Polymer Bulletin 21, 563–569 (1989)

Polymer Bulletin

Thermotropic poly(ester-β-sulfide)s

A new polymer series containing the *p*-phenylene di(*p*-oxybenzoate) unit

Giancarlo Galli[1], Emo Chiellini[1,*], Michele Laus[2], and Annino S. Angeloni[3]

[1]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, I-56100 Pisa, Italy
[2]Dipartimento di Ingegneria Meccanica, Università di Brescia, I-25060 Brescia, Italy
[3]Dipartimento di Chimica Industriale e Materiali, Università di Bologna, I-40136 Bologna, Italy

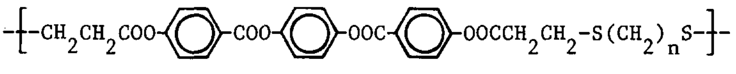
SUMMARY

A new series of thermotropic liquid-crystalline poly(ester-β-sulfide)s (HQH-n) was prepared which contained the p-phenylene di(p-oxybenzoate) (HQH) unit. The thermodynamic parameters of the nematic-isotropic melt phase transition were analyzed in terms of the number n of methylene groups in the sulfide spacer segment (n = 2 to 10). It is found that the flexible segment behaves principally as a diluent of the mesogen, in contrast with previously studied poly(ester-β-sulfide)s containing different mesogenic groups.

INTRODUCTION

The p-phenylene di(p-oxybenzoate) (HQH) unit is a very effective mesogenic core (1-3) which has been used in various molecular architectures of thermotropic liquid-crystalline polymers (4-9). Among these, side chain polymers with the mesogenic groups laterally attached to the polymer backbone have been shown to exhibit biaxial nematic phases (9). However, the HQH unit has never been incorporated into semiflexible liquid-crystalline polymers in combination with sulfide segments. Such systems constitute polymeric liquid-crystalline materials and may be taken as macromolecular precursors suitable for further transformations to new series of modified mesomorphic polymers.

Accordingly, we are investigating liquid-crystalline poly(ester-β-sulfide)s derived from various mesogenic groups, including p-oxybenzoate diads and triads (10-14). In the present paper we report on the liquid-crystalline properties of a series of poly(ester-β-sulfide)s (HQH-n) consisting of the phenylene di(p-oxybenzoate) core and sulfide spacers of various lenghts (n = 2 to 10):



HQH-n

EXPERIMENTAL

Synthesis of precursors

4-(benzyloxycarbonyloxy)benzoic acid (2): 88.7g (0.52mol) of benzyl chloroformate were added dropwise at 0°C to 900ml of a 1M NaOH solution containing 60.0g (0.43mol) of 4-hydroxybenzoic acid (1). After 2hr, the mixture was poured into 1.5l of 2M HCl. The precipitate was filtered and crystallized

---

[*] To whom offprint requests should be sent

from acetone/water (1:1 by volume): m.p.181-182°C; yield 90%.

1,4-phenylene di(4-benzyloxycarbonyloxy)benzoate (4): A solution of 53.8g (0.20mol) of 2 in 200ml of 1,2-dichloroethane and 18ml (0.25mol) of $SOCl_2$ was heated at reflux for 2hr and then dried under vacuum. The acid chloride 3 formed was dissolved in 50ml of 1,2-dichloroethane and added dropwise to a solution of 10.0g (0.09mol) of hydroquinone and 57ml of triethylamine in 250 ml of 1,2-dichloroethane. After 2hr at reflux, the reaction mixture was cooled, filtered and the organic phase was washed with water and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the solid obtained was crystallized from toluene: m.p.192°C; yield 84%.

1,4-phenylene di(4-hydroxybenzoate) (5): A suspension of 25g (0.04mol) of 4 and 2.5g of 5% Pd-C in 200ml of tetrahydrofuran was hydrogenated in a Parr apparatus at 2atm pressure till no more hydrogen was absorbed (about 3hr). The mixture was filtered and the solution dried under vacuum. Diphenol 5 was used without any further purification: m.p.320°C (dec.); yield 100%.

1,4-phenylene di|4-(acryloyloxy)benzoate| (6): 12ml (0.14mol) of freshly distilled acryloyl chloride were added dropwise to a solution of 17.0g (0.05 mol) of 5, 67ml of triethylamine, and 0.1g of 2,6-di-t.butyl-4-methylphenol in 100ml of anhydrous tetrahydrofuran at 0°C. After reacting 30min at room temperature, the mixture was filtered and dried under vacuum. The crude product was repeatedly crystallized from toluene: m.p.151°C; yield 70%.

^1H-NMR (DMSO-d_6): δ (in ppm from TMS) = 8.2 (d, 4H, oxybenzoate); 7.5 (d, 4H, oxybenzoate); 7.4 (s, 4H, hydroquinone); 6.7-6.0 (m, 6H, vinyl).

Polymerization experiments

In a typical polymerization reaction, a solution of 1.00g (2.17mmol) of 6 in 50ml of anhydrous dioxane was added dropwise over 60min to a solution of 0.38g (2.17mmol) of 1,8-octanedithiol (n = 8), 1ml of triethylamine and 0.1g of 2,6-di-t.butyl-4-methylphenol in 200ml of the same solvent. The mixture was let to react at room temperature for 2 days and at 60°C for 30min. The polymeric product was then precipitated into petroleum ether and purified by several precipitations from dioxane solution into petroleum ether. Yield 95%.

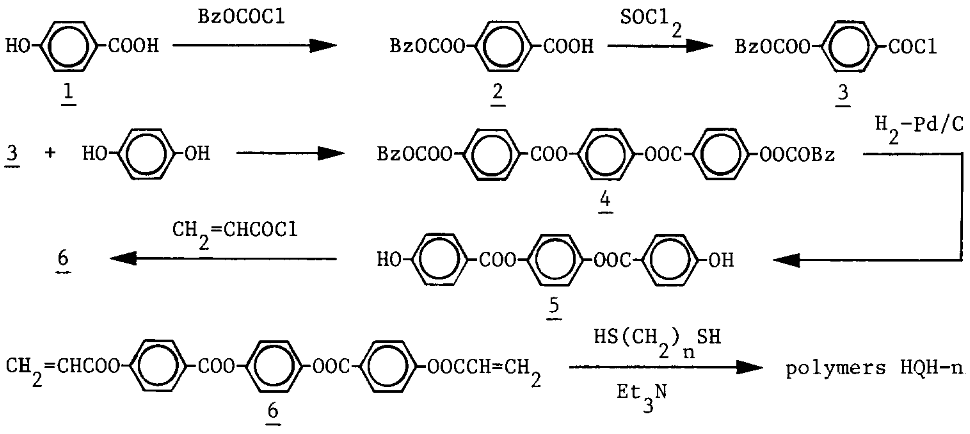
Physicochemical characterizations

Differential scanning calorimetry (DSC) analysis was made with a Perkin-Elmer DSC-2 apparatus at a heating/cooling rate of 20K/min under dry nitrogen flow. Whenever possible (see Tables I and II), the transition temperatures refer to samples crystallized from the isotropic melt and were taken for polymers as corresponding to the maximum in the relevant enthalpic peaks, while for monomeric precursors they corresponded to the intercept on the baseline. The enthalpy changes were determined from the integrated areas using indium standard samples for calibration, and were referred to one mole of repeating unit (r.u.). Observations of optical textures were performed with a Reichert Polyvar polarizing microscope equipped with a Mettler FP-52 hot stage.

RESULTS AND DISCUSSION

Polymers HQH-2 to HQH-10 were prepared by a Michael-type polyaddition reaction of dithiols of varying length (n = 2 to 10) to the diacrylate of 1,4-phenylene di(4-hydroxybenzoate) (6), in the presence of triethylamine as a catalyst, according to Scheme 1. This nucleophilic polyaddition reaction

SCHEME 1. Synthetic route for the preparation of polymers HQH-n



typically goes to completion in one-two days at room temperature (12), but in the present case the temperature was raised to 60°C in order to allow the polymerization to occur mostly under homogeneous conditions. Nearly quantitative yields were obtained in all experiments, and the polymers were soluble in hot DMSO and DMF, higher homologues ($n > 5$) also being soluble in dioxane. Inherent viscosity values of the polymer samples were in the range 0.30 to 0.80dl/g in p-chlorophenol/chloroform mixture (1:1 by weight).
All polymers exhibit liquid-crystalline properties, as summarized in Table I. The DSC melting transitions are generally structured in several endothermic components, but in no sample could they be associated to the onset of smectic phases, as was tha case of other HQH-containing main chain polymers (4,15). The melting temperatures, taken as corresponding to the maximum of the higher temperature endotherm, vary in an irregular way on changing the number n of methylene groups in the spacer segment (Figure 1). Microscopy observations of optical textures with numerous defects such as dark brushes or schlieren, disclination points and inversion walls clearly indicate the the mesophase is nematic (16).
The transition from the nematic phase to the isotropic liquid could not be studied accurately in lower homologues of the series with $n < 5$ due to thermal degradation, and the quoted temperatures may represent a lower bound. The isotropization temperature greatly decreases on lengthening the flexible segment from $Ti \approx 598$ K to $Ti = 511$ K and the mesophasic range narrows from ≈ 90 K to 40 K for polymers with $n = 2$ and $n = 10$, respectively (Figure 1). For the higher homologues ($n \geqslant 5$), the decrease in Ti is steeper for polymers with odd-numbered spacers, while it is less marked for polymers incorporating spacer segments with even values of methylene units. On cooling, the crystallization process is supercooled and the mesophase spans a much wider temperature range (60 K to 170 K).

The isotropization enthalpy and entropy changes, ΔHi and ΔSi in Table I, also show an overall descending trend with increasing number n, which is more pronounced for the former. Within the range of spacer lengths examin-

TABLE I. Liquid-crystalline properties of thermotropic poly(ester-β-sulfide)s HQH-n containing the p-phenylene di(p-oxybenzoate) mesogen

Polymer	n	η_{inh} [a] dl/g	Tm [b] K	Ti [b] K	ΔHi kJ/mol	ΔSi J/mol·K	Tc [b] K
HQH-2	2	0.37	507	598 [c]	nd [c]	nd [c]	nd [c]
HQH-3	3	0.39	497	595 [c]	nd [c]	nd [c]	nd [c]
HQH-4	4	0.35	498	590 [c]	nd [c]	nd [c]	nd [c]
HQH-5	5	0.46	495	576	3.3	5.7	404
HQH-6	6	0.62	478	551	4.3	7.8	421
HQH-7	7	0.38	468	542	3.8	7.0	436
HQH-8	8	0.80	478	528	4.2	8.0	447
HQH-9	9	0.30	472	510	2.7	5.2	442
HQH-10	10	0.31	470	511	3.7	7.2	450

a) Inherent viscosity, in p-chlorophenol/chloroform (1:1 by weight) at 30°C (c = 1.00g/dl). b) Phase transition temperatures, by DSC at a scanning rate of 20K/min: Tm, melting; Ti, nematic-isotropic; and Tc, crystallization temperatures. c) With partial polymer decomposition.

ed, we note that even members exhibit slightly higher values of the thermodynamic parameters than adjacent odd members (Figure 2). This results in a somewhat irregular zig-zag alternation with varying length of the flexible spacer, and indicates a better tendency of the even homologues to stabilize the nematic mesophase (17,18), as is well established in a number of thermotropic liquid-crystalline polymers (14,19,20). However, the low values and weak oscillations of ΔSi with parity of n suggest that the sulfide spacers do not provide a significant conformational contribution at the elevated temperatures of the nematic-isotropic liquid transition. Consistently, the depression in Ti with increasing length of the flexible segment can be attributed essentially to a large decrease in enthalpy which overrides the effect of the decrease in entropy.

The marked tendency of the HQH molecular system to give rise to liquid-crystalline (nematic) properties has been correlated to its strong dipolar character, resulting from electron donation by the oxygen to conjugated ester carbonyl of the oxybenzoate group (2,3). This ability is also recognized in low molar mass precursors 4, 5, and 6, whose mesomorphic properties (Table II) one would not have simply anticipated. Above melting, all compounds exhibit a nematic phase, but the liquid-crystalline behavior of diacrylate monomer 6 could not be fully characterized because of concomitant polymerization at high temperatures, nor was it possible to investigate

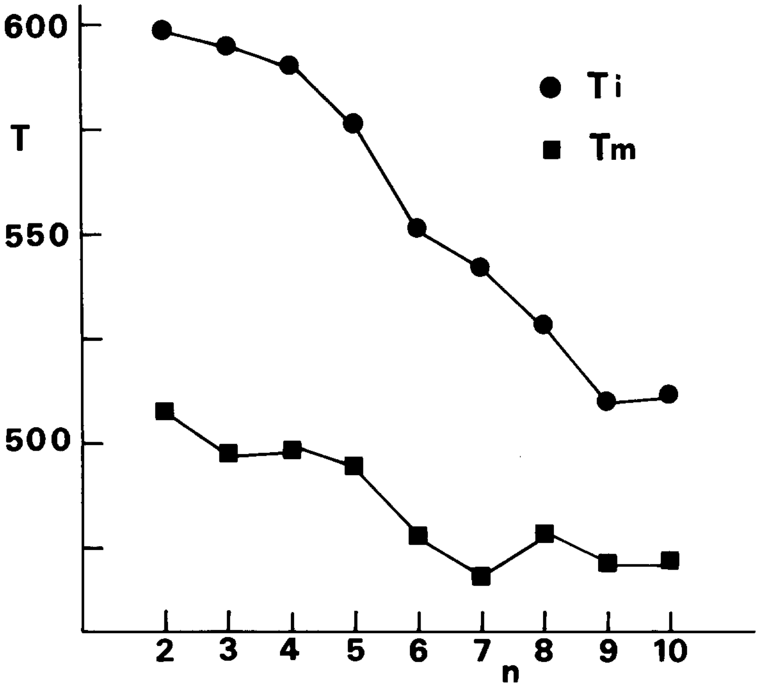


FIGURE 1. Variation of phase transition temperatures, Tm and Ti (in K), as function of the number n of methylene units in the sulfide spacer of polymers HQH-n

TABLE II. Liquid-crystalline properties of low molar mass precursors <u>4</u>-<u>6</u> of polymers HQH-n

Precursor	$Tm^{a)}$ / K	$Ti^{a)}$ / K	ΔHi / kJ/mol	ΔSi / J/mol.K
<u>4</u>	465	495	1.6	3.2
<u>5</u>	≈ 593	$> 630^{b)}$	$nd^{b)}$	$nd^{b)}$
<u>6</u>	424	$454^{c)}$	$nd^{c)}$	$nd^{c)}$

a) Phase transition temperatures, by DSC at a scanning rate of 20K/min.
b) With extensive decomposition.
c) With partial polymerization.

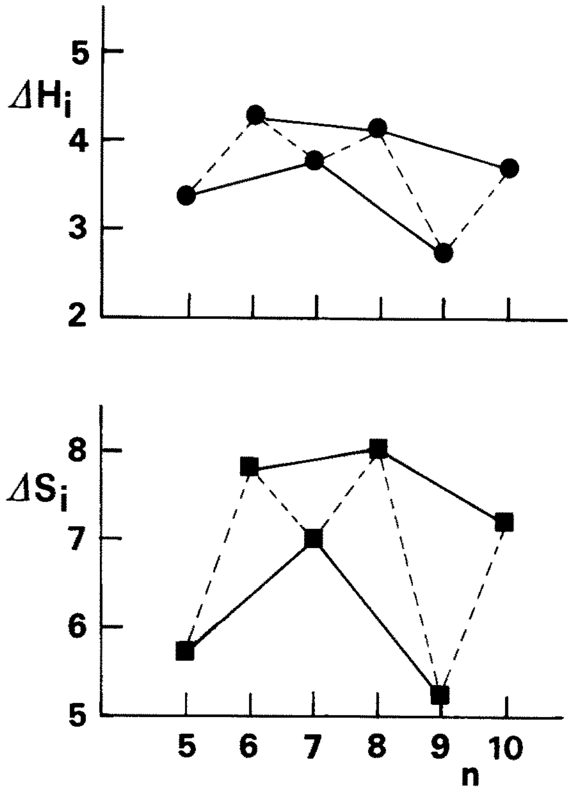


FIGURE 2. Variation of isotropization enthalpy, ΔHi (in kJ/mol), and isotropization entropy, ΔSi (in J/mol·K), as function of the number n of methylene groups in the sulfide spacer of polymers HQH-n

diphenol 4 because of extensive thermal degradation (21). However, it is pertinent to note that this last precursor is one of a few known examples of mesomorphic diphenols (21,22).

CONCLUSIONS

The *p*-phenylene di(*p*-oxybenzoate) unit can be inserted into thermotropic semiflexible poly(ester-β-sulfide)s to produce nematic mesophases which consistently possess a great thermal stability. The spacer segment, including two sulfide moieties, principally acts as a diluent of the mesogenic unit. This effect contrasts what is found with other poly(ester-β-sulfide)s containing *p*-oxybenzoate diads (14), in which the flexible segments serve to enhance intermolecular interactions and propagate intramolecularly the orientational order in the nematic mesophase.

ACKNOWLEDGMENT

The authors wish to thank the Ministero Pubblica Istruzione of Italy for financial support of the work.

REFERENCES

(1) M.J.S.Dewar, J.P.Schroeder, J.Org.Chem., 30, 2296 (1965).
(2) M.J.S.Dewar, R.S.Goldberg, J.Org.Chem., 35, 2711 (1970).
(3) J.P.Schroeder, D.W.Bristol, J.Org.Chem., 38, 3160 (1973).
(4) L.Strzelecki, D. vanLuyen, Eur.Polym.J., 16, 299 (1980).
(5) S.Antoun, R.W.Lenz, J.I.Jin, J.Polym.Sci., Polym.Chem.Ed., 19, 1901 (1981).
(6) Q.F.Zhou, H.M.Li, X.D.Feng, Macromolecules, 20, 233 (1987).
(7) S.Berg, V.Krone, H.Ringsdorf, Makromol.Chem., Rapid Commun., 7, 387 (1986).
(8) B.Valenti, V.Trefilletti, F.Silanus, G.Costa, Mol.Cryst.Liq.Cryst., 155, 511 (1988).
(9) F.Hessel, H.Finkelmann, Makromol.Chem., 189, 2275 (1988).
(10) G.Galli, M.Laus, A.S.Angeloni, P.Ferruti, E.Chiellini, Eur.Polym.J., 21, 727 (1985).
(11) A.S.Angeloni, M.Laus, E.Burgin, G.Galli, E.Chiellini, Polym.Bull. (Berlin), 13, 131 (1985).
(12) E.Chiellini, G.Galli, A.S.Angeloni, M.Laus, R.Pellegrini, Liq.Cryst., 2, 529 (1987).
(13) M.Laus, V.Milanesi, A.S.Angeloni, G.Galli, E.Chiellini, Polymer Commun., 28, 82 (1987).
(14) G.Galli, E.Chiellini, M.Laus, A.S.Angeloni, Macromolecules, in press.
(15) C.K.Ober, T.L.Bluhm, Polym.Bull.(Berlin), 15, 233 (1986).
(16) D.Demus, L.Richter, Textures of Liquid Crystals, Verlag Chemie, Weinheim, 1978.
(17) A.Abe, Macromolecules, 17, 2280 (1984).
(18) D.Y.Yoon, S.Bruckner, W.Volksen, J.C.Scott, A.C.Griffin, Faraday Discuss.Chem.Soc., 79, 41 (1985).
(19) A.Blumstein, O.Thomas, Macromolecules, 15, 1264 (1982).
(20) A.Roviello, A.Sirigu, Makromol.Chem., 183, 895 (1982).
(21) D.C.Schroeder, J.P.Schroeder, J.Am.Chem.Soc., 96, 4347 (1974).
(22) See for instance: H.K.Hall, Jr., T.Kuo, R.W.Lenz, T.M.Leslie, Macromolecules, 20, 2041 (1987) and references therein.

Accepted March 22, 1989 C