibrations (possibly hydrogen-bonded and free amine) and two bands at 1309cm^{-1} and 1148cm^{-1} assigned to the antisymmetric and symmetric stretch vibrations of the sulfone group.

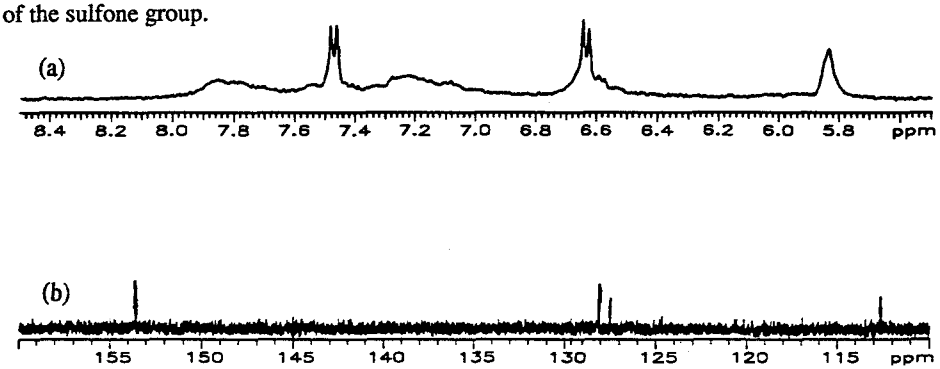
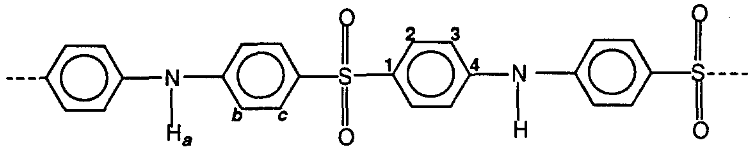


Figure 3. **(a)** ^{1}H-NMR and **(b)** ^{13}C-NMR spectrum of a dilute solution (*ca.* 3 mgml^{-1}) of the polymer in DMSO-d$_6$.

Figure 3a shows the ^{1}H-NMR spectrum of a dilute solution (*ca.* 3mgml^{-1}) of the same material in DMSO-d$_6$. The spectrum exhibits two sets of doublets at 7.49ppm and 6.64ppm and a broad singlet at 5.84ppm. Two broad peaks at about 7.2ppm and 7.9ppm are also present; these are attributed to hydrogen bonding interactions and will be discussed in more detail later. The ^{13}C-NMR spectrum of the polymer in DMSO-d$_6$ (figure 3b) exhibits four resonances at 153.7ppm 128.2ppm 127.4ppm and 112.6ppm with assignments shown in table 1. The ^{1}H-NMR and ^{13}C-NMR spectra were assigned by analogy with the signals observed in DMSO-d$_6$ solution for the "model compound", 4,4'-diaminophenylsulfone, which exhibits ^{1}H-NMR resonances at 7.46ppm, 6.59ppm and 6.00ppm and ^{13}C-NMR absorptions at 152.7ppm, 128.5ppm, 128.1ppm and 112.8ppm, respectively.

Table 1. ^{1}H-NMR and ^{13}C-NMR resonances in DMSO-d$_6$solution.



carbon	^{13}C-NMR/δ(ppm)	proton	^{1}H-NMR/δ(ppm)
1	153.7	*a*	5.84
2	112.6	*b*	6.64
3	128.2	*c*	7.49
4	127.4		

The complete solid-state ^{13}C-NMR spectrum of the polymer is shown in figure 4 together with spectra for the protonated and non-protonated carbon resonances. The absorptions at 149.8ppm, 114.2ppm, 129.4ppm and 137.2ppm are assigned to carbons **1**, **2**, **3**and **4**, respectively. The resonance at 40.6ppm is attributed to the presence of trapped DMSO within the polymer matrix. It was found that the intensity of this absorption varied with sample drying times (the spectrum shown in figure 4 was obtained for a sample dried at 180°C for five hours). The main difference between the solution and solid-state ^{13}C-NMR spectra is associated with the relative intensities due to carbons **2** and **3**; in solution, resonances of approximately equal intensity are observed whereas in the solid state that due to carbon **3** is substantially greater than that due to carbon **2** and is not fully suppressed in the non-protonated spectra. This anomaly is not understood and, along with the shift differences is attributed to unidentified solid-state effects, possibly hydrogen bonding, and is discussed below in the light of further NMR and WAXS analysis results.

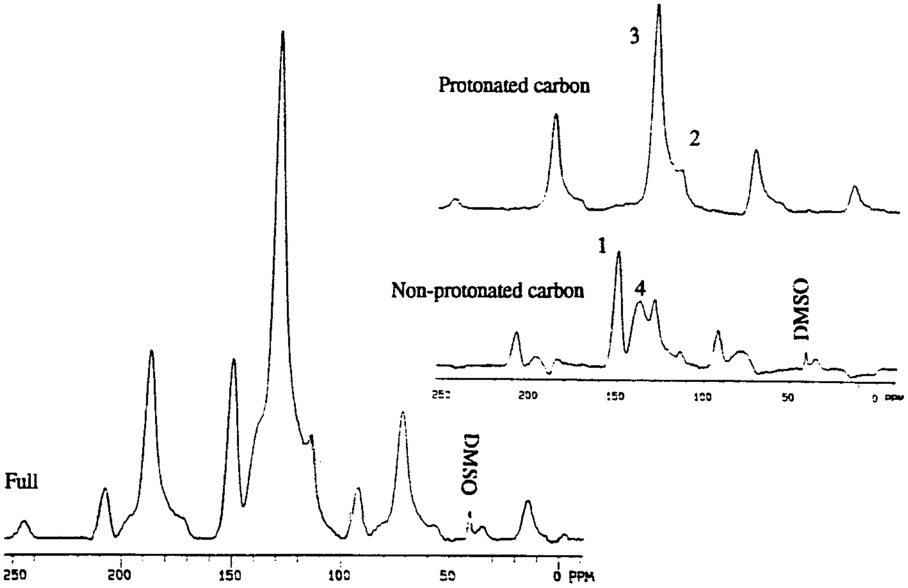


Figure 4. ^{13}C-NMR spectrum of the polymer in the solid state; the protonated and non-protonated carbon resonances are also shown.

In figure 5 the ^{1}H-NMR spectra of a concentrated solution of the polymer in DMSO-d_6 (*ca.* 20mgml^{-1}) recorded at 20°C, 60°C, 80°C and 120°C, are reproduced. In these solutions, the broad resonances (7.9ppm and 7.2ppm) are more pronounced than those observed in dilute solution and a number of new, less intense absorptions at about 7.5ppm and 6.0ppm are also present. Addition of D_2O resulted in the disappearance of all the resonances between 5.3 and 6.3ppm indicating that these are due to N-H protons; the positions and relative intensities of all other resonances were unaffected. The line broadening with increasing temperature is fully reversible.

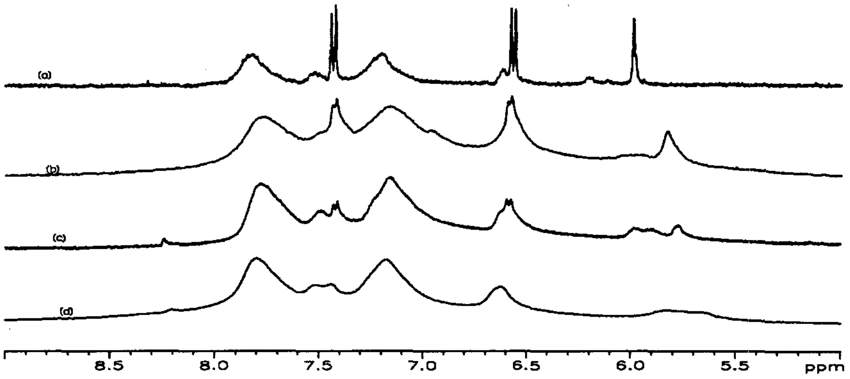


Figure 5. ^{1}H-NMR spectrum of a concentrated solution (ca. 20mgml^{-1}) of the polymer in DMSO-d_6 recorded as a function of temperature at **(a)** 20°C; **(b)** 60°C; (c)80°C; and **(d)** 120°C.

The broad absoptions may be a consequence of a hydrogen bonding process involving solvent molecules and interchain interactions such as those shown in figure 6. If this suggestion has any validity, the observed reversible line broadening must be associated with the temperature dependence of the organisation of polymer chains *via* hydrogen bonds. The presence of trapped DMSO within the polymer matrix (as observed by solid-state ^{13}C-NMR) even for samples which had been subjected to intensive vacuum drying supports the hypothesis that DMSO molecules are also involved in hydrogen bonding.

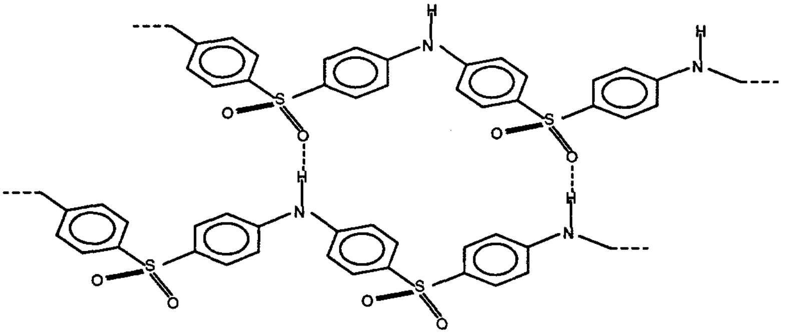


Figure 6. Possible interchain hydrogen-bonding.

The WAXS powder diffraction pattern of a polymer sample at room temperature is shown in figure 7. The sharp peaks are due to background (sample holder). The sample exhibits an "amorphous halo" at high angle and a sharper peak at a lower angle indicating a measure of order. The d-spacing (4.86Å) calculated from the low angle peak is consistent with the hydrogen bonded structure shown in figure 6 and is attributed to the intermolecular distance between the centres of gravity in adjacent chains. In a further attempt to investigate the temperature dependence of the hydrogen bonded interactions, the WAXS profiles of powdered samples were recorded at various temperatures up to 120°C. In all cases the observed patterns were identical to those shown in figure 7 indicating that within this temperature range the extent of hydrogen bonding in solid samples of the material is not temperature dependent.

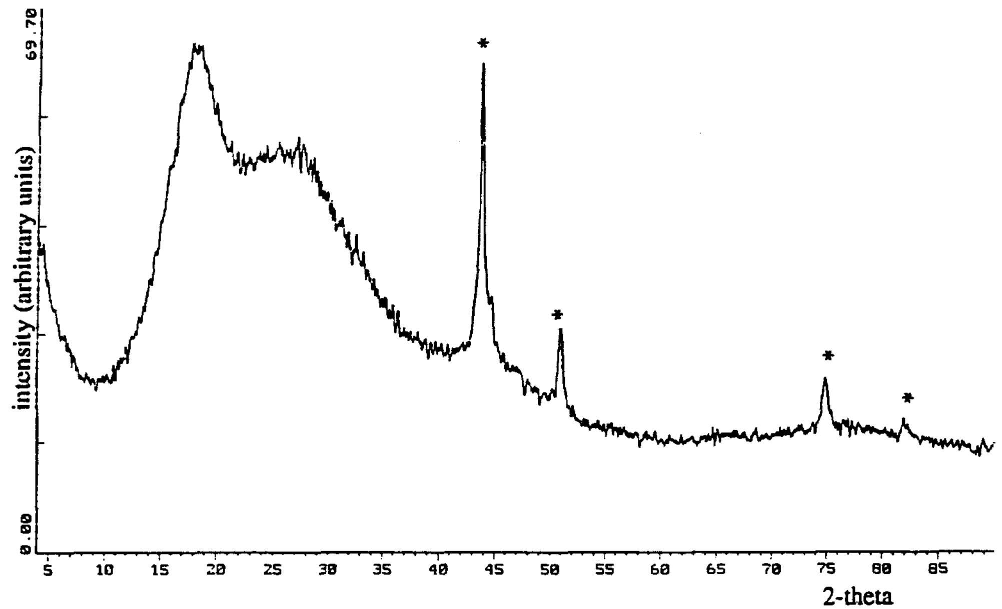


Figure 7. WAXS profile of the powdered polymer at room temperature; the sharp peaks marked * are due to the sample holder.

The thermal properties of the polymer were studied by thermogravimetry (TGA) and differential scanning calorimetry (DSC). Thermogravimetric analysis revealed that polymer samples dried under vacuum at 180°C for five hours contained about 2% DMSO which could be removed on heating to 350°C at 10°Cmin^{-1}. Polymer samples heated isothermally at 350°C for three hours did not loose any further weight. The onset of the degradation process as determined by heating a polymer sample at 5°Cmin^{-1} under a nitrogen atmosphere is at about 410°C. The 50% weight loss point is at 770°C. In accord with the WAXS experiments the DSC thermogram (temperature range: -50°C to +300°C) of the vacuum dried polymer (180°C/5hours) in the first and subsequent heating cycles is completely featureless, neither a melting endotherm nor a glass transition were detected. The failure to observe any such transitions for this material is cosistent with degradation occurring prior to either of these transitions in what appears to be a structure which is effectively cross-linked via strong hydrogen bonding interactions.

Conclusions

The reaction of 4,4'-difluorophenyl sulfone and 4,4'-diaminophenyl sulfone in refluxing dimethyl sulfoxide results in the formation of a polymer which possesses a significant degree of order in both the solid state and in solution. Variable temperature NMR and WAXS experiments indicated that this order is due to strong hydrogen bonding interactions involving adjacent polymer chains and solvent molecules.

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12. This work was supported through ESPRIT Basic Research Project 7282, Tailored Oligomers and Polymers for Information Technology.

Accepted March 10, 1994 C