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LIQUID-CRYSTALLINE SIDE-CHAIN POLYACRYLATES CONTAINING CHIRAL SULFOXIDE SUBSTITUENTS

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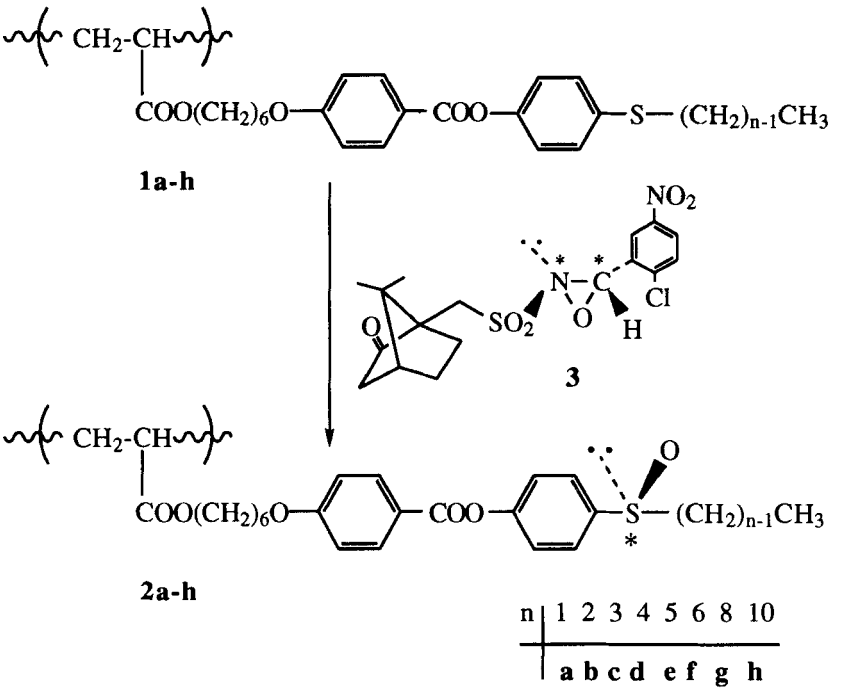
Abstract A series of side-chain polyacrylates containing chiral, optically active sulfoxide substituents was prepared by the enantioselective oxidation of the corresponding prochiral polyacrylates containing prochiral sulfide substituents. A chiral sulfonyloxaziridine was used as the oxidant. The chemical modification was selective from chemical and stereochemical standpoints. The resulting polymers formed chiral nematic and/or smectic phases with a slightly decreased propensity to give stable and persistent mesophases with respect to the parent sulfide containing polymers.

INTRODUCTION

Considerable attention is being paid to the design and synthesis of chiral thermotropic side-chain liquid-crystalline (LC) polymers[1]. Their ability to generate chiral nematic and chiral smectic supramolecular assemblies endowed with a macroscopic twist may result in specific optical and electrooptical properties for advanced technology application[2].

Very recently, a novel approach to the preparation of chiral LC polymers has been proposed[3-5], involving the enantioselective modification of prochiral polymeric substrates. This synthetic procedure is fairly straightforward and attractive for its apparent simplicity and the manifold opportunities it offers to design macromolecular architectures otherwise unfeasible by ordinary synthetic procedures. Following this approach, we presented[5] the chemical modification of prochiral alkyl sulfide substituents of LC side-chain polymers (such as polymers **1b** and **1d** below) leading to chiral, optically active sulfoxide groups (Scheme 1). In this paper we describe the synthesis and LC properties

SCHEME 1. Synthetic procedure for the preparation of chiral polymers **2a-h**.



of a series of chiral polymers **2a-h** obtained by the enantioselective oxidation of the corresponding prochiral polymers **1a-h**[6].

The length of the alkyl tail substituent (n = 1-6, 8, or 10) was varied systematically in order to tune the mesophase behavior of the parent polymers **1a-h** and of the modified chiral polymers **2a-h**. The modification of a sulfide to a sulfoxide moiety introduces a strong dipole moment directly located at the chiral center and perpendicular to the molecular long axis of the mesogenic group. These structural features may be expected to be conducive to chiral LC polymers suitable for electrooptical and non-linear optical applications.

EXPERIMENTAL PART

Synthesis

Prochiral polymers **1a-h** were prepared according to literature[5,6]. (-)-(*S,S*)-3-(2-chloro-5-nitrophenyl)-2-(*d*-2-oxo-10-bornylsulfonyl) oxaziridine (**3**) (m.p. 149°C, $[\alpha]^{25}_{D}$ = -79.1° ($CHCl_3$)) was synthesized following the procedure of Davis *et al.*[7].

Polymers **2a-h** were prepared by an enantioselective oxidation of polymers **1a-h** (Scheme 1) which is here described in detail for polymer **1b**, as a typical example. A solution of 0.87 g (2.1 mmol) of **3** in 20 ml of anhydrous chloroform was added dropwise to a solution of 1.0 g (2.1 mmol repeat unit) of polymer **1b** in 20 ml of the same solvent at -50°C. The mixture was let to react for an additional 1 h. The solution then was evaporated to a small volume and poured into a large excess of methanol. The polymeric product **2b** was purified by several precipitations from chloroform solutions into hexane (yield 95 %).

Physicochemical Characterization

^1H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer. Average molar masses were determined by size exclusion chromatography (SEC) of chloroform solutions with a 590 Waters chromatograph equipped with a Shodex KF-804 column. Polystyrene standard samples were used for the universal calibration method. Optical rotatory power measurements were performed with a Perkin-Elmer 141 spectropolarimeter. Circular dichroism (CD) absorption spectra were recorded on dioxane dilute solutions of the polymers ($c \approx 10^{-4}$-10^{-5} M repeat unit) using a Jasco J500C spectrophotometer (path length 0.1 cm). Differential scanning calorimetry (DSC) analyses were carried out under dry nitrogen flow with a Perkin Elmer DSC 7 apparatus. The transition temperatures were taken from the DSC traces of samples annealed by cooling from the isotropic melt, as corresponding to the maximum of the enthalpic peaks at a scanning rate of 10 $Kmin^{-1}$. X-ray measurements were performed by using a Rigaku Denki RV300 rotating anode generator equipped with a pin-hole flat camera. Ni-filtered CuK_α ($\lambda = 1.54$ Å) radiation was used.

RESULTS AND DISCUSSION

Synthesis

Polymers **2a-h** cotaining chiral sulfoxide substituents were prepared by the enantioselective oxidation of polymers **1a-h** containing prochiral sulfide groups, in chloroform solution at -50°C using a stoichiometric amount of the chiral 2-sulfonyloxaziridine **3** (Scheme 1). The reaction is believed to be a S_N2 nucleophilic attack by the substrate on the highly electrophilic oxaziridine oxygen atom[7,8]. It occurred with nearly quantitative yields. Polymers **2a-h** have average molar mass (M_n) and first polydispersity index (M_w/M_n) (Tab.1) very similar to those of the corresponding polymers **1a-h**[6], thus indicating that the oxidation reaction occurred without appreciable chain degradation. NMR and IR spectra of polymers **2a-h** are in full agreement with the expected structures and no signals denoting the presence of residual sulfide or of

TABLE 1. Physico-chemical properties of chiral LC polymers **2a-h**.

	n	M_n[a]	M_w/M_n[a]	$[\alpha]^{25}_D$	T_g	T_{S-i}	T_{N^*-i}	ΔS_{S-i}	ΔS_{N^*-i}
		(10^{-3})		(deg)	(K)	(K)	(K)	($Jmol^{-1}K^{-1}$)	($Jmol^{-1}K^{-1}$)
2a	1	13	1.1	-17.7	301	-[b]	-[b]	-[b]	-[b]
2b	2	28	1.6	-26.2	308	-	333	-	2.0
2c	3	70	1.2	-23.8	304	-	334	-	3.9
2d	4	56	1.5	-21.1	304	-	362	-	5.2
2e	5	54	1.5	-17.5	306	347	332[c]	18.2	8.5[c]
2f	6	23	1.4	-20.6	303	356	341[c]	29.4	13.6[c]
2g	8	15	1.5	-18.0	345	363	-	30.5	-
2h	10	109	2.1	-20.4	363	374	-	39.4	-

[a]By SEC, in chloroform at 25 °C. [b]Not mesomorphic. [c]On cooling from the isotropic melt.

overoxidized sulfone moieties are detected. This indicates that the oxidation reaction is highly chemoselective.

Polymers **2a-h** are optically active (Tab.1) with optical rotation ($[\alpha]^{25}_D$) values in the range -17.5 to -26.2°. The close similarity among the $[\alpha]^{25}_D$ values suggests that the enantioselectivity of the reaction is substantially controlled by the local stereochemical environment in the vicinity of the prochiral center. These optical rotatory powers should correspond to an asymmetric induction of about 20%, in agreement with previous NMR measurements on a model compound using chiral shift reagents[5]. The CD spectra in dilute solutions of polymers **2a-h** all show the same strong absorption profiles in correspondence with the electronic transitions of the arylalkyl sulfoxide chromophore[9], see Fig.1 for a typical example. Therefore, the overall optical activity of the polymers seems to be dominated by the prevailing chirality of the sulfoxide moieties. It is not known to what extent the sign and the rotatory strength ($\Delta\varepsilon$) of the CD absorption bands depend on the local conformation of the macromolecular chain. Similar Cotton effects were detected in model compounds characterized by the (*S*) absolute configuration at the sulfur atom[9].

LC properties

The phase transition temperatures and relevant thermodynamic parameters (Tab.1) were determined by DSC measurements. The LC behavior was investigated by qualitative

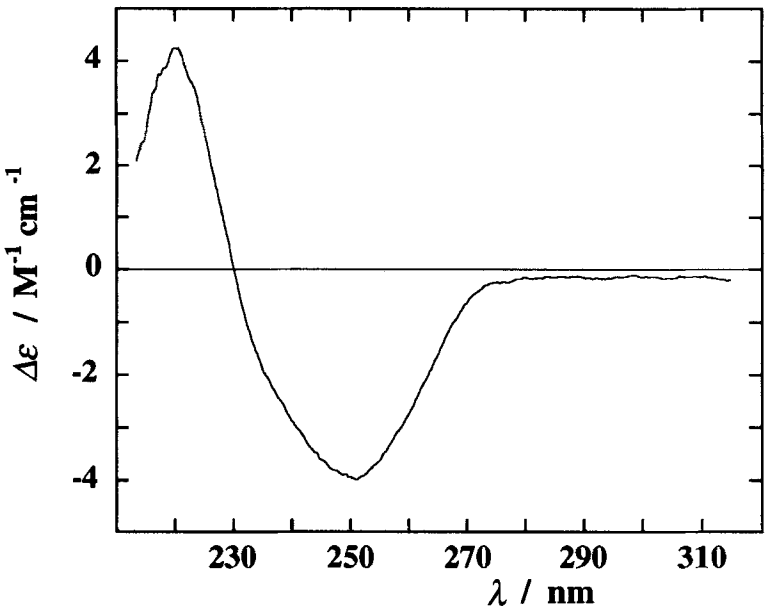


FIGURE 1. Circular dichroism absorption spectrum of polymer **2c** in dilute dioxane solution.

observations of the optical textures on the hot stage of a polarizing microscope and by X-ray diffraction

The LC properties of polymers **1a-h** were previously described[6] and are reconsidered here for comparison. The lower homologues **1a-f** ($n \leq 6$) displayed smectic B1 and smectic A1 mesophases, whereas the higher homologue **1h** ($n = 10$) formed a bilayer, partly interdigitated smectic C mesophase. A special place was held by polymer **1g** with an intermediate length ($n = 8$) of the sulfide substituent for which the coexistence of monolayer and bilayer smectic mesophases was observed over a broad temperature range[10].

Polymers **2a-h** are amorphous, as evidenced by X-ray analysis. No mesophase was observed for **2a** having the shortest ($n = 1$) tail substituent. In contrast, all the other members of this series exhibit LC behavior in the melt (Tab.1). In particular, **2b**, **2c** and **2d** form a nematic mesophase, whereas **2g** and **2h** form a smectic mesophase. Both **2e** and **2f** exhibit a smectic mesophase on heating, and an additional nematic mesophase on cooling that can be detected beacause of the supercooling of the smectic phase. Accordingly, for the latter polymers the nematic mesophase is metastable with respect to the smectic one. The X-ray diffraction investigation of the smectic mesophase of polymers **2e-2h** reveals that they have disordered bilayer smectic (A2 or C2) structures

(Fig.2). However, no oriented specimens could be obtained and a detailed characterization of the mesophase structure was not possible.

The trends of the phase transition temperatures of polymers **2a-h** as function of the length of the tail substituent (n) are illustrated in Fig.3. For comparison, the same figure reports the isotropization (smectic-isotropic) temperature for the parent polymers **1a-h**. Both the glass temperature (T_g) and the transition temperatures associated with the LC transitions of polymers **2a-h** generally increase with n. The phase transition entropies associated with both the chiral nematic-isotropic and smectic-isotropic transitions strongly increase with n (Fig.4), revealing an enhanced conformational contribution of the alkyl substituent to the disordering transition. Therefore, both the stability of the mesophase, as evaluated by the isotropization temperature, and its degree of order, as estimated by the isotropization entropy, increase with lengthening the tail substituent.

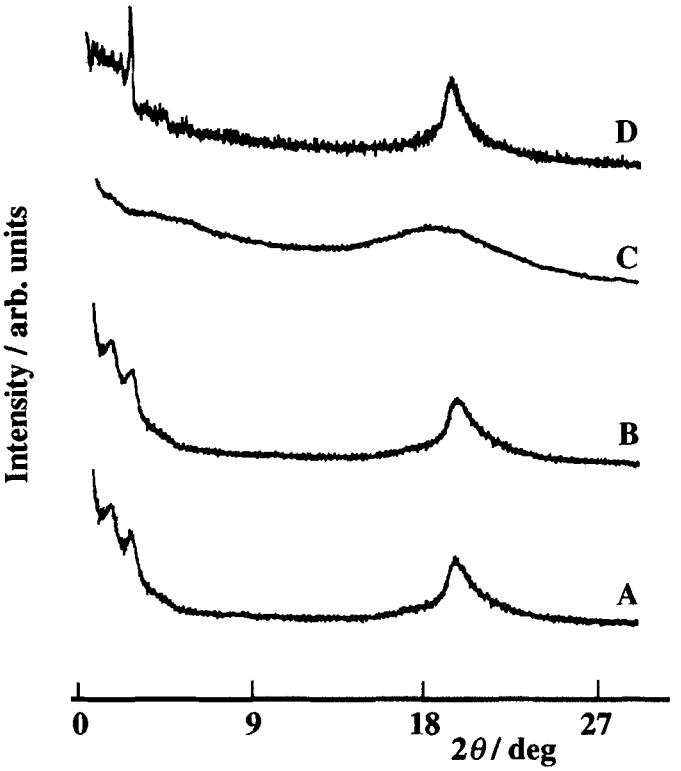


FIGURE 2. X-ray diffraction diagrams of polymer **2g** at different temperatures: A, 300 K (virgin sample); B, 343 K; C, 369 K; D 300 K (after cooling from the isotropic melt).

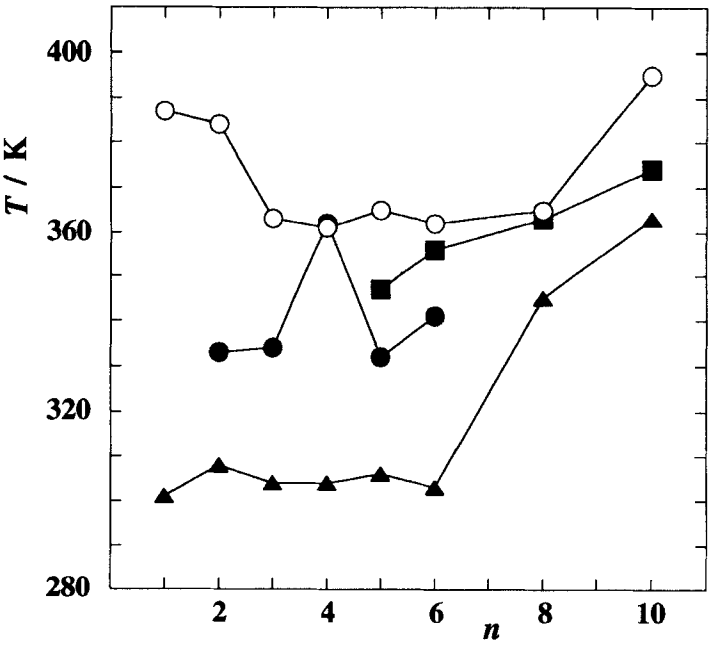


FIGURE 3. Transition temperatures of polymers **2a-h** (▲, glass; ■, S-i; ●, N*-i (or i-N*)) and polymers **1a-h** (○, S-i) as function of *n*.

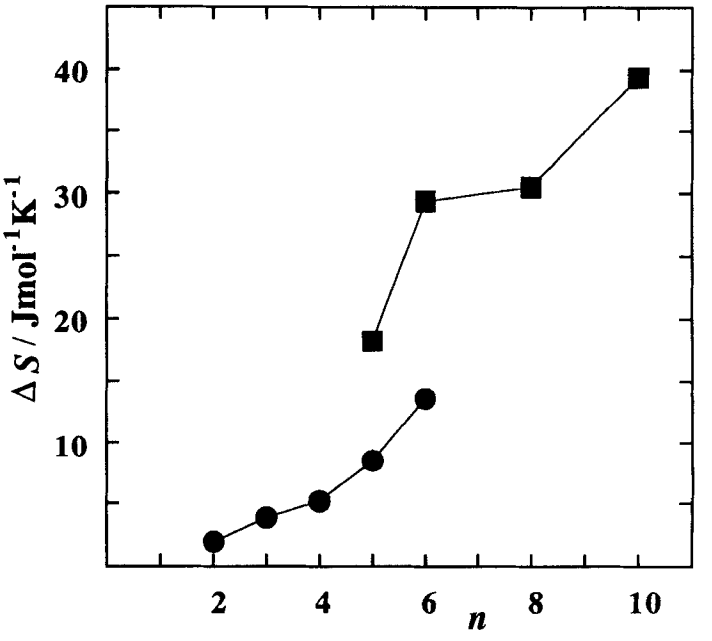


FIGURE 4. Transition entropies of polymers **2a-h** (■, S-i; ●, N*-i (or i-N*)) as function of *n*.

By comparing the transitional properties of polymers **2a-h** with those of the prochiral counterpart polymers **1a-h**, it appears that the modification of the sulfide group to the sulfoxide group causes a decrease of both isotropization temperature and entropy, that is a depression of the mesogenic power of the chiral repeat units. This is especially evident for the lower homologues (n = 1-5) for which the mesophase nature turns from smectic to nematic in going from the sulfide polymers to the corresponding sulfoxide polymers. It would be to verify whether this behavior may may connected to and driven by the enantiomeric purity of the chiral sulfoxide units.

CONCLUSION

The synthesis of LC polymers incorporating chiral sulfoxide moieties can be accomplished by the enantioselective modification of prochiral sulfide polymers. By this procedure, it is possible to tune on a structural ground the formation of different chiral nematic and chiral smectic mesophases in the sulfoxide polymers. This chemical modification slightly depresses the propensity of the resulting polymers to form stable and persistent mesophases.

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REFERENCES

1 P. Le Barny, J.C.Dubois, in: Side-chain Liquid Crystal Polymers, edited by C.B.McArdle, Blackie, Glasgow 1989, p. 130; V.P.Shibaev, Ya.S.Freidzon, ibid., p.260.
2 E.Chiellini, G.Galli, F.Cioni, E.Dossi, Makromol. Chem., Makromol. Symp. **69**, 51 (1993).
3 A.S.Angeloni, M.Laus, D.Caretti, E.Chiellini, G.Galli, Makromol. Chem. **191**, 2787 (1990).
4 E.Chiellini, G.Galli, A.S.Angeloni, M.Laus, in: Liquid-Crystalline Polymers, edited by R.A.Weiss, C.K.Ober, ACS Symposium Series 435, 1990, p. 79.
5 A.S.Angeloni, M.Laus, D.Caretti, E.Chiellini, G.Galli, Chirality **3**, 307 (1991).
6 M.Laus, A.S.Angeloni, G.Galli, E.Chiellini, O.Francescangeli, B.Yang Polymer in press.
7 F.A.Davis, R.H.Jenkins, Jr., S.B.Awad, O.D.Stinger, W.H.Watson, J.Galloy, J. Am. Chem. Soc. **104**, 5412 (1982).
8 F.A.Davis, J. M.Billmers, D.J.Gosciniak, J.C.Towson, R.D.Bach, J. Org. Chem. **51**, 4240 (1986) and references therein.
9 K.Mislow, M.M.Green, P.Laur, J.T.Melillo, T.Simmons, A.L.Ternay, Jr., J. Am. Chem. Soc. **87**, 1958 (1965).
10 G.Galli, E.Chiellini, M.Laus, A.S.Angeloni, O.Francescangeli, B.Yang, Macromolecules, **27**, 303 (1994).