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Thermotropic Liquid Crystalline Poly(ester β-sulfide)s Based on Twin Hexamethylene-Spaced *p*-Oxybenzoyl Diads

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ABSTRACT: A series of poly(ester β-sulfide)s, 6S*n*, has been prepared by reacting the mesogenic hexamethylene bis[4-[[4-(acryloyloxy)benzoyl]oxy]benzoate] (1) with α,ω-alkanedithiols with a different number *n* of methylene units (*n* = 2-10). All of the polymers exhibit a nematic phase whose stability depends on the length of the dithiol segment. The nematic phases are enantiotropic with the only exception being that of the last term of the series, for which monotropic character has been detected. Onset and isotropization temperatures of the mesophase show a pronounced even-odd alternation that also holds for the isotropization entropy. A detailed study of the dependence of thermal properties upon the molecular weight is reported and indications are provided on their practical independence of the molecular weight at $\overline{DP}_n \geq 4$-5.

Introduction

Polymers in which rigid anisotropic moieties and flexible units are incorporated along the main chain backbone can exhibit liquid crystalline behavior in the melt.[1,2] The mesogenic units, which normally contain aromatic structures, introduce both limited flexibility and anisotropic interactions. However, as the mesogenic groups form part of the main chain, the polymer molecule must adopt a configurational packing whose features define the structure, the symmetry, and the stability of the mesophase. The strong overlap between the polymeric and the mesomorphic properties of the single mesogens leads to large intra- and intermolecular interactions affecting not only the rigid but also the flexible part of the repeating units in semiflexible systems.[3,4]

At the molecular level, the conformationally flexible segments can propagate intramolecularly, via the pattern of rotational states, the orientational correlation from a rigid group to the successive one. In turn, the intermolecular ordering of rigid groups, originated by the orientational and eventually positional anisotropic potential, may impose specific constraints on the flexible spacers, thus altering the statistical weight of their configurations established in the isotropic phase.[5-7] Consequently, the overall mesophase properties depend on the critical interplay between the order of the mesogenic units and the conformational changes induced by the local environment on the flexible spacer. They may be extremely sensitive to even subtle structural modifications on both the rigid and the flexible components of the repeat units.

With the objective of gaining a better insight into the control exerted by the structural factors on the onset and stability of the liquid crystalline state, a systematic investigation[8-14] was undertaken concerning the thermotropic behavior of different series of functional liquid crystalline semiflexible polyesters. Among them a series of poly(ester β-sulfide)s of general structure I was prepared by reacting mesogenic diacrylates with α,ω-alkanedithiols. Generally,

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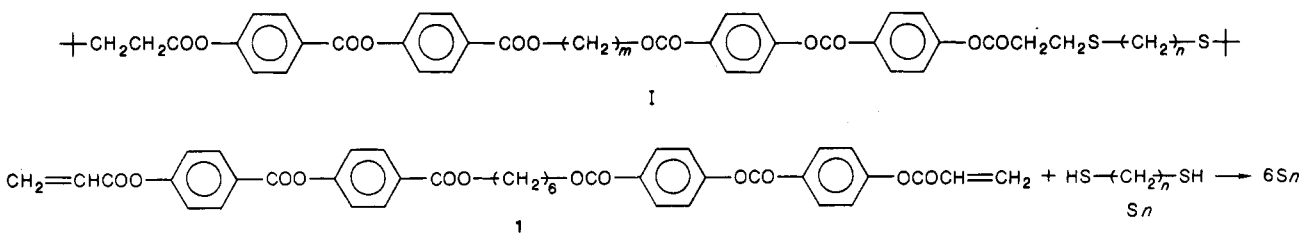

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they are characterized by *p*-oxybenzoyl diads interconnected by linear aliphatic chains of variable length (m = 6–10, 12) and linear aliphatic dithiols Sn comprising a variable number n of methylenic units (n = 2–10). For convenience they are grouped in series designated as mSn.

By allowing independent variations in either flexible spacer, a large variety of mesomorphic polymers was obtained. In the present paper we report on the synthesis and characterization of poly(ester β-sulfide)s 6Sn, with n being between 2 and 10.

Experimental Section

Hexamethylene bis[4-[[4-(acryloyloxy)benzoyl]oxy]benzoate] (1) (T_m = 418 K, T_i = 450 K) was prepared as previously described.[15]

Commercial α,ω-dithiopolymethylenes Sn (n = 2–6, 8–10) were purified by distillation under vacuum and treated under nitrogen atmosphere. 1,7-Heptanedithiol (S7) (bp 107–112 °C/20 mm, yield 58%) was prepared from 1,7-heptanediol according to the procedure described for the preparation of (*R*)-3-methyl-1,6-hexanedithiol.[12]

Poly(ester β-sulfide)s 6S2–6S10 were prepared by the following experimental procedure used for sample 6S2 as a typical example.

Diacrylate 1 (2.00 g, 2.8 mmol) and 1,2-ethanedithiol (S2) (0.26 g, 2.8 mmol) were dissolved in 60 mL of anhydrous dioxane with 1 mL of triethylamine and 0.1 g of 2,6-di-*tert*-butyl-4-methylphenol. The reaction mixture was stirred at 60 °C for 24 h and then poured into 300 mL of *n*-hexane. The coagulated polymer product was purified by repeated precipitations from chloroform solution into *n*-hexane (yield 95%).

^{1}H NMR ($CDCl_3$) δ (in ppm from TMS) 8.4 (d, 4 H, Ar), 8.2 (d, 4 H, Ar), 7.4 (d, 8 H, Ar), 4.4 (t, 4 H, OCH_2), 3.0 (s, 8 H, $COCH_2CH_2S$), 2.6 (s, 4 H, CH_2S), 1.2–1.8 (m, 8 H, $-(CH_2)_4-$).

^{13}C NMR ($CDCl_3$) δ (in ppm) 169.7 (3), 165.8 (13), 163.7 (8), 154.8 (4), 154.4 (9), 131.8 (6), 131.2 (11), 128.1 (12), 126.7 (7), 121.8 (5), 121.7 (10), 65.0 (14), 35.0 (1), 32.2 (17), 28.6 (15), 26.9 (2), 25.7 (16). The chemical shifts were referenced to the central peak of the chloroform-d_1 triplet (77.0 ppm from TMS). Numbers in parentheses represent assignments to carbon atoms as reported in Figure 1.

Polymer samples with different molecular weight 6S3(a)–(d) and 6S4(a)–(f) were obtained by using appropriate ratios of the reagents in the feed mixture. The diacrylate/dithiol mole ratios employed were 2.0 for sample 6S3(a), 1.5 for 6S3(c), 1.2 for 6S3(d), 2.0 for 6S4(a), 1.5 for 6S4(b), 1.3 for 6S4(c), 1.1 for 6S4(d), and 1.05 for 6S4(e). In all cases, after the polymerization was completed, an excess of methanethiol was added to the reaction mixture. The end-capped polymeric products were then precipitated into *n*-pentane and washed several times with the same solvent. Oligomers 6S3(a) and 6S4(a) were dissolved in boiling dioxane solution, which by cooling to room temperature gave rise to soluble fractions 6S3(a1) and 6S4(a1) and to insoluble fractions 6S3(a2) and 6S4(a2), respectively.

Samples 6S3(b), 6S3(e)–(h), 6S4(f), and 6S4(g) were obtained by fractional precipitation of crude polymer samples 6S3 and 6S4 prepared under stoichiometric conditions with chloroform/diethyl ether as the solvent/nonsolvent pair, using the experimental apparatus described in ref 16, as follows. A dilute solution of 10.0 g of polymer in 1 L of chloroform was poured in a 2-L fractionation vessel at 30 °C. Diethyl ether (200 mL) was added dropwise to the solution under vigorous stirring while a stream of nitrogen was conducted into the system. The vessel was then heated at 50 °C and, after homogeneity was reached, stirring was stopped. The system was cooled down slowly to the initial temperature and allowed to settle for 24 h. The polymer-rich phase was separated and evaporated under vacuum. The fractionation cycle was continued by addition of successive fresh portions of diethyl ether. Fractions of 1.5–2.0 g were thus typically recovered.

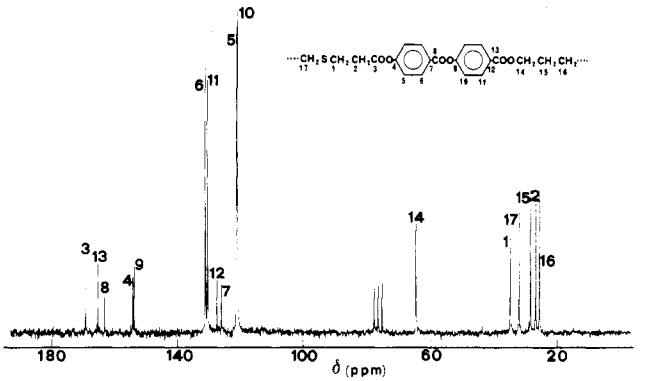


Figure 1. ^{13}C NMR spectrum of poly(ester β-sulfide) 6S2 (only half of the symmetrical repeating unit is reported).

Physicochemical Characterizations. Intrinsic viscosity measurements were performed in chloroform at 30 °C.

Average molecular weights of polymers were determined by gel permeation chromatography by a liquid chromatograph, consisting of a Waters 590 pump, a Waters U6K injector, and a Waters R-401 spectrophotometric detector, equipped with a Shodex KF-804 column. Monodisperse polystyrene samples (Shodex) were used for calibration by universal standard methods. No corrections to the GPC spectra for the axial spreading were applied in consideration of the relatively short retention times of oligomer samples.[17]

NMR spectra were recorded by using a Varian XL-100 spectrometer in $CDCl_3$ solutions.

Differential scanning calorimetry analyses were carried out under dry nitrogen flow on polymer samples (8–12 mg) by a Perkin-Elmer DSC-2 calorimeter. In all cases the maximum in DSC enthalpic peaks, with heating/cooling rate of 10 K/min, was taken as the phase transition temperature. Indium and tin standards were employed for temperature calibration, while indium reference samples were used for enthalpy evaluation.

Texture observations were performed on polymer films between glass slides without any previous treatment, by means of a Reichert Polyvar microscope equipped with a programmable Mettler FP52 heating stage at a scanning rate of 10 K/min.

X-ray diffraction measurements were performed in a transmission mode by means of a conventional X-ray powder diffractometer. The Ni-filtered Cu Kα radiation (λ = 1.54 Å) was used.

Results and Discussion

Synthesis. Polymers 6S2–6S10 were obtained by a stepwise polymerization reaction involving a base-catalyzed Michael-type polyaddition of dithiols Sn to the activated double bonds of diacrylate 1. The polymerization reactions were carried out at room temperature in dioxane under strictly anhydrous conditions. Triethylamine was employed as a nucleophilic catalyst. The polymer samples obtained with yields greater than 90% were characterized by intrinsic viscosity values of 0.27–0.56 dL/g (chloroform at 30 °C), to which average molecular weights of 9×10^3–1.8×10^4 Da (Da = dalton) correspond (Table I).

The structure of polymers was confirmed by ^{1}H NMR and ^{13}C NMR spectra. The ^{13}C NMR spectrum, with relevant assignments, of polymer 6S2 is presented in Figure

Table I
Molecular Weight Characteristics of Poly(ester β-sulfide)s 6S*n*

sample	n	$\lvert\eta\rvert$,[a] dL/g	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$[b]
6S2	2	0.42	12500	1.6
6S3(e)	3	0.31	9000	1.6
6S4(e)	4	0.33	10400	1.6
6S5	5	0.27	7900	1.5
6S6	6	0.45	15100	1.6
6S7	7	0.39	12300	1.7
6S8	8	0.43	14200	1.7
6S9	9	0.56	18400	1.8
6S10	10	0.43	13700	1.6

[a] In chloroform, at 30 °C. [b] By GPC, in chloroform.

Table II
Molecular Weight Characteristics of the Poly(ester β-sulfide) 6S3 and 6S4 Series

sample	$\lvert\eta\rvert$,[a] dL/g	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$[b]	sample	$\lvert\eta\rvert$,[a] dL/g	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$[b]
6S3(a1)	0.05	1600	1.2	6S4(a1)	0.07	2100	1.1
6S3(b)	0.10	3200	1.3				
6S3(a2)	0.16	4300	1.5	6S4(a2)	0.11	3500	1.3
6S3(c)	0.21	6900	1.6	6S4(b)	0.13	4200	1.5
6S3(d)	0.27	8600	1.7	6S4(c)	0.19	6200	1.6
6S3(e)	0.31	9000	1.6	6S4(d)	0.28	8500	1.5
6S3(f)	0.34	10900	1.7	6S4(e)	0.33	10400	1.6
6S3(g)	0.39	11800	1.6	6S4(f)	0.42	13400	1.6
6S3(h)	0.44	14100	1.8	6S4(g)	0.52	17000	1.8

[a] In chloroform, at 30 °C. [b] By GPC, in chloroform.

1 as a typical example. The low-field region of the spectrum was assigned by chemical shift calculations[18] and off-resonance decoupling data are as described for strictly related polymeric structures.[14] In the high-field region the assignment of carbons 14, 15, and 16 becomes straightforward by comparing the spectrum with those of monomer 1. Carbon 1 may be differentiated from 2 and 17 by chemical-shift calculations. Assignment of carbon 2 was unequivocally performed by comparison of the spectra of the polymer samples based on ethanedithiol and ethanedithiol-d_2.

Several samples of polymers 6S3 and 6S4 with different molecular weights were also prepared and characterized by intrinsic viscosity measurements and gel permeation chromatography. Molecular characteristics of the fractionated samples 6S3(a1)–(h) and 6S4(a1)–(g) are reported in Table II.

Samples 6S3(a), 6S3(c), 6S3(d), and 6S4(a)–(e) were obtained by adjusting the stoichiometric ratios of the reagents. An excess of diacrylate was always employed and in the final product the vinyl end groups were blocked by reaction with methanethiol.

Samples 6S3(a1), 6S3(a2), 6S3(b), 6S3(e)–(h), 6S4(a1), 6S4(a2), 6S4(f), and 6S4(g) were obtained by fractional precipitation from dilute solution of the relevant crude polymer samples.

Liquid Crystalline Properties. The liquid crystalline properties of the polymers were studied by combined differential scanning calorimetry (DSC), observations of textures on the hot stage of a polarizing microscope, and X-ray diffraction analysis.

The values of the phase-transition temperatures together with the relevant enthalpies and entropies (Tables III and IV) were determined from DSC traces on samples annealed by cooling at 10 K/min from the isotropic melt.

Polymers 6S2–6S9 show on heating two distinct endothermic transitions. The first corresponds to melting and generally appears structured in a set of peaks whose relative magnitude depends on the thermal history of the sample. The second transition corresponds to isotropization. Both transformations are reversible on cooling and, accordingly, these polymers are enantiotropic in character. A supercooling of a few degrees (5–10 K) for the higher temperature transition is observed, but it is greater (30–40 K) for the crystallization, indicating a more pronounced off-equilibrium nature for the latter transition. Polymer 6S10 melts directly to the isotropic phase but on cooling exhibits two exothermic peaks, the first of which is associated with the onset of a monotropic liquid crystalline phase and the second to the crystallization process.

Table III
Thermal Properties of Poly(ester β-sulfide)s 6S*n* Prepared under Stoichiometric Conditions

sample	$\lvert\eta\rvert$, dL/g	T_m, K	ΔH_m, kcal/mol	T_i, K	ΔH_i, kcal/mol	ΔS_i, cal/mol·K
6S2	0.42	446	2.7	476	1.8	3.8
6S3(e)	0.31	412	1.8	448	1.2	2.6
6S4(e)	0.33	447	3.5	471	1.9	4.0
6S5	0.27	416	2.6	444	1.5	3.3
6S6	0.45	431	2.4	455	2.2	4.9
6S7	0.39	415	2.3	436	1.9	4.3
6S8	0.43	430	2.5	446	2.4	5.5
6S9	0.56	421	2.4	434	2.2	5.1
6S10	0.43	432	5.5	427[a]	2.6	6.1

[a] Monotropic transition.

Table IV
Thermal Properties of Poly(ester β-sulfide) 6S3 and 6S4 Samples with Different Molecular Weights

sample	$\lvert\eta\rvert$,[a] dL/g	T_m, K	ΔH_m, kcal/mol	T_i, K	ΔH_i, kcal/mol	ΔS_i, cal/mol·K
6S3(a1)	0.05	358	1.0	425	1.0	2.2
6S3(b)	0.10	380	2.2	433	0.8	1.8
6S3(a2)	0.16	405	3.0	442	1.1	2.4
6S3(c)	0.21	410	2.5	445	1.2	2.6
6S3(d)	0.27	413	2.4	440	1.0	2.3
6S3(e)	0.31	412	1.8	448	1.2	2.6
6S3(f)	0.34	410	2.6	445	1.2	2.8
6S3(g)	0.39	416	2.1	451	1.1	2.5
6S3(h)	0.44	418	2.4	449	1.1	2.4
6S4(a1)	0.07	405	5.1	449	1.7	3.9
6S4(a2)	0.11	429	4.8	464	2.1	4.5
6S4(b)	0.13	433	4.2	468	2.2	4.6
6S5(c)	0.19	444	4.1	473	1.9	4.0
6S4(d)	0.28	445	5.7	474	1.8	3.7
6S4(e)	0.33	447	3.5	471	1.9	4.0
6S4(f)	0.42	445	2.5	464	1.5	3.1
6S4(g)	0.52	445	3.0	467	1.7	3.7

[a] In chloroform, at 30 °C.

No unambiguous information is gained about the nature of the liquid crystalline phases by observation of the relevant textures. The high viscosity of the anisotropic polymer melts most likely prevents the development of well-defined textures. Only in the vicinity of the isotropization temperature can nematic schlieren textures be detected. In contrast, clear threaded and schlieren textures are observed for the nematic phase of low molecular weight fractions of samples 6S3 and 6S4 (see below).

X-ray diffraction spectra of unoriented samples 6S3, 6S4, 6S8, and 6S9, recorded at intermediate temperatures between melting and isotropization, are only constituted by an outer broad halo, indicating a nematic structure for the mesophase independent of the length of the sulfide segment.

Melting and isotropization temperatures as functions of the number n of methylene units of the dithiol spacer are illustrated in Figure 2. Both melting and isotropization temperatures decrease in a regular alternating manner as the series is ascended. The downward trend is a result of

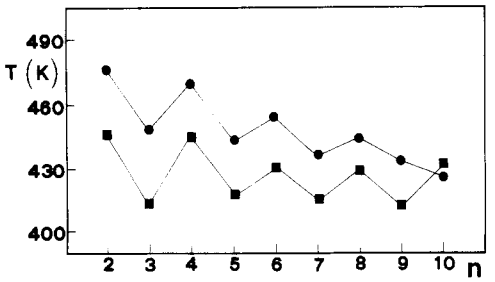


Figure 2. Melting (■) and isotropization (●) temperatures for poly(ester β-sulfide)s 6S*n* as function of the number *n* of methylene units in the dithiol segment.

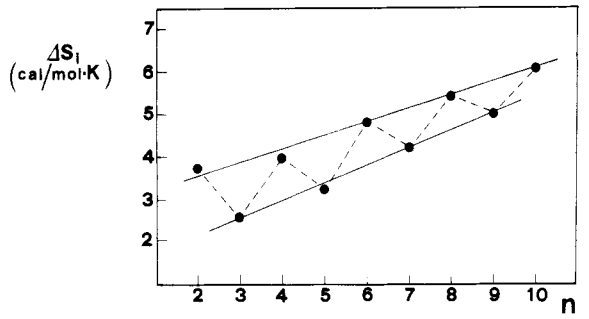


Figure 3. Isotropization entropy for poly(ester β-sulfide)s 6S*n* as a function of the number *n* of methylene units in the dithiol segment.

the overall decreasing polarity and molecular rigidity with increasing *n*. Polymers with even-numbered spacers show higher transition temperatures than adjacent polymers with odd-numbered spacers. This even–odd alternation is more pronounced for the lower homologues and diminishes as *n* increases.[19-21]

The dependence of the isotropization entropies upon the length of the sulfide segment (Figure 3) is characterized by a persistent even–odd alternation. The nematic–isotropic transition entropies for even and odd members lie on two smooth curves which rise with increasing spacer length, even members being placed on the upper curve. This increase of isotropization entropies has to be connected with an increased conformational entropy of the molecules in the isotropic phase. The even–odd alternation of the phase-transition parameters clearly indicates that the spacer plays an integral role in determining the degree of organization in the liquid crystalline phase.

In a nematic structure the more extended conformers are selectively preferred for steric packing reasons.[22] This preference results in a change of their statistical weight in the anisotropic phase with respect to the isotropic one.[22-24] Calculations based on the rotational isomeric state (RIS) method[5] indicate that the conformational distribution of a linear polymethylenic chain, connected to two rigid groups by ester functions, is strongly dependent on its parity. An even-numbered polymethylenic spacer possesses a set of low-energy extended conformers that force the rigid groups to adopt a colinear disposition. In contrast, an odd-numbered spacer possesses a relatively small fraction of extended conformers which places the mesogenic groups in angled orientations, unfavorable for the onset of nematic ordering. This basic difference between the configurational character of the extended conformers should be responsible for the large even–odd oscillations of the thermodynamic phase transition parameters and may explain the higher mesogen order assumed by even members. The first- and second-order interactions of a sulfur atom inserted in a polymethylenic chain should not modify substantially the conformational distribution relative to the corresponding fully polymethylenic chain.[25,26] On this ground we infer that the above results could be extended, at least in a qualitative manner, to the present polymer system. Comparisons between the thermodynamic behavior of poly(ester β-sulfide)s I and homologous polyesters II from our laboratories,[27] in which the sulfur atoms are replaced by methylenic units, strongly corroborate this conclusion. The perturbation introduced by the sulfur atoms results in fact in a systematic decrease of 15–20 K in the nematic–isotropic transition temperatures with respect to the corresponding homologues. A comparable behavior was already detected in other series of functional polyesters containing azoxybenzene mesogenic groups.[11]

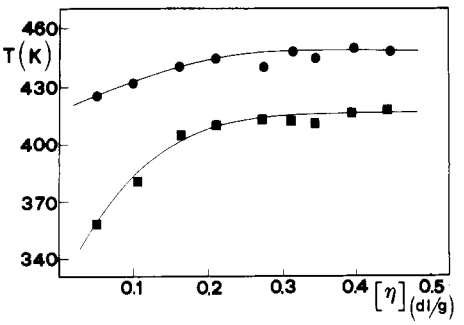
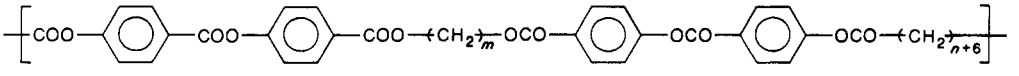


Figure 4. Melting (■) and isotropization (●) temperatures for poly(ester β-sulfide) 6S3 samples as function of the intrinsic viscosity.

The molecular weight dependence of the thermodynamic phase transition parameters has been investigated for two series of polymer samples 6S3 and 6S4, characterized by different molecular weights and molecular weight distributions. Molecular weight polydispersity causes the occurrence of broad isotropization transitions, particularly evident in the lower molecular weight samples, and is responsible for the coexistence of anisotropic and isotropic phases in the polymer melt over fairly extended temperature ranges. For both series of samples, the width of the DSC isotropization endotherm, taken as a rough indicator of the extent of the biphasic gap,[28] decreases from 40 to 20 K with increasing molecular weight from 1500 to 4000 Da and then levels off for higher molecular weight values. We may expect that higher molecular weight species should be incorporated sequentially into the anisotropic phase. This partitioning phenomenon, which is well documented for lyotropic polymer solutions[29,30] and has been recently demonstrated to occur also in thermotropic main-chain polymers,[28,31] is responsible for the asymmetric profile of the isotropization peaks as a function of the oligomeric composition of the samples. For all samples the isotropization temperatures were taken as corresponding to the maximum of the DSC peaks, irrespective of the extension of the biphasic region. On the basis of DSC and optical microscopy observations, all samples, including the diacrylate monomer 1, present a nematic phase, independent of molecular weight. The nematic–isotropic transition temperatures increase in oligomer samples up to a value of intrinsic viscosity equal to 0.2 dL/g ($\overline{DP}_n$ = 4–5) (Figures 4 and 5), the increase being



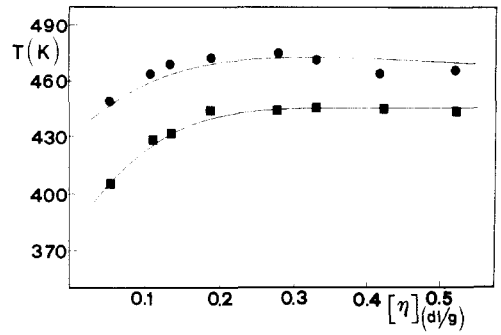


Figure 5. Melting (■) and isotropization (●) temperatures for poly(ester β-sulfide) 6S4 samples as function of the intrinsic viscosity.

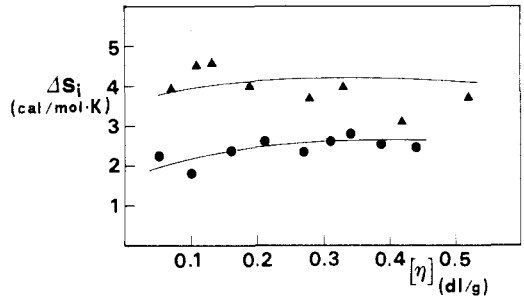


Figure 6. Isotropization entropy for poly(ester β-sulfide)s 6S3 (●) and 6S4 (▲) samples as a function of the intrinsic viscosity.

more pronounced for 6S4 samples. After that value is reached, the isotropization temperatures remain practically constant for samples 6S3, while a slight downward trend is detected for samples 6S4. An analogous trend is observed for the melting temperatures even though a more marked dependence can be appreciated for the lower molar mass samples. This results in a wider mesophasic region particularly for 6S3 oligomers.

The isotropization entropies (Figure 6) appear to slightly increase with increasing molecular weight up to the saturation value of $|\eta| = 0.2$ dL/g ($\overline{DP}_n = 4$–5). The increase of the thermodynamic parameters with increasing molecular weight has been ascribed to the increased cooperativity between repeating units in the anisotropic phase.[30] Consistently, the orientational correlation between distant segments, belonging to the same polymer backbone, may be propagated via the local environment,[32] thus conferring an even more marked first-order character to the nematic–isotropic liquid phase transition.[32-34] However, these cooperative effects appear not to be operating in the investigated poly(ester β-sulfide)s, either even or odd homologues, within a substantial range of molecular weights.

Conclusions

A new series of functional semiflexible liquid crystalline polyesters has been prepared by reacting different α,ω-alkanedithiols with a mesogenic bisacrylate consisting of two *p*-oxybenzoyl diads spaced by a hexamethylene–dioxy segment.

The synthetic strategy has been adapted to the production of different samples in a distinct series characterized by a variable average degree of polymerization in the approximate range from 2 to 20. All the polymer samples, independent of molecular weight, exhibit a nematic mesophase, whose isotropization temperature and relevant entropy increase with molecular weight to level off at $\overline{DP}_n \geq 5$, corresponding to an intrinsic viscosity value $|\eta| = 0.2$ dL/g. Such behavior has been observed in other series of analogous poly(ester β-sulfide)s and seems to be a common feature for these functional liquid crystalline polymers.

The isotropization temperature and entropy as a function of the dithiol spacer length follow a distinct even–odd alternation in which the even members possess a greater propensity to establish more stable mesophases.

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Registry No. 652 (copolymer), 117162-62-6; 652 (SRU), 117162-71-7; 653 (copolymer), 117162-63-7; 653 (SRU), 117162-72-8; 654 (copolymer), 117162-64-8; 654 (SRU), 117162-73-9; 655 (copolymer), 117162-65-9; 655 (SRU), 117162-74-0; 656 (copolymer), 117162-66-0; 656 (SRU), 117162-75-1; 657 (copolymer), 117162-67-1; 657 (SRU), 117162-76-2; 658 (copolymer), 117162-68-2; 658 (SRU), 117162-77-3; 659 (copolymer), 117162-69-3; 659 (SRU), 117162-78-4; 6510 (copolymer), 117162-70-6; 6510 (SRU), 117162-79-5.

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