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Synthesis and characterization of naphthalene-containing polythioamides

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New semi-aromatic polythioamides have been synthesized, based on aliphatic diamines and a new bis(dithioester) derived from 2,6-naphthalenedicarboxylic acid. Polythioamides were prepared by solution polycondensation at low temperature, in high yields and moderate to high inherent viscosities. The presence of naphthalene rings instead of benzene rings or aliphatic groups affected the thermal transitions in these polythioamides. By comparison with aliphatic or benzene polythioamides, polythioamides containing naphthalene revealed lower glass transition temperatures and a tendency to form liquid crystal mesophases. Noticeable solubility improvements were also observed. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: semi-aromatic polythioamides; liquid crystalline polythioamides; thioamidation)

INTRODUCTION

The synthesis of thiocarboxamides from dithioesters and aliphatic amines is a well-known reaction[1]. Levesque and Gressier have prepared many aliphatic polythioamides[2] and some aromatic and semi-aromatic polythioamides[3] from bis(dithioester)s and diamines. Synthesis are usually carried out in solution at low temperature (0–50°C). Compared to the homologous polyamides, polythioamides afford lower melting and glass transition temperatures[2,3]. Semi-aromatic and fully aromatic polythioamides were also obtained[4,5], often as low molecular weight samples.

Thioamidation kinetics have been investigated in solution for reaction between aliphatic amides and aliphatic mono- and bis(dithioester)s[6] as well as some aromatic bis(dithioester)s[5]. Thioamidation is very fast, highly specific and irreversible.

The goal of the present research was to design and prepare a novel family of polythioamides characterized by an alternating sequence of naphthalene bis(thiocarboxamide) units and flexible spacer groups containing even numbers of methylene units (*Figure 1*): their synthesis, study and properties have not been reported. Naphthalene was chosen as the bulky group because it offers good advantages concerning the stability and thermal resistance of the resulting polymer[7].

RESULTS AND DISCUSSION

Monomer **1** (*Scheme 1*) used for the synthesis of naphthalene-containing polythioamides was prepared from 2,6-naphthalenedicarboxylic acid **2** and trimethyl tetrathiophosphate **3**, according to the synthetic route shown in *Scheme 1*. This one-step synthesis gives high yields, so that monomer **1** could be obtained in considerable amounts. The method is a variation of the route described by Davy and others[8–13] for aliphatic and aromatic compounds bearing a monofunctional dithioester.

Parallel to the synthesis and purification of the monomer, we made an estimate of its structural characteristics. We were mainly interested in the reactivity of the functional groups, and in the influence of the molecular geometry on the accessibility of the nucleophiles to the functional group of **1** involved in the polythioamidation reaction.

Six polythioamides, **6a**–**f**, have been prepared by polycondensation of bis(dithioester) **1** and diamines **5** at 50–60°C in chloroform without catalyst according to *Scheme 2*. Polymer particles were formed from an initially homogeneous reaction mixture. Yields, inherent viscosities and glass transition temperatures of polythioamides **6a**–**f** are summarized in *Table 1*.

Good to high yields were obtained, and inherent viscosities lying in the range 0.70–1.08 $\mathrm{dl\,g^{-1}}$ were observed.

The structure and purity of the polythioamides **6** were confirmed in each case by ^{1}H, ^{13}C n.m.r., i.r. and u.v.-visible spectroscopy.

A first characterization of the chemical structures was made by n.m.r. spectroscopy. The absence of the methylthio singlet at 2.8 ppm, normally present in dithioester **1**, indicates that the reaction is complete. Compounds **6a**–**f** exhibit characteristic n.m.r. signals of polythioamides listed in the Experimental section and show good agreement with those determined from ^{13}C n.m.r. spectra. The assignments were based on the comparison of spectra from different copolymer samples. The assignments for the naphthalene carbons are described elsewhere[14,15]. The polythioamides **6a**–**f** structures are confirmed by ^{13}C n.m.r. shifts at *ca.* 196 ppm related to the thioamide functions. No dithioester thiocarbonyl signal (from some eventually remaining dithioester) could be observed near 228 ppm.

All polythioamides show characteristic i.r. absorption for the thioamide group: ν (KBr) at 3210 and 1530 $\mathrm{cm^{-1}}$.

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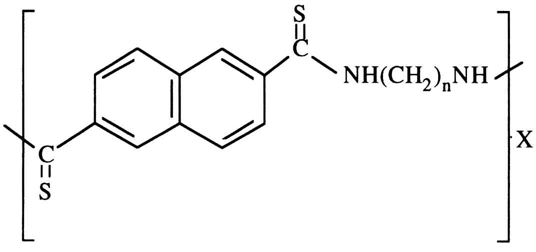
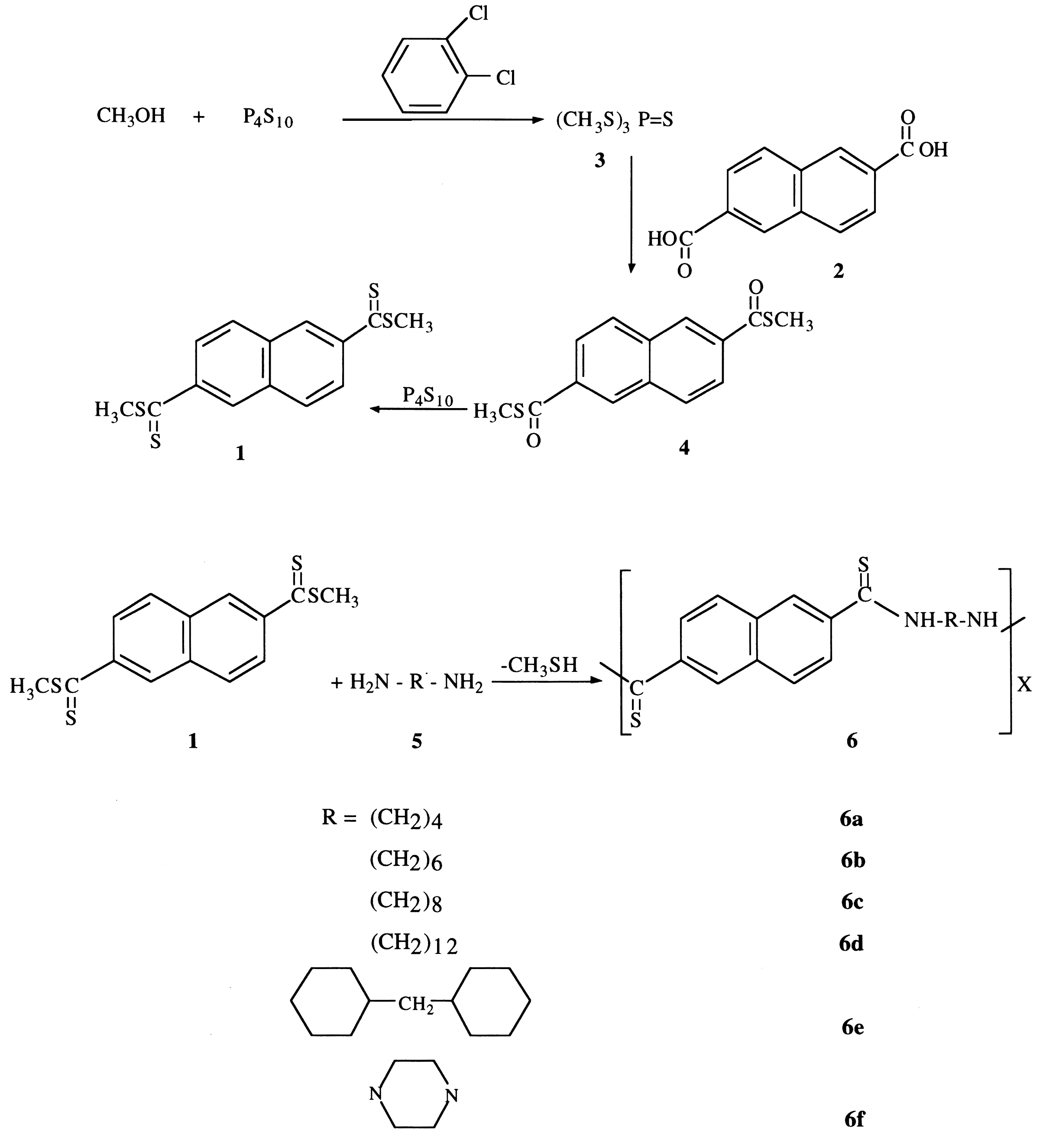
U.v.-visible spectra (DMF or DMSO) exhibit a maximum at 306–308 nm and 233–234 nm, and again the absence of absorptions at *ca*. 500 nm and *ca*. 338 nm confirms the complete thioamidation of bis(dithioester) **1** into polythioamides **6**.



A

Figure 1 Structure of polythioamides **A**

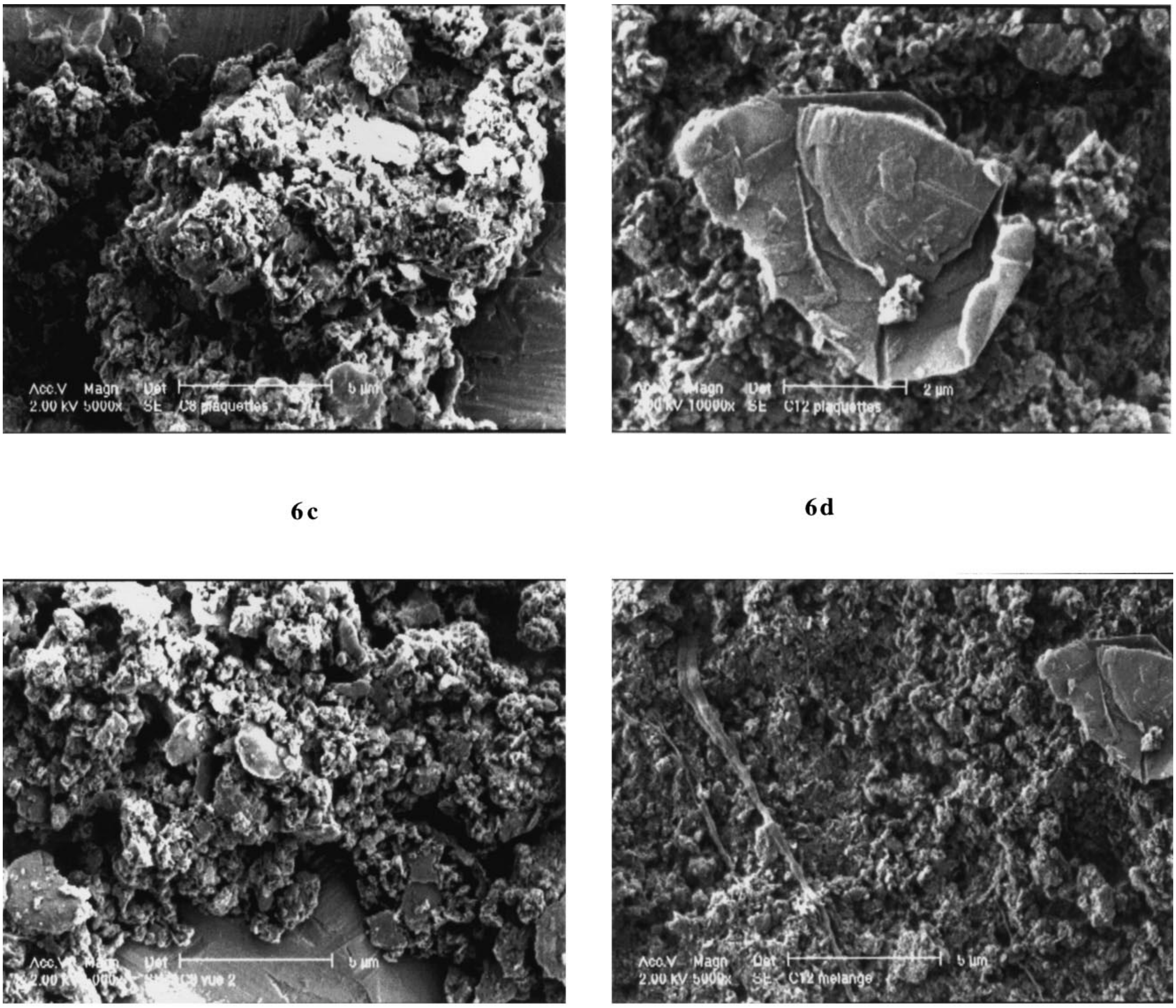
Although this kind of polymer synthesis involves the precipitation of polythioamide during reaction, the experimental conditions have similar effects as in the usual solution polycondensation. Fairly high-molecular weight polymers are obtained: this is of great importance in the case of low solubility or nearly insoluble polythioamide **6f**. Semi-aromatic polythioamides **6** were obtained as yellow powders. As can be seen from *Figure 2*, the particles of polythioamide **6d** are aggregates of smaller particles, characterized by a nearly equal size among larger plates, than those from polythioamide **6c**. The morphology of the amorphous polythioamide **6c** appears homogeneous at this microscopic observation scale (*Figure 2*): polymer **6c** is constituted by a multitude of smaller plates. It can be clearly seen that the augmentation of CH$_2$/NHC=S ratio increases the plate size, and diminishes the particle size of polythioamides.



Scheme 2 Synthesis of polythioamides **6** via dithioester aminolysis of dimethyl 2,6-naphthalenebis(dithiocarboxylate) **1** by diamines **5**

Table 1 Synthesis and characteristics of polythioamides **6** from bis(dithioester) **1** and diamines **5**

Polythioamides **6**	Diamines **5**	Reaction		Yields (%)	η_{inh} (dl g^{-1})	T_g (°C)
		Temp. (°C)	Times (h)			
6a	1,4-Diaminobutane	50	112	97	0.88	180
6b	1,6-Diaminohexane	50	112	83	0.90	151
6c	1,8-Diaminooctane	60	112	65	0.78	140
6d	1,12-diaminododexane	50	112	82	0.70	111
6e	4,4′-Diaminodicyclohexylmethane	60	192	41	1.08	245
6f	Piperazine	60	192	44	—	254



6c **6d**

6c **6d**

Figure 2 SEM photographs of polythioamides **6c** and **6d**

A characteristic difference between **6a**–**e**, on the one hand, and **6f**, on the other hand, is the extremely rapid precipitation of **6f** in polycondensation reaction.

As can be clearly seen from *Table 1* and *Figure 3*, the glass transition temperatures (T_g) follow the usual structural dependence: short methylene spacers lead to amorphous polymers, while the longer ones generate liquid crystal mesophases. In the series **6a**–**d**, the glass transition temperature decreases with the increase of the spacer length (*Figure 3*). This effect results from the increasing flexibility of the main chain. Therefore, in polythioamides **6e**,**f** the relative rigidity imposed on the polymer chain by the ring system leads to the higher transition temperatures.

A characteristic difference between series **6a**–**d**,**f** and **6e** concerns the melting temperature (T_m) (*Figure 4*). Only the polythioamide **6e** offers a behaviour which looks like a liquid crystalline one, although polymers **6a**–**d** and **6f** are amorphous. It is obviously a consequence of the varying sizes of the polymethylene spacer group in the main chain.

EXPERIMENTAL

All reactions were run under a positive nitrogen pressure. All materials and solvents were commercially available and they were used as received unless otherwise indicated.

^{1}H n.m.r. 60 and 250 MHz spectra were run on Varian EM 360 and Bruker AC 250 spectrometers with TMS as an internal reference. The products were dissolved in the mentioned solvent. Data are given in the following order: chemical shift in ppm, multiplicity (s, singlet; d doublet; t, triplet; q, quartet; hept, heptet; m, multiplet), coupling constant in Hz, assignment. ^{13}C n.m.r. spectra were determined at 20.15 MHz with a Bruker WP 80 SY spectrometer operating with broad band ^{1}H decoupling or a Bruker AC 250 spectrometer at 62.89 MHz, with TMS as an internal standard. The solvents used are indicated.

I.r. absorption spectra were recorded as liquid thin films or as solutions in $CDCl_3$ between NaCl plates or as solids in KBr pellets, on a Perkin-Elmer 257 i.r. spectrophotometer and a Pye-Unicam SP 3-100 or a Perkin-Elmer 16 PC FT-spectrometer. The mentioned i.r. absorptions were observed as strong bands in cm^{-1}. U.v.-vis spectra were executed on Perkin-Elmer λ 15 or Beckman DU-7. The products were dissolved in $CHCl_3$, DMSO, DMSO + LiCl or DMF.

Elemental analyses were performed by 'Service Central d'Analyse' of CNRS at Vernaison (France). The results were described as percentages.

Scanning electron microscopy of the polymers was performed on a SEM (Philips FEG XL 30) at an accelerating voltage of 10 kV.

*Synthesis of dimethyl-2,6-naphthalene bis(dithiocarboxylate) **1***

The bis(dithioester) **1** was prepared from the reaction of reagent **3** toward 2,6-naphthalenedicarboxylic acid **2** followed by the facile thionation of the resulting thiocarboxylic ester **4** by P_4S_{10} in 1,2-dichlorobenzene according to the procedures described by Davy and Metzner[11].

A stirred suspension of P_4S_{10} (4 equiv) (16.45 g, 37 mmol) and dry methanol (8.54 g, 266 mmol) in 1,2-dichlorobenzene (30 ml) was preheated at 40°C to initiate the reaction, then to 120°C and finally at the reflux temperature (178°C) for 10 min. The solution containing **3** was cooled at 100°C before addition of 2,6-naphthalenedicarboxylic acid (2.00 g, 9.25 mmol). The mixture was stirred and heated at 178°C for some minutes then allowed to cool gradually to 130°C. P_4S_{10} (8.22 g, 18.49 mmol) was introduced into the red mixture containing thiolester **4**.

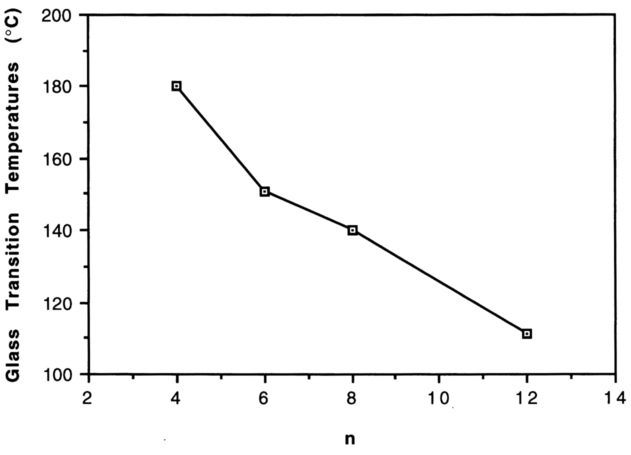


Figure 3 The dependence of glass transition temperatures on the length (n) of flexible spacer $(CH_2)_n$

The reaction mixture was stirred and heated again at 160°C for 20–30 min. The inorganic phosphorus compounds were precipitated by pouring the reaction mixture into an excess of cyclohexane (about 3 vol.) and removed by filtration. After solvent evaporation under reduced pressure, the bis(dithioester) **1** was purified by flash chromatography (silica gel), in cyclohexane. Yield = 30%, red powder, m.p = 188°C. ^{1}H n.m.r. ($CDCl_3$): 2.7 (6H, s, SCH_3), 8.0–8.5 (6H, m, H naphthalene); ^{13}C n.m.r. ($CDCl_3$): 20.86 (SCH_3), 125.60, 126.17, 129.79, 130.40 (CH=CH arom.), 143.72 (C=C arom.), 228.25 (C=S); u.v.-vis ($CHCl_3$): 338 ($\log \epsilon = 4.64$), 501 ($\log \epsilon = 2.91$); Anal. Calcd. for $C_{14}H_{12}S_4$: C, 54.51; H, 3.92; S, 41.57. Found: C, 54.54; H, 3.92; S, 41.56%.

*Synthesis of polythioamides **6a–f***

Typical polycondensation conditions. To a 50 ml three-necked, round-bottomed flask, equipped with a small magnetic stirring bar were placed **1** (1 g, 3.24 mmol) and diamine (1 equiv) in chloroform (5 ml). The mixture was subjected to nitrogen deaeration, which was continued during the polymerization. The reaction was carried out at 50–60°C under conditions indicated in *Table 1*. The precipitate formed and the resulting polymer solution was poured into the precipitant described below (mixture of acetone/water (1/1) or cyclohexane or methanol) then filtered and washed with acetone. The crude polythioamides formed was purified by reprecipitation at least once from DMSO using acetone as non-solvent, and dried *in vacuo*.

*Polythioamide **6a**.* Bis(dithioester) **1** (1 g, 3.24 mmol) and 1,4-diaminobutane (285.6 mg, 3.24 mmol) were used. Yield = 97%, yellow powder. ^{1}H n.m.r. (DMSO): 1.8 (4H, m, CH_2–CH_2), 3.7 (4H, m, NCH_2), 7.9–8.3 (6H, m, H arom.), 10.5 (2H, m, NH=CS); ^{13}C n.m.r. (DMSO): 38.77, 40.11, 40.35, 40.44 (CH_2, NCH_2), 125.57, 126.17, 128.36 (CH=CH arom), 132.60, 139.66 (C=C arom.), 197.29 (NC=S); i.r. (KBr pellets): 1530 (C–N), 3400 (N–H); u.v.-vis (DMSO): 234 ($\log \epsilon = 4.53$), 307 ($\log \epsilon = 4.25$); Anal. Calcd. for $(C_{16}H_{16}N_2S_2)_n$: C, 63.97; H, 5.37; N, 9.32; S, 21.34. Found: C, 64.16; H, 5.45; N, 9.22; S, 21.16%.

*Polythioamide **6b**.* The polymer **6b** was obtained from bis(dithioester) **1** (1 g, 3.24 mmol) and 1,6-diaminohexane (376.7 mg, 3.24 mmol) and 1,6-diaminohexane (376.7 mg, 3.24 mmol). Yield = 83%, yellow powder. ^{1}H n.m.r. (DMSO): 1.4–1.7 (8H, m, CH_2CH_2), 3.7 (4H, m, NCH_2), 7.8–8.2 (6H, m, H arom.), 10.5 (2H, m, NHC=S); ^{13}C n.m.r. (DMSO): 26.28, 27.06 (CH_2), 46.00 (NCH_2), 125.50, 126.15, 128.33 (CH=CH arom), 132.17, 139.13 (C=C arom.), 196.52 (NC=S); i.r. (KBr pellets): 1520 (C–N), 3220 (N–H); u.v.-vis (DMSO): 234 ($\log \epsilon = 4.15$), 307 ($\log \epsilon = 3.86$); Anal. Calcd. for $(C_{18}H_{20}N_2S_2)_n$: C, 65.82; H, 6.13; N, 8.53; S, 19.52. Found: C, 65.69; H, 5.97; N, 8.62; S, 19.71%.

*Polythioamide **6c**.* The reaction of bis(dithioester) **1** (1 g, 3.24 mmol) with 1,8-diaminooctane (467.4 mg, 3.24 mmol) gave the polythioamide **6c**. Yield = 65%, yellow powder. ^{1}H n.m.r. (DMSO): 1.2–1.8 (12H, m, CH_2), 3.8 (4H, m, NCH_2), 7.9–8.3 (6H, m, H arom.), 10.5 (2H, m, NHC=S); ^{13}C n.m.r. (DMSO): 26.57, 27.17, 28.72 (CH_2), 46.33 (NCH_2), 125.63; 126.27, 128.57 (CH=CH arom.), 132.70, 140.50 (C=C arom), 196.56 (NC=S); i.r. (KBr pellets): 1529 (C–N), 3309 (N–H); u.v.-vis (DMSO): 252 ($\log \epsilon = 4.63$), 305 ($\log \epsilon = 4.07$).

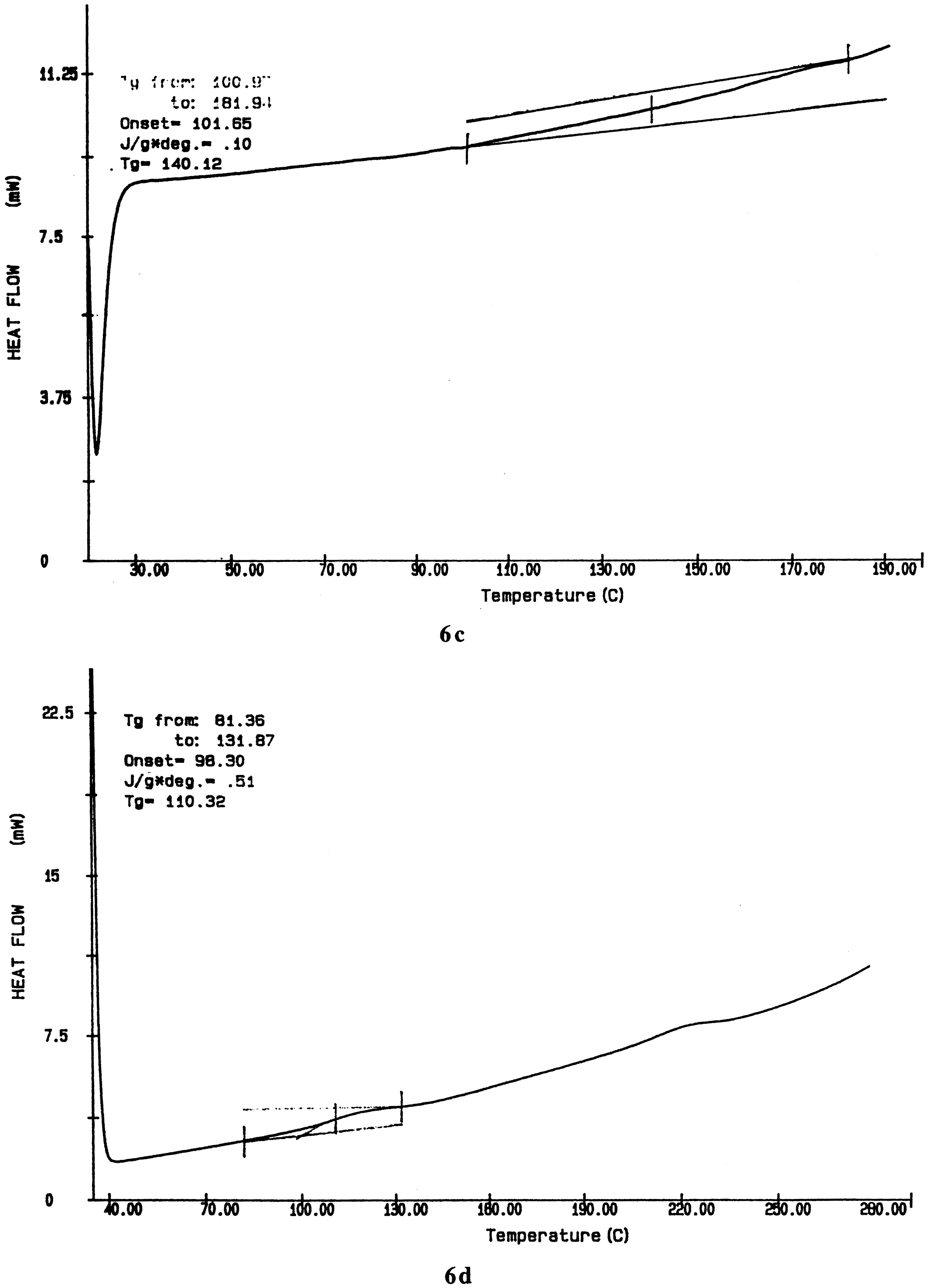


Figure 4 D.s.c. curves of polythioamides **6c** and **6d**

*Polythioamide **6d**.* The polythioamide **6d** was given by the reaction of bis(dithioester) **1** (1 g, 3.24 mmol) with 1,12-diaminododecane (649.2 mg, 3.24 mmol); the precipitant was cyclohexane. Yield = 82%, yellow powder. ^{1}H n.m.r. (DMSO): 1.2–1.8 (20 H, m, CH_2CH_2), 3.7 (4 H, m, NCH_2), 7.8–8.3 (6H, m, H arom.), 10.5 (2H, m, NHC=S); ^{13}C n.m.r. (DMSO): 26.48, 27.00, 28.68, 28.87 (CH_2), 46.09 (NCH_2), 125.72, 126.18, 128.25 (CH=CH arom.), 132.52, 139.28 (C=C arom.), 196.00 (NC=S); i.r. (KBr pellets): 1517 (C–N), 3300 (N–H); u.v.-vis (DMSO + 5%/LiCl): 235, 307. $T_g = 111°C$; $T_m = 237°C$.

*Polythioamide **6e**.* Bis(dithioester) **1** (1 g, 3.24 mmol) reacted with 4,4′-diaminodicyclohexylmethane (681.6 mg, 3.24 mmol) to provide the polythioamide **6e** (cyclohexane or methanol was used as precipitant). Yield = 41%, orange powder. ^{1}H n.m.r. (DMSO): 0.9–2.2 (18H, m, CH_2), 4.3–4.5 (2H, m, NCH), 7.9–8.2 (6H, m, H arom.), 10.3–10.4 (2H, m, NHC=S); i.r. (KBr pellets): 1513 (C–N), 3200, 3357 (N–H); u.v.-vis (DMSO + 5% LiCl): 233 ($\log \epsilon = 4.05$), 308 ($\log \epsilon = 3.77$).

*Polythioamide **6f**.* The polycondensation of bis(dithioester)

1 (1 g, 3.24 mmol) with piperazine (279.2 mg, 3.24 mmol) furnished the polymer **6f** (diethyl ether was used as precipitant). Yield = 44%, yellow powder. ^{1}H n.m.r. (DMSO): 2.9 (4H, m, NCH), 4.3 (4H, m, NCH), 7.4–8.7 (6H, m, H arom); i.r. (KBr pellets): 1510 (C–N), 3260, 3400 (N–H).

CONCLUSION

A convenient synthetic method has been developed to prepare dimethyl 2,6-naphthalene bis(dithiocarboxylate) **1**. Polycondensation of **1** with aliphatic diamines at low temperatures gives high-molecular weight semi-aromatic polythioamides.These polymers are generally amorphous and a good correlation between T_g and molecular structures is noted in the aliphatic series. The polythioamide from 1,12-diaminododecane could be a liquid crystalline polymer. This preliminary work has stimulated us to carry out further studies on liquid crystalline polythioamides with various other mesogenic hardening compounds.

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