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Synthesis and structural study of poly(thioether-imide-sulfones) based on 3,3′- and 4,4′-bis(4-chloro-1,8-naphthalimido)diphenylsulfone

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Abstract

3,3′-Bis(4-chloro-1,8-naphthalimido)diphenylsulfone (**1a**) and 4,4′-bis(4-chloro-1,8-naphthalimido)diphenylsulfone (**1b**) and model imides have been synthesized and characterized by n.m.r. and i.r. spectroscopies and by d.s.c. The results of the structural investigations indicate that **1a** and **1b** are pure naphthalimides, without traces of isoimides. **1a** and **1b** were used to generate three series of poly(thioether-imide-sulfones). The polymer synthesis involved a nucleophilic displacement polymerization between **1a** or **1b** and Li_2S or dithiol reactants such as 1,3-benzenedithiol and 2,5-dimercapto-1,3,4-thiadiazole under basic conditions in NMP or DMAc. The copolymers were characterized by i.r., n.m.r. and thermal analysis. Model compounds were synthesized for the correct assignment of ^{13}C n.m.r. chemical shifts. All the copolymers showed a good thermal stability, exhibiting 10% mass loss in the range 400–500°C. The copolymers containing parasubstituted phenylsulfone units and/or the ones containing thiadiazole units were soluble in common polar solvents such as DMSO, DMF, NMP and DMAc.

Keywords: Soluble poly(thioether-imide-sulfone); 1,8-Naphthalimide copolymers; Thiol/aryl chloride reaction

1. Introduction

The synthesis of sulfur containing polymers such as polythioarylenes has been studied extensively, since they have excellent thermomechanical stability, chemical resistance and flame retardant properties. The most frequent method utilized for the synthesis of polythioarylenes is the nucleophilic displacement polymerization of dihalo-terminated reactants with alkali metal sulfides in polar aprotic solvents like *N*-methylpyrrolidinone (NMP) at elevated temperature and pressure [1–4]. An alternate method of synthesis of these polymers is the analogue polythioetherification reaction between dithiol reactants and activated dihalo compounds in the presence of a base [5]. Most of polythioarylenes are insoluble in organic solvents and their melt processing requires very high temperatures. In order to improve their solubility and processability, many attempts have been made, the most successful being the introduction of flexible or substituted comonomer units within polymer backbone [6–10]. Polyetherimides or their thio analogues have been receiving great attention as they may provide good thermal stability owing to the presence of flexible ether or thioether links. The synthesis of polythioetherimides derived from the reaction between diamine-terminated oligothiophenylenes and five-membered anhydride has been reported [11,12]. Polyimides with thioarylene and sulfone group have found applications in membrane technology due to their remarkable gas-selective and permselective properties [13]. Polythioetherimides may be either synthesized by polyimidation reaction between dianhydrides and diamines containing thioether units or by the halogen displacement reaction of dihalo-terminated imide monomers with sulfur reagents. This article describes poly(imide-sulfone-thioethers) synthesized following the latter strategy, from dichloro terminated six-membered imide monomers.

The synthesis and characterization of pure imide monomers is challenging as a number of side reactions, isoimide formation, cross chain imidation as well as reaction termination due to reactivity changes of amino groups are known to occur [14–16]. The synthesis of six-membered polyimides has also been documented recently [17]. In the first part of this article, we report the synthesis and the detailed structural characterization of new imide monomers, namely 3,3′- and 4,4′-bis(4-chloro-1,8-naphthalimido)diphenylsulfone (**1a** and **1b**, respectively). The advantage of using these

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chloro monomers for copoly(thioether-imide) synthesis lies in that, the Cl atoms present in the para position to the six-membered imide ring are highly susceptible to nucleophilic displacement with oxygen or sulfur reagents [18] and thus enhance the possibility to obtain high molar mass copolymers. Such facile nucleophilic displacement of nitro groups in 4-position of naphthalimides by bisphenolate ions has been reported [19]. The heterocyclic six-membered imide should also impart thermal stability while the diphenylsulfone moieties should impart solubility to the resultant copolymers. The second part of this article describes the synthesis, characterization and properties of poly(imide-sulfone-thioethers) obtained by the chloro displacement polymerization of the imide-sulfone monomers **1a** and **1b** with lithium sulfide and 1,3-benzenedithiol. Since the incorporation of heterocycles such as 1,3,4-thiadiazole or oxadiazole in the main chain of polymers usually imparts solubility and results in copolymers with high thermal and oxidative stabilities [20,21], 2,5-dimercapto-1,3,4-thiadiazole has also been used as a sulfur reagent.

2. Experimental

2.1. Materials

4-Chloro-1,8-naphthalic anhydride (CNA) (Janssen), bis(3-aminophenyl)sulfone, 2,5-dimercapto-1,3,4-dithiadiazole (DMTD), 1,8-naphthalic anhydride (NA), lithium sulfide, 1,3-benzenedithiol, aniline, *m*-cresol, anhydrous potassium carbonate (Aldrich), and bis(4-aminophenyl)sulfone (Fluka), were of reagent grade and used as received. *N*-Methylpyrrolidinone (NMP) and *N,N*-dimethylacetamide (DMAc) were of puriss. grade from SDS and Prolabo, respectively, and used as received.

2.2. Measurements

Infrared measurements were recorded using a Bruker IFS-45 FTIR instrument and KBr discs.

D.s.c. and t.g.a. were carried out on a TA Instruments 9900 apparatus equipped with DSC910 and TGA951 modules at rate of 20°C/min under nitrogen. Melting points were taken at the maximum of the melting endotherm and glass transition temperatures at the mid-point of baseline shift. Calibrations were made using indium.

^{1}H and ^{13}C n.m.r. 1D analysis were carried out using Bruker ARX 250 or AM 500 instruments. ^{13}C{^{1}H} decoupling, Spin-echo, 2D ^{1}H–^{1}H COSY and 2D $^1J_{CH}$ heteronuclear ^{13}C–^{1}H correlation n.m.r. experiments were carried out using Bruker 500 MHz n.m.r. instrument. For **1a** and **1c**, n.m.r. spectra were recorded in *N*-methylpyrrolidinone (NMP) and few drops of DMSO-d6, whereas for **1d**, n.m.r. spectra were recorded in DMSO-d6. The spectra of polymers **3e–g** and **4e–g** and of their model compounds were recorded in *N*-methylpyrrolidinone (NMP) using dimethylsulfoxide-d6 (DMSO-d6) as an external deuteriated reference.

Inherent viscosities were measured from *m*-cresol solutions (0.25 g/dl) at 40°C, using a Schott Geräte automatic viscometer with a Canon Ubbelhode Nr. Ic micro-viscometer.

2.2.1. 3,3′-Bis(4-chloro-1,8-naphthalimido)diphenylsulfone (1a)

4-Chloro-1,8-naphthalic anhydride (CNA) (1.28 g, 5.5 mmol) was dissolved in 50 ml *m*-cresol. Then, bis(3-aminophenyl) sulfone (0.62 g, 2.5 mmol) and benzoic acid catalyst (0.61 g, 5 mmol) were added. The reaction mixture was heated at 202°C (reflux) for 12 h under argon flow. It was cooled to room temperature and isoquinoline (0.66 g, 5 mmol) was added. The reaction mixture was again heated at 202°C for another 12 h. To the cooled mixture, MeOH was added. The yellow solids obtained were washed several times with hot MeOH and dried at 60°C under vacuum. Yield 80%, m.p. (d.s.c.), 376°C.

Elemental analysis, calculated for $C_{36}H_{18}Cl_2N_2O_6S$ (677.51): C 63.82, H 2.68, N 4.13, O 14.17, S 4.73, Cl 10.47. Found: C 63.17, H 2.64, N 3.84, O 14.73, S 4.54, Cl 10.58.

N.m.r. characterization: see Section 3.

2.2.2. 4,4′-bis(4-Chloro-1,8-naphthalimido)diphenylsulfone (1b)

The method was similar as described for **1a**, using bis(4-aminophenyl) sulfone instead of bis(3-aminophenyl) sulfone. **1b** was recrystallized from NMP, washed with hot MeOH and dried at 60°C under vacuum. Yield, 57%; m.p. (d.s.c.), 387°C.

Elemental analysis, calculated for $C_{36}H_{18}Cl_2N_2O_6S$ (677.51): C 63.82, H 2.68, N 4.13, S 4.73, Cl 10.47. Found: C 63.70, H 3.03, N 4.00, S 4.59, Cl 9.82. I.r. (KBr): 1714 cm^{-1}; 1674 cm^{-1} (imide); 1590 cm^{-1} (phenyl). ^{13}C n.m.r. (NMP/DMSO-d6 (90/10 vol/vol), 62.9 MHz, ref TMS) ppm: 163.40 and 163.20 (imide carbonyls), 141.45 ($\underline{C}$–SO_2), 141.20 ($\underline{C}$–N $<$), 137.95 ($\underline{C}$–Cl), 132–120 (13 peaks, aromatic C).

2.2.3. 3,3′-Bis(1,8-naphthalimido)diphenylsulfone (1c)

The method was similar to that described for **1a**, using 1,8-naphthalic anhydride instead of 4-chloro-1,8-naphthalic anhydride. Yield, 80%; m.p. (d.s.c.), 363°C.

Elemental analysis, calculated for $C_{36}H_20N_2O_6S$ (608.62): C 71.04, H 3.31, N 4.60, O 15.77, S 5.27. Found: C 70.12, H 3.30, N 4.52, O 15.33, S 5.37. ^{13}C n.m.r. (62.9 MHz, NMP + DMSO-d6, ref. TMS): 122.39, 126.82, 127.04, 127.70, 128.44, 129.88, 130.28, 131.38, 134.08, 134.61, 137.10, 141.64 and 163.20 ppm.

2.2.4. N-Phenyl-4-chloro-1,8-naphthalimide (1d)

The method was similar as described for **1a**, using aniline in place of bis(3-aminophenyl) sulfone. After cooling, solids were isolated out by adding 4 times by volume of MeOH to the *m*-cresol solution and then adding water slowly. After filtration the solids were recrystallized from EtOH. Yield, 80%; m.p. (d.s.c.), 218°C.

Elemental analysis, calculated $C_{18}H_{10}ClNO_2$ (307.74): C 70.25, H 3.28, N 4.55 O 10.40, Cl 11.52. Found: C 69.92, H 3.55, N 4.43, O 10.51, Cl 11.41. ^{13}C n.m.r. (125.76 MHz, DMSO-d6, ref. TMS): 122.12, 123.41, 127.82, 128.41, 128.66, 128.73, 128.92, 129.00, 129.14, 130.23, 130.95, 131.70, 135.88, 137.64, 163.06 and 163.36 ppm.

*2.2.5. Poly(thioether-imide-sulfone) (**3e** and **4e**)*

1a or **1b** (0.966 g, 1.425 mmol) and lithium sulfide (0.0653 g, 1.425 mmol) were mixed in 10 ml *N*-methylpyrrolidinone in a cylindrical pressure reactor. The reaction mixture was stirred under nitrogen atmosphere and polymerization was started by immersing the reactor in a oil bath at 180°C. The reaction was continued for 4 h. After cooling, the polymer was precipitated by pouring the reaction mixture into water. The polymer was filtered, washed with hot methanol, soxhlet extracted with methanol and finally dried at 60°C under vacuum. Yield, 95% and 94% for **3e** and **4e**, respectively.

Elemental analysis, calculated for $(C_{36}H_{18}N_2O_6S_2)_n$: C 67.70, H 2.84, N 4.38, S 10.04. Found (**3e**): C 64.6, H 3.18, N 4.62, S 8.65, Cl 0.38. Found (**4e**): C 63.8, H 3.28, N 4.89, S 8.80, Cl 0. 20. I.r. (KBr) (**3e**,**4e**): 1714 cm^{-1}; 1674 cm^{-1} (imide); 1590 cm^{-1} (phenyl); ^{13}C n.m.r. (**4e**) (NMP/DMSO-d6 (90/10 vol/vol), 62.9 MHz, ref TMS) ppm: 163.4 and 163.2 (imide carbonyls), 141.45 ($\underline{C}$–SO_2), 141.20 ($\underline{C}$–N <), 139.1 ($\underline{C}$–S), 132–120 (nine peaks, aromatic).

*2.2.6. 4,4′-Thio-bis(N-phenyl-1,8-naphthalimide) (**2e**)*

2e was synthesized by the same procedure as above by reacting Li_2S and **1d** in NMP at 180°C for 3 h. Yield, 98%. The compound did not show any melting point.

Elemental analysis, calculated for $C_{36}H_{20}N_2O_4S$: C 74.99, H 3.50, N 4.86 S 5.56. Found: C 72.1, H 3.60, N 4.65, S 5.29. I.r.: 1712 cm^{-1}; 1666 cm^{-1} (imide carbonyls); 1587 (phenyl). ^{13}C n.m.r. (NMP/DMSO-d6 (90/10 vol/vol), 62.9 MHz, ref TMS) ppm: 163.49 and 163.32 (imide carbonyls), 139.06 ($\underline{C}$–S), 136.4 ($\underline{C}$–N) and 12 peaks in the 132–120 region (aromatic).

*2.2.7. Poly(imide-sulfone-thiophenylenes) (**3f** and **4f**)*

1a or **1b** (1.295 g, 1.912 mmol) was stirred in 20 ml dimethylacetamide in a 50-ml three-way round-bottomed flask. 1,3-Benzenedithiol (0.272 g, 1.912 mmol) and powdered anhydrous potassium carbonate (0.264 g, 1.912 mmol) were then added under nitrogen atmosphere. The polymerization was started by immersing the flask in a preheated oil bath at a temperature of 140°C. The temperature was then raised to 160°C and maintained for 4 h. The polymer was precipitated by pouring reaction mixture into water, purified by repeated washing with hot methanol followed by soxhlet extraction with methanol and finally dried at 60°C under vacuum. Yield, 95% each.

Elemental analysis, calculated for $C_{42}H_{22}N_2O_6S_3$: C 67.55, H 2.96, N 3.75 S 12.87. Found (**3f**): C 63.6, H 3.21, N 4.00, S 11.92, Cl 0.83. Found (**4f**): C 63.9, H 3.25, N 3.75, S 12.1, Cl 0.40. I.r. (KBr) (**3f**,**4f**): 1714 cm^{-1}; 1674 cm^{-1} (imide); 1590 cm^{-1} (phenyl). ^{13}C n.m.r. (NMP/DMSO-d6 (90/10 vol/vol), 62.9 MHz, ref TMS) ppm: (**4f**) 163.04 and 162.90 (imide carbonyls), 141.94 ($\underline{C}$–S naphthyl), 141.29 ($\underline{C}$–SO_2),141.08 ($\underline{C}$–N), three small peaks at 136–134 region ($\underline{C}$–S phenyl), 13 peaks 132–120 region (aromatic C).

*2.2.8. S,S′-(1,3-Phenylene)bis(4-mercapto-N-phenyl-1,8-naphthalimide) (**2f**)*

2f was synthesised by the same procedure as above with **1d** and 1,3-benzenedithiol in a 2:1 molar ratio. Yield, 96%. The compound did not show any melting point.

Elemental analysis, calculated for $C_{42}H_{24}N_2O_4S_2$: C 73.69, H 3.53, N 4.09, S 9.37. Found: C 71.00, H 3.26, N 4.04, S 8.94. I.r. (KBr): 1712 cm^{-1}; 1666 cm^{-1} (imide carbonyls); 1587 (phenyl). ^{13}C n.m.r. (NMP/DMSO-d6 (90/10 vol/vol), 62.9 MHz, ref TMS) ppm: 163.22 and 163.10 (imide carbonyls), 141.98 ($\underline{C}$–S naphthyl), 136.4 ($\underline{C}$–N) and 13 peaks in the 135–120 ppm region (aromatic C).

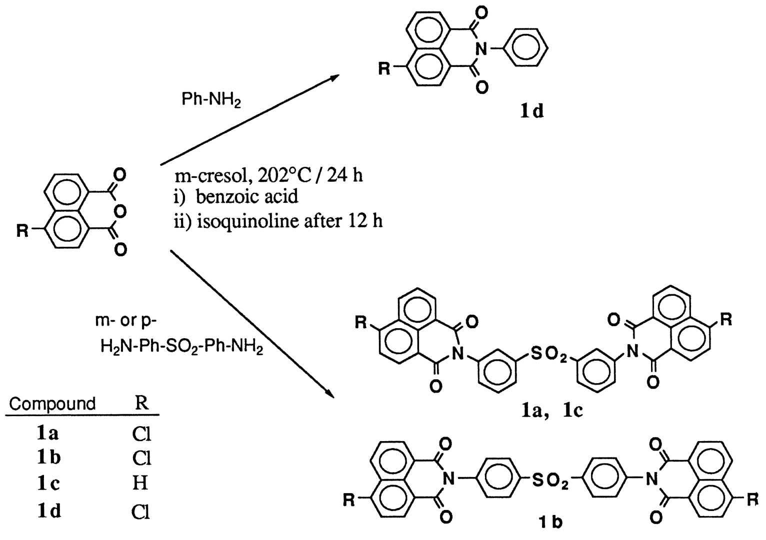
*2.2.9. Poly(imide-sufone-1,3,4-thiadiazole thioethers) (**3g** and **4g**)*

1a or **1b** (0.726 g, 1.072 mmol) was stirred in 15 ml dimethylacetamide in a 50-ml three-way round-bottomed flask. 2,5-Dimercapto-1,3,4-thiadiazole (0.163 g, 1.072 mmol) and powdered anhydrous potassium carbonate (0.149 g, 1.072 mmol) were added under nitrogen atmosphere. The reaction flask was then placed in an oil bath at 160°C for 4 h. The polymer was precipitated by pouring the reaction mixture into water, purified by repeated washing with hot methanol followed by soxhlet extraction with methanol and finally dried at 60°C under vacuum. Yield, 95% and 93% for **3g** and **4g**, respectively.

Elemental analysis, calculated for $C_{38}H_{18}N_4O_6S_4$: C 60.47, H 2.40, N 7.42, S 16.99. Found (**3g**): C 61.28, H 3.01, N 7.56, S 13.27, Cl 0.38. Found (**4g**): C 59.0, H 2.55, N 6.68, S 12.44, Cl 0.35. I.r. (KBr) (**3g**,**4g**): 1714 cm^{-1}; 1674 cm^{-1} (imide); 1590 cm^{-1} (phenyl). ^{13}C n.m.r. (NMP/DMSO-d6 (90/10 vol/vol), 62.9 MHz, ref TMS) ppm: 163.07 and 162.92 (imide carbonyls), 162.79 ($\underline{C}$–N thiadiazole), 141.29 ($\underline{C}$–SO_2), 141.08 ($\underline{C}$–N), seven main peaks in the 132–120 ppm region (aromatic).

*2.2.10. S,S′-(2,5-(1,3,4-Thiadiazolylene))bis(4-mercapto-N-phenyl-1,8-naphthalimide) (**2g**)*

2g was synthesised by the same procedure as above with **1d** and 2,5-dimercapto-1,3,4-thiadiazole in a 2:1 mol ratio for 2 h at 160°C. Yield, 95%. The compound did not show any melting point.



Compound	R
1a	Cl
1b	Cl
1c	H
1d	Cl

Scheme 1.

Elemental analysis, calculated for $C_{38}H_{20}N_4O_4S_3$: C 65.88, H 2.91, N 8.09, S 13.88. Found: C 65.7, H 2.93, N 8.04, S 13.1. I.r.: 1712 cm^{-1}; 1666 cm^{-1} (imide carbonyls); 1587 (phenyl). ^{13}C n.m.r. (NMP/DMSO-d6 (90/10 vol/vol), 62.9 MHz, ref TMS) ppm: 163.07; 162.92 (imide carbonyl), 162.79 ($\underline{C}$–N thiadiazole), 139 ($\underline{C}$–S); 136.4 ($\underline{C}$–N), 15 peaks in the 132–120 ppm region (aromatic C).

3. Results and discussion

3.1. 3,3′ and 4,4′-bis(4-chloro-1,8-naphthalimido)diphenylsulfone (*1a* and *1b*)

The first attempts of reacting 4-chloronaphthalic anhydride (CNA) with 3,3′-diamino diphenyl sulfone using acetic acid as reaction medium—a solvent commonly used for the synthesis of five membered ring polyimides [12]—failed due to the high stability of the six-membered anhydride, which remained unreacted. The synthesis of six-membered ring polyimides has been reported to be successful at 190°C in *m*-cresol, in the presence of catalysts such as benzoic acid and isoquinoline [22]. In the absence of catalyst, only low MW polymers were obtained [22]. The best results were obtained when the catalysts were used sequentially, i.e. benzoic acid at the beginning and isoquinoline after 12 h of reaction. Hence, we have employed the reaction conditions depicted in Scheme 1 for the synthesis of imide monomers **1a** and **1b** as well as for model compounds **1c** and **1d**.

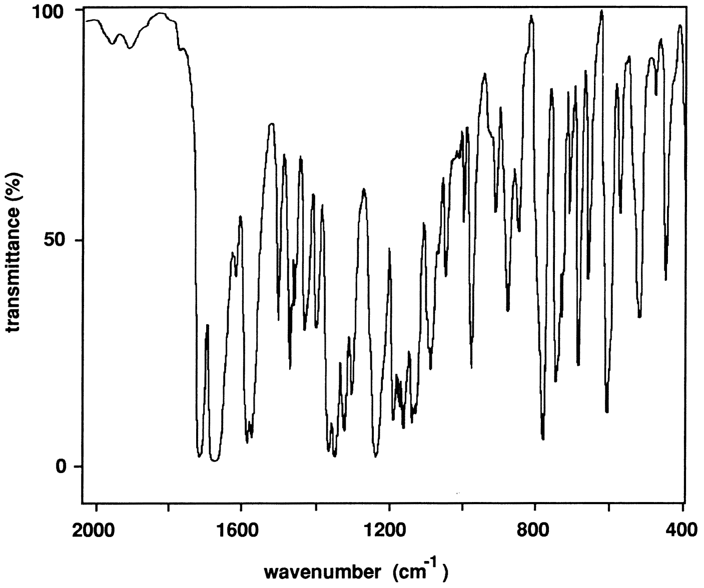
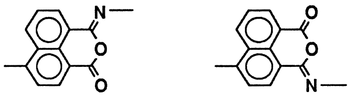


Fig. 1. FT-i.r. spectrum (KBr disc) of bis(4-chloro-1,8-naphthalimido)diphenyl sulfone (**1a**).



Scheme 2.

The formation of *cis*- and *trans*-isoimide along with imide had been reported for systems based on 4-benzoyl-1,8-naphthalic anhydride and aromatic amines [16]. On heating above melting temperature *trans*-isoimide was converted into infusible imide, whereas *cis*-isoimide remains unaltered on successive heating. Monomers **1a** and **1b** melt at 376 and 387°C, respectively, as observed from d.s.c. Model **1c** obtained from aniline melts at 218°C and **1d** at 363°C. Melting peaks remained unchanged on successive cooling and heating. Thus, the d.s.c. study of our compounds seems to rule out the possibility of formation of *trans*-isoimide.

The completion of reaction was confirmed on the basis of disappearance of anhydride carbonyl peaks (symmetric and asymmetric stretching) at 1780 and 1740 cm^{-1} in i.r. spectra and appearance of new absorptions at 1715 and 1673 cm^{-1} (Fig. 1). Similar peaks were also observed for model compounds **1b**, **1c** and **1d**. Unlike five-membered cyclic imides, six-membered ones such as 1,8-naphthalimides have not been much studied, and discrepancies exist in literature on the assignments of these i.r. absorptions. They were reported to be due to naphthalimide (symmetrical and unsymmetrical C=O stretching) 23 or to naphthalisoimide (C=N and six-membered lactone O–C=O stretchings) [16,17]. N.m.r. assignments of the *N*-phenyl peaks of model compounds (*N*-aryl 4-benzoyl-1,8-naphthalimides or isoimides) based on calculated spectra were claimed to support the isoimide structure [16]. However, the naphthalimide moiety was not assigned and no other data is available in literature on such compounds. In order to further investigate whether our compounds are isoimides, desired imides or mixtures of two, their characterization was carried out using various n.m.r. experiments.

A main difference between naphthalisoimide and naphthalimide structures is the symmetry of the latter. Consequently, the number of peaks expected in the ^{13}C n.m.r. spectra of imides is lower than in the spectra of isoimides. This has been observed on *N*-phenylphthalimide and isoimide [24]. In the present case, the two carbonyls of starting CNA are not equivalent. The formation of isoimide should therefore lead to the two isomers depicted in Scheme 2 having a total of 24 different naphthalisoimide carbons, while imide should present only 12 different ones.

In the unlikely case of the formation of only one of the two isoimide isomers, the same number of naphthalisoimide peaks as in the imide (12 peaks) would be obtained. However in the imide two C=O will be expected against one C=N and only one C=O in the isoimide. The resonance of imide C=O (ca. 165 ppm) [23,24] being quite different from that of isoimide C=N (ca. 145 ppm) [24], distinction between the two structures is possible in this case too.

In the ^{13}C n.m.r. spectrum of **1a** (Fig. 2), two resonances appear close to 163 ppm, i.e. in the carbonyl resonance area. The total number of peaks, 18, corresponds exactly to what is expected for the 18 different C atoms of pure imide monomer. This assignment of **1a** to imide is supported by the spectrum of 3,3′-bis(1,8-naphthalimido) phenylsulfone (**1c**). Since naphthalimide moiety is unsubstituted in this model, imide structure results in a symmetrical molecule, while isoimide would lead to a non-symmetrical one. Only 13 peaks are seen in the ^{13}C n.m.r. spectrum of **1c**. This, and the single carbonyl peak at 163.2 ppm, correspond exactly to what is expected for the symmetrical imide structure. Similar conclusions were drawn from the spectra of **1b** (18 peaks, two C=O resonances at 163 ppm) and of *N*-phenyl-4-chloro-1,8-naphthalimide **1d** (16 peaks, two C=O resonances at 163 ppm). From this study, it is concluded that **1a–d** are the expected naphthalimides.

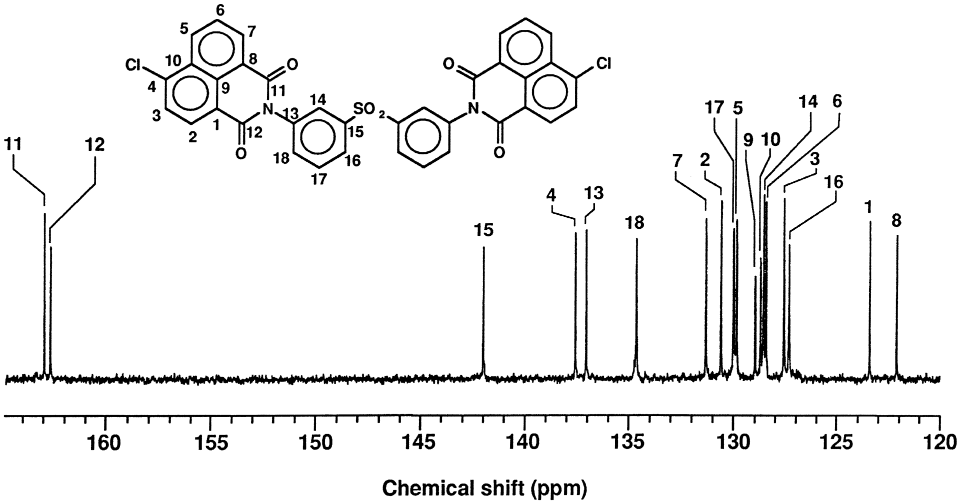


Fig. 2. $^{13}C\{^1H\}$ n.m.r. spectrum (125.76 MHz, NMP + DMSO-d6, ref. TMS) of 3,3′-bis(4-chloro-1,8-naphthalimido)diphenyl sulfone (**1a**).

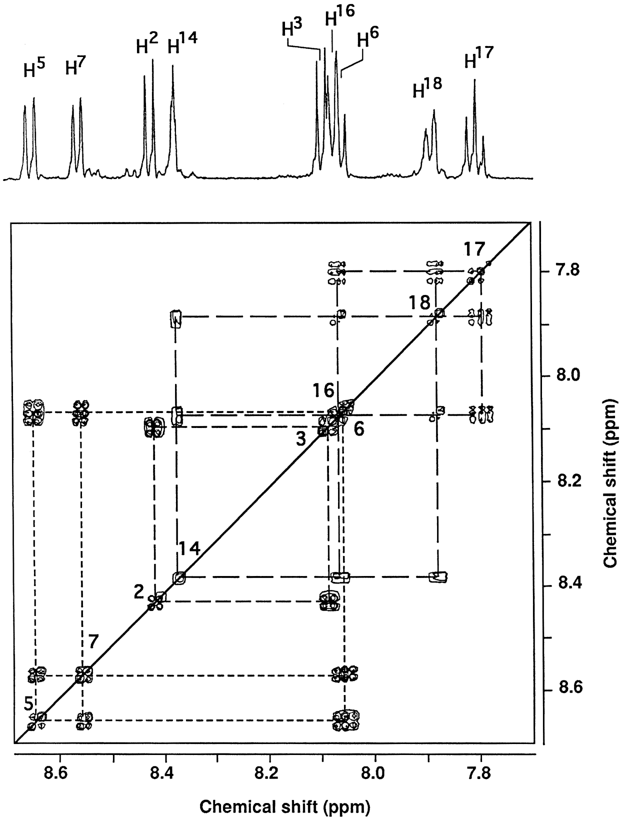


Fig. 3. 2D ^1H–^1H COSY spectrum (500.14 MHz, NMP + DMSO-d6, ref. TMS) of 3,3′-bis(4-chloro-1,8-naphthalimido)diphenyl sulfone (**1a**).

The ^1H,^1H-COSY spectrum of **1a** is given in Fig. 3. As expected, one 2-spin and one 3-spin system (1,4,8-substituted naphthyl moiety) and one 4-spin system (1,3-substituted phenyl) are observed, corresponding, respectively, to H^2–H^3, H^5–H^6–H^7 and to H^{14}–$H^{16}H^{17}$–H^{18} systems. This spectrum, together with the 2D $^1J_{C,H}$ ^{13}C–^1H spectrum, the non-decoupled ^{13}C spectrum and a series of ^{13}C n.m.r. spectra of carbonyl region with selective proton decoupling allowed the assignments given in Fig. 2. The assignments of the quaternary carbons of naphthalene ring were based on long-range (C,H) couplings: in naphthalene derivatives, the predominant long-range coupling is always the three-bond $^3J_{C,H}$ coupling [25–27]. *Ortho* $^2J_{C,H}$, *para* $^4J_{C,H}$ and higher range couplings are weak (0–2 Hz). In the same way, the existence of the long-range couplings C^{12}–H^2 and C^{11}–H^7 allowed the assignments of carbonyls and of the corresponding protons. Some ambiguities remained, which were removed as follows:

Table 1
Calculated and experimental ^{13}C n.m.r. chemical shifts (125.76 MHz, NMP + DMSO-d6, ref. TMS) of *m*-phenylene carbons C^{13-18} in 3,3′-bis(4-chloro-1,8-naphthalimido)diphenylsulfone (**1a**)

δ (ppm)	C^{13}	C^{14}	C^{15}	C^{16}	C^{17}	C^{18}
Experimental	136.9_9	129.5_2	141.9_5	127.2_8	129.9_6	134.6_0
Calculated	137.3	127.9	141.8	127.5	130.5	134.5
Difference	− 0.3	+ 0.6	− 0.1	− 0.2	− 0.5	+ 0.1

Table 2
^1H and ^{13}C n.m.r. (500.14 MHz(1H) or 125.76 MHz (13C), NMP + DMSO-d6, ref. TMS) assignments of 3,3′-bis(4-chloro-1,8-naphthalimido)diphenyl sulfone (**1a**)

Number	δC (ppm)	δH (ppm)
1	123.39	—
2	130.56	8.42
3	127.53	8.10
4	137.52	—
5	129.81	8.67
6	128.40	8.06
7	131.28	8.56
8	122.09	—
9	128.92	—
10	128.67	—
11	162.90	—
12	162.60	—
13	136.99	—
14	128.52	8.38
15	141.95	—
16	127.28	8.08
17	129.96	7.81
18	134.60	7.89

C^{13} and C^{15}

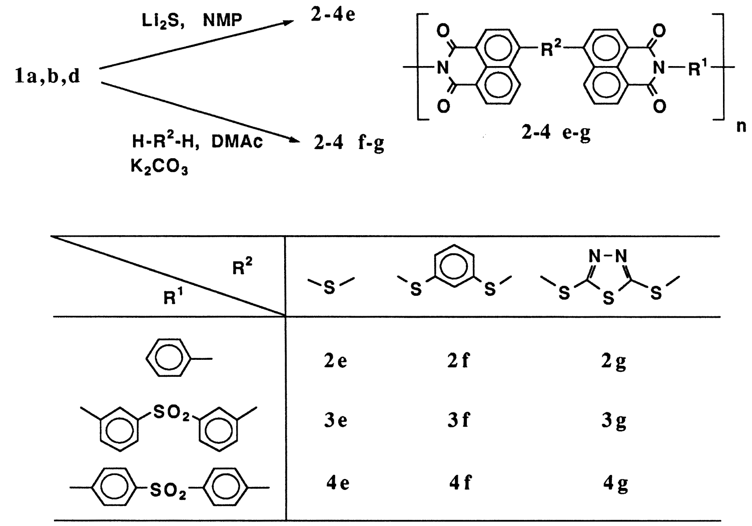
The deshielded quaternary carbon signals obtained at 141.9 and 137.0 ppm are due to the phenylene carbons C^{13} and C^{15} attached to heteroatoms, either N or SO_2 group. As a general rule, the chemical shifts of phenyl carbons are only slightly influenced by *meta* substituents [28]. This is illustrated by the close resonances of C–SO_2 in phenyl sulfone (141.2 ppm) [29] and 3-aminophenyl sulfone (142.1 ppm). Thus, conversion of amino group to imide will not influence peak due to *meta* carbon, i.e. the carbon attached to SO_2, drastically. This carbon (C^{15}) appears at 141.9 ppm in **1a**. This leaves the peak at 137.0 ppm, i.e. 5 ppm upfield, to C^{13}–N $<$. This assignment is confirmed by the spectrum of **1d**. This compound does not contain SO2 group and its spectrum does not exhibit any peak close to 140 ppm.

C^1 and C^8

C^1, with the Cl substituent in *para* position, is assigned to the more deshielded signal. This agrees with the spectrum of **1c**: in this compound, naphthyl moiety does not have a 4-Cl group. Only one $\underline{C}$–CO signal is found, the chemical shift of which, at 122.4 ppm, is very close to the value assigned to C8.

C^{18} and C^{16} (resp. H^{18} and H^{16})

From the spectrum of **1d**, the effect of 4-chloro-1,8-naphthalimido substituent on the ^{13}C n.m.r. chemical shift of benzene can be determined (1, *o*, *m*, *p*: + 7.4, + 0.6, + 0.6, + 0.2 ppm). Applying these substituent effects [28] to the ^{13}C chemical shifts of phenyl sulfone [29], in order to



Scheme 3.

calculate the chemical shifts of the phenylene group shifts in **1a**, a very good agreement is obtained between calculated and experimental values (Table 1), especially for C^{16} and C^{18} (ca ± 0.2 ppm). This allows the assignments of the attached protons H^{16} and H^{18} (Table 2).

The ^{13}C and ^{1}H n.m.r. studies therefore reveal that monomer **1a** is pure imide and not isoimide, nor a mixture of isoimide and imide. The same holds for models **1b–d**. The absorptions close to 1710 and 1670 cm^{-1} observed in the i.r. spectra of imides and polyimides derived from naphthalic anhydride [16,17,23,30] (1715 and 1673 cm^{-1} for **1a** and **1b**) must, therefore, be assigned to the naphthalimide structure and not to the naphthalisoimide one proposed by some authors [16,17].

The reactivity of aromatic chloro group towards nucleophilic substitution can be estimated through ^{13}C n.m.r. chemical shift of $\underline{C}$–Cl [31]. Reactivity towards nucleophiles increases as the electron density of the $\underline{C}$–Cl decreases, that is for more deshielded carbons. High reactivity was found for carbons with $\delta > 132.5$ ppm [31]. The $\underline{C}$–Cl ^{13}C n.m.r. chemical shift being 137.52 ppm for **1a** and 137.95 ppm for **1b**, good reactivities are expected for these two imide monomers with sulfur nucleophiles.

Table 3
Characterization of polymers **3** and **4**: inherent viscosity (η), glass transition temperature (T_g) and 5% and 10% mass loss temperatures ($T_{5\%}$ and $T_{10\%}$)

Polymer	η^a (dl/g)	T_g^b (°C)	$T_{5\%}^c$ (°C)	$T_{10\%}^c$ (°C)
3e	—[d]	234	445	495
4e	1.90	220	447	490
3f	—[d]	220	428	473
4f	1.30	210	385	445
3g	0.84	—[e]	442	474
4g	1.20	—[e]	353	422

[a] Determined in *m*-cresol at (0.25 g/dl) at 40°C.
[b] Determined by d.s.c. at 20°C/min (second heating curves).
[c] Determined by t.g.a. at 20°C under nitrogen.
[d] Not determined due to low solubility.
[e] Not detected.

3.2. Poly(thioether-imide-sulfones)

Poly(thioether-imide-sulfones) **3e** and **4e** were synthesized by the chloro displacement polymerization of imide-sulfones **1a** and **1b** in *N*-methylpyrrolidinone (NMP) using lithium sulfide as the sulfur source, at a temperature of 180°C for 4 h (Scheme 3).

Polymers **3f**,**g** and **4f**,**g** were synthesised by the nucleophilic substitution polymerization of **1a** or **1b** with 1,3-benzenedithiol and 2,5-dimercapto-1,3,4-thiadiazole (DMTD), respectively, using potassium carbonate as a base and dimethyl-acetamide (DMAc) as solvent (Scheme 3). Attempted nucleophilic polycondensation reactions of the imide monomers with the dipotassium salt of DMTD in NMP at 200°C yielded low-molecular weight compounds. Better results were obtained with DMAc, which is widely used as a solvent in the synthesis of polythioethers and polyether ketones [5,20].

The low values of elemental chlorine content indicate that the nucleophilic substitution has proceeded efficiently. The infrared spectra of all polymers show similar peaks as monomers **1a**,**b**, especially the peaks close to 1713 and 1674 cm^{-1}, characteristic of six-membered imides and those at 1580 cm^{-1} due to aromatic rings. The polymers do not contain any i.r. detectable thiol group, observable at 2550 cm^{-1}. From the inherent viscosity data presented in Table 3, it is clear that high molar mass polymers were formed. The values lie between 0.84 and 1.9 dl/g, which is remarkably higher than reported for other thioether-imide polymers [12].

All polymers were insoluble in $CHCl_3$ and THF. However, the polymers obtained from para substituted monomer **1b** (**4e–g**) exhibited good solubilities in common

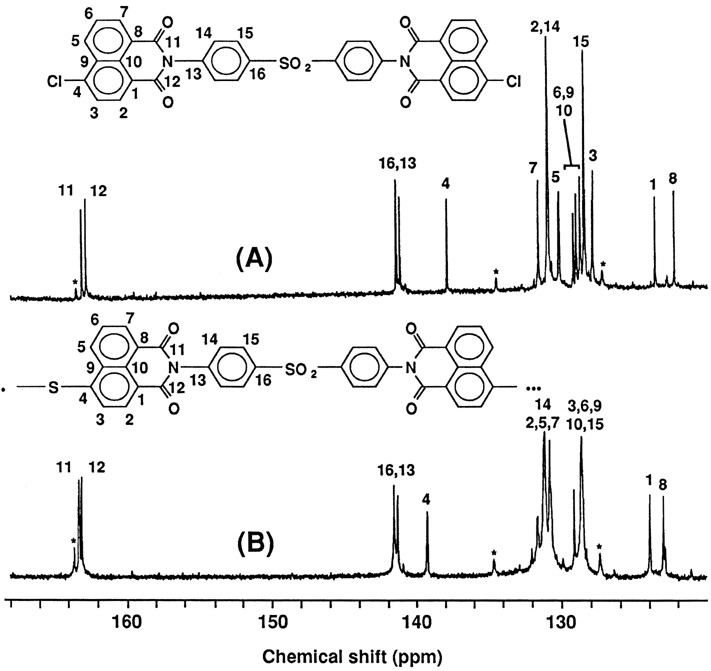


Fig. 4. ^{13}C n.m.r. spectra (62.9 MHz, NMP, external DMSO-d6, ref. TMS) of (A) monomer **1b**, (B) polymer **4e** (*, see text).

polar solvents (*m*-cresol, NMP, DMAc, DMF, DMSO), whereas polymers **3e** and **3f** obtained from *meta*-substituted monomer **1a** had only low solubility in these solvents. The results imply that the *meta*-substituted diamino diphenylsulfone moieties does not have any effect in increasing the solubility of the resultant polymer. This result is quite surprising as the kink in the diamines generally increase the solubility of the polyimide generated [32].

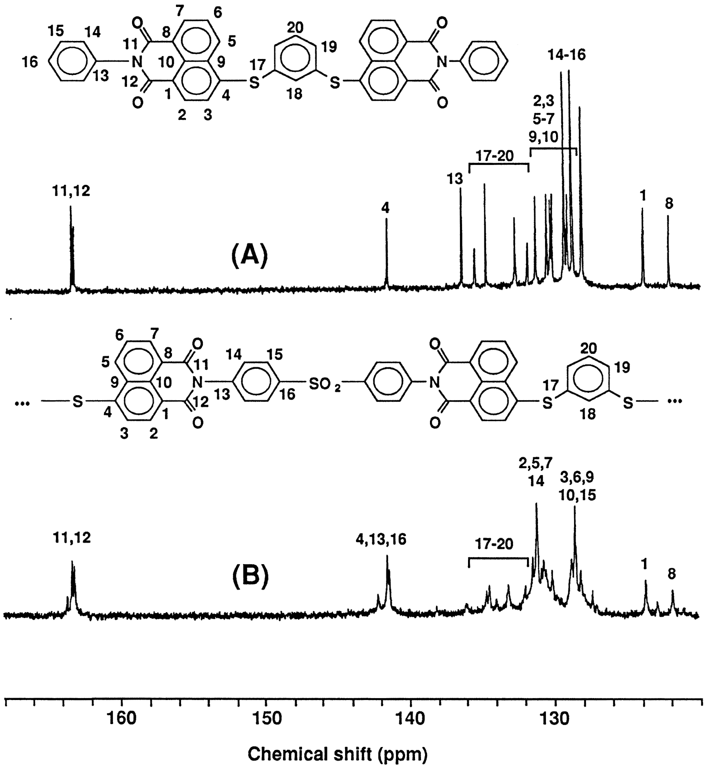


Fig. 5. ^{13}C n.m.r. spectra (62.9 MHz, NMP, external DMSO-d6, ref. TMS) of (A) model **2f**, (B) polymer **4f**.

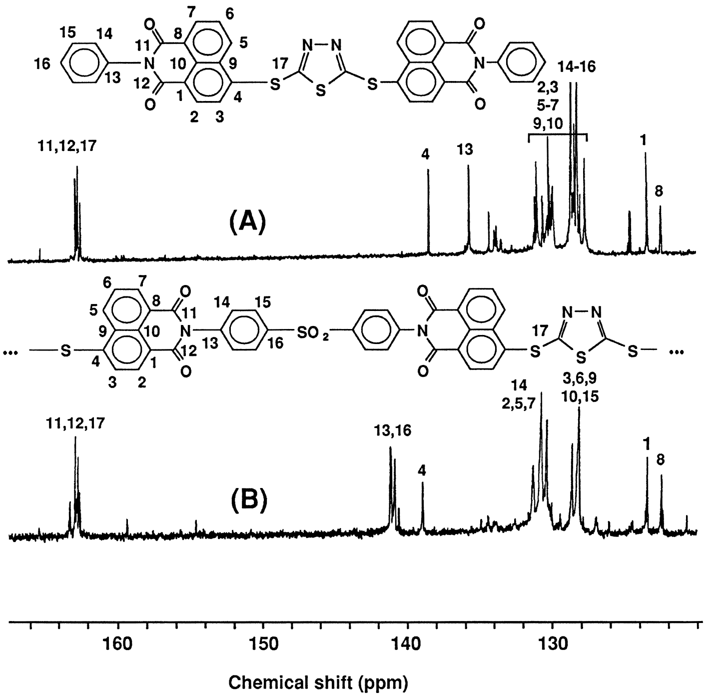


Fig. 6. ^{13}C n.m.r. spectra (62.9 MHz, NMP, external DMSO-d6, ref. TMS) of (A) model **2g**, (B) polymer **4g**.

Higher solubility in these solvents was observed for polymers **3g** and **4g** with respect to **3e**,**f** and **4e**,**f**. This may be attributed to the presence of polar thiadiazole groups in the former ones.

Though polyimides have been used in electronic industry as a high-cost polymers, the solution n.m.r. of these materials is not well documented, due to their insolubility. Recently several attempts have been made on the study of polymer chain mobility of soluble polyetherimides, polyketoneimides and polythioetherimides by n.m.r. spectroscopy [33,34]. However, the synthesis and n.m.r. characterization of polythioetherimides derived from dihalo compounds have not been described in literature and thus the corresponding side reactions as well as the C–S chemical shift have not been presented.

The n.m.r. spectra were assigned with the help of model compounds **2e–g** of similar structure (Scheme 3). From the spectra it is clear that nucleophilic substitution of chlorine has taken place with the sulfur nucleophile and generated polymers. For example, as presented in Fig. 4, the $\underline{C}$–Cl peak of monomer **1b** at 137.9 ppm has disappeared in polymer **4e** while a new peak is observed at 139 ppm, i.e. at the $\underline{C}$–S chemical shift of model compound 2e.

The presence of the same small unassigned peaks (starred peaks) in the spectra of **1b** and **4e** (Fig. 4) indicate that side reactions have occurred during imidation. On the other hand, no supplementary unassigned peaks appear in the spectrum of polymer **4e**, meaning that the polymerization proceeded quite nicely.

The spectrum of model compound **2f**, assigned from the spectra of starting compounds, shows that reaction between 1,3-benzenedithiol and 4-chloronapthalimide can proceed in the expected manner (Fig. 5A). The ^{13}C n.m.r. spectrum of polymer **4f** (Fig. 5B) is close to that of model **2f**, with naphthyl $\underline{C}$–S peak appearing close to 142 ppm and 1,3-dithiophenylene carbons in the 132–135 ppm region. However, the presence of unassigned peaks indicate that side reactions have taken place during the polymerization.

The reaction between 2,5-dimercapto-1,3,4-thiadiazole with model compound **1d** yields model compound **2g**. It is clear from the spectrum (Fig. 6A) that the $\underline{C}$–Cl to $\underline{C}$–S nucleophilic substitution has taken place, since the C4 peak has shifted from 137.9 to 139 ppm as discussed earlier. However, a number of unassigned peaks appear, specially at 125 ppm and in the 130 and 135 ppm regions. This indicates that the reaction was accompanied with side reactions. The same is noted for polymer **4g** (Fig. 6B) although the relative importance of the side reactions is somewhat lower. It should be noted, however, that the side reactions do not hinder the formation of high molecular weight polymer as shown by the inherent viscosity of 0.84 dl/g for **3g** and 1.20 dl/g for **4g**.

The evaluation of the thermal properties of all poly(thioether imide sulfones) was carried out by thermogravimetry (t.g.a.) and differential scanning calorimetry (d.s.c.).

The polymers do not exhibit any melting point below their decomposition temperature. They behave as amorphous compounds, a glass transition being observed around 220°C for polymers **3e**, **3f**, **4e** and **4f** (Table 3). Polymers obtained from monomer **1a**, with the *m*-phenylenesulfone group, show more distinct glass transitions compared to that obtained from their para homologue **1b**, but the value of T_g

does not vary much with the nature of the diamine. Polymers **3g** and **4g**, containing thiadiazole units, do not show any T_g below their onset of decomposition. This may be explained by the existence of inter-chain interactions, originating from the polar thiadiazole units, but also by the greater angle, ca. 150°, introduced in polymer chains by 2,5-disubstituted five-membered rings with respect to the angle of 120° introduced by 1,3-disubstituted aromatics. This increases the stiffness of polymer chains and, therefore, T_g.

Thermogravimetry results are given in Table 3. The decomposition of all these polymers was similar. Ten percent mass loss was obtained in the range 400–500°C, results quite higher than reported for naphthalene-imide-ether containing polymers [17]. In polymers of similar skeleton, viz **3** or **4**, the **3** series polymers obtained from bis(*m*-amino-phenyl)sulfone were found to be more thermally stable.

4. Conclusion

Three series of copoly(thioether-imide-sulfone) based on 1,8-naphthalimide, a six-membered imide, were synthesised by the reaction of *meta* or *para* bis(chloro-1,8-naphthalimido)diphenylsulfones with lithium sulfide or dithiol reactants. The dichloro imide-sulfone monomers were fully characterized and proved to be imides, and not isoimides or mixtures of the two. The $\underline{C}$–Cl and $\underline{C}$–S ^{13}C n.m.r. resonances were clearly assigned, and prove that the polymerization proceeded through the expected substitution of chlorine by the sulfur nucleophiles. Although the spectra reveal the occurrence of side reactions, specially in the case of the thiadiazole polymers, inherent viscosity measurements indicate that high molar mass polymers were formed. DMAc was found to be a better reaction medium for thioetherification reactions with dimercapto-terminated monomers, while NMP should be used for the reactions with lithium sulfide. The copolymers based on bis(4-aminophenyl)sulfone exhibited good solubility in polar solvents, better than that of polymers based on the *meta* derivative. All copolymers were amorphous and thermally stable compounds, with a 10% mass loss temperature in the 400–500°C range, that may find applications as soluble high-performance coatings.

Acknowledgements

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