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Chirality induction in liquid crystalline side-chain polyethers prepared by copolymerization of oxiranes with mesogenic and non mesogenic groups

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Abstract

Copolymers prepared by anionic initiation from racemic or optically active styrene oxide and a racemic oxirane bearing cyanobiphenyl mesogenic group in the side chain are liquid crystalline when the content of the mesogenic monomer exceeds 60 mole %. Copolymers prepared from a mesogenic oxirane with a short spacer and racemic styrene oxide exhibit a nematic phase, while those prepared with optically active styrene oxide exhibit a cholesteric phase, thus indicating a transfer of chirality from the main chain towards the mesophase. Such a transfer of chirality is no more observed in the case of a copolymer prepared from a mesogenic oxirane with a long spacer.

Introduction

During the last twenty years a large number of side-chain liquid crystalline polymers (SCLCP's) have been synthesized and investigated (1). The backbones that have been most commonly employed are those of the acrylate, methacrylate and siloxane types. However, in recent years the interest in polyether backbones has increased because of their intrinsic flexibility which allows to observe a LC behavior even with short spacers. The synthesis of SCLC polyethers may be performed either by chemical modification reaction on a polyether backbone which contains functional groups such as polyepichlorohydrin (2-4), or by ring-opening polymerization of cyclic ethers, e.g. oxiranes, bearing mesogenic groups (5-11). A major interest in polyether backbone comes from the presence of chiral centers which allow to study the influence of chirality and tacticity of the macromolecular chain on the thermal properties and more precisely on the type of the LC phases formed. In a previous work we have demonstrated (7) that polyethers with cyanobiphenyl mesogenic groups attached to a racemic main chain through short spacers form a nematic phase while those with an optically active chain exhibit a cholesteric phase. The formation of a cholesteric phase indicates a transfer of the chirality from the chiral centers in the main chain towards the mesophase. By contrast no transfer effects were observed for polymers with long spacers (10). Copolymerization is another convenient way to obtain polymers with different LC properties, the thermotropic behavior depending on the composition of copolymers. In this paper we report on copolymerization of a racemic oxirane bearing cyanobiphenyl group in the side chain with racemic or optically active styrene oxide. This approach allows to study the influence of a chiral monomer unit in the main chain on the mesophase organization induced by the mesogenic groups of the neighboring comonomer units.

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Experimental part

Reagents

Racemic [(R,S)-[SO]] and optically active [(R)-[SO]] styrene oxides were purchased from Aldrich and purified before polymerization by distillation on calcium hydride under vacuum.

Racemic [(4-cyano-4'-biphenylyl)oxy] methyloxirane [(R,S)-[CBO-MO]] was prepared by an analogous procedure to that developed by Mc Clure et al (12) for aryloxymethyloxiranes. Into a 250 mL three-necked flask fitted with a reflux condenser and magnetic stirrer were introduced 2.50 g (0.013 mol) of 4-cyano-4'-hydroxybiphenyl (Aldrich) in 100 mL of anhydrous acetone. 1.95 g (0.0141 mol) of K_2CO_3 and 1.8 mL (0.023 mol) of distilled epichlorohydrin (Carlo Erba) were then added. The suspension mixture was refluxed for 7 days under stirring. Upon completion of reaction (followed by thin layer chromatography) the reaction mixture was poured into a large excess of water. The precipitate was filtered off, washed several times with water and dried. The recovered solid was purified by chromatography on silica-gel (40-63 μm, Merck) using dichloromethane with 2% of methanol as eluent. Yield = 50% (1.60g). Mp = 114°C (lit. (8) mp = 113°C). All other characteristics are identical to those given in lit. (8).

Racemic [(4-cyano-4'-biphenylyl)hexyloxy]methyloxirane [(R,S)-[CBHO-MO]] was prepared by the procedure already described elsewhere (10).

Dimethylsulfoxide (DMSO) was distilled on calcium hydride before polymerization.

Copolymerization

Commercial tBuOK (Fluka) was introduced into the apparatus and dried under vacuum. The appropriate amounts of monomers and freshly distilled DMSO were then added under nitrogen. The mixture was outgassed several times by the freeze-thaw technique and the apparatus sealed under high vacuum. All the polymerizations were run at 80°C. At the end of polymerization a small amount of DMSO containing few drops of acetic acid was added to the solution and the mixture was poured into an excess of methanol. The copolymer was recovered by centrifugation of the solution and then dried *in vacuo*. All the copolymers were characterized by Size Exclusion Chromatography (SEC) in THF and by ^1H and ^{13}C NMR in $CDCl_3$.

Characterization of polymers

The molecular weights of the copolymers were determined by SEC in THF on a Waters apparatus equipped with μ-styragel columns: 10^4, 10^3, 10^2, 50, 10 nm (refractive index and UV (254nm) detections : flow rate 1 mL/min ; calibration vs polystyrene standards).

The assignments of signals for [CBO-MO] and [SO] units in ^1H and ^{13}C spectra are taken from (8) and (13), respectively. The composition of copolymers was determined from ^1H NMR (200MHz) in $CDCl_3$. Protons corresponding to [CBO-MO] unit are found at 7.39-7.58 (large d pattern, Ar, 6H), 6.91 (large s, Ar, 2H), 3.87-4.04 (m, CH_2, CH, 5H). Protons corresponding to [SO] units are found at 7.28 (large s, Ar, 5H), 4.56-4.87 (large d, CH, 1H) and 3.37 (large, CH_2, 2H). The composition of copolymers was established from the ratio of integrated 6.91ppm/other aromatic signals. In the ^{13}C spectra the following signals were assigned to (R,S)-[CBO-MO] units : 67.92, 69.90, 78.15, 110.30, 115.30, 118.77, 126.83, 128.23, 128.53, 131.64, 132.52 and the following to [SO] units: 46.5, 82.5, 126.11, 144.74.

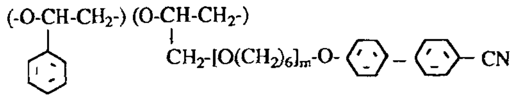
Phase transition temperatures were measured using a differential thermal analyzer (Perkin Elmer 7 or Du Pont 1090). A scanning rate of 20°C/min was used. Tg was estimated from the point of intersection between the initial base line and the sloping portion of the line obtained as the base line shifts during the glass transition. Peak maximum positions were taken as the clearing temperatures. The textures of the mesophases were observed with a polarizing microscope (Olympus BHA-P) equipped with a Mettler FP 52 hot-stage and FP5 control unit.

Results and discussion

Synthesis of copolymers

The anionic copolymerization of racemic oxirane (R,S)-[CBO-MO] with racemic (R,S) or optically pure (R) styrene oxide was carried out at 80°C using tBuOK/DMSO as initiator system. This initiator was found to be active for the polymerization of various oxiranes (14) and was successfully used for polymerization of (R,S)-[CBO-MO] (8). The results of copolymerization are reported in Table 1. It appears that several days are required to obtain substantial yields of copolymers and that the composition of recovered copolymers is not too far from the composition of the initial mixtures of comonomers.

The optical rotation of the copolymer C 3 (23% of (R)-[SO]) was found to be $[\alpha]^{25}_{578}=-11.5$ (c=1.5, $CHCl_3$). Optically pure poly (R)-[SO] exhibits a value of $[\alpha]^{25}_{578}=-118$ (c = 1, dioxane) (15). On the other hand optically pure poly (R)-[CBO-MO] shows an optical rotation value of $[\alpha]^{25}_{589}=-13.6$ (c = 1.5, $CHCl_3$) (8). It can be expected that the same type of chirality, i.e., (R)-type, is present in these three polymers.



[CBO-MO] m=0

[CBHO-MO] m = 1

Table 1. Copolymerization of (R,S)-[CBO-MO] (M_1) with racemic (R,S) or optically active (R)-[SO] (M_2) in DMSO at 80°C using tBuOK (I) as initiator system [I]/[M] = 5 mole %. [I] = 0.08-0.18 mol L^{-1}

Run	Monomer		t (day)	Yield (%)	Copolymer		
	M_2	M_1/M_2 (mole)			M_1/M_2 (a)	$\overline{Mn}$ (b)	$\overline{Mw}$ / $\overline{Mn}$ (b)
C 1	(R, S)-SO	13 / 87	4	86	13 / 87	4300	1.5
C 2	(R,S)-SO	75 / 25	8	85	79 / 21	4700	1.3
C 3	(R)-SO	80 / 20	5	74	77 / 23	3700	1.3
C 4	(R)-SO	70 / 30	6	35	93 / 7	2800	1.2
H 1	-	100 /0 (c)	6	80	100 / 0	3500	1.4
H 2	(R,S)-SO	0 / 100	1	38	0 / 100	2100	1.2

(a) composition of the copolymer from ^1H NMR (b) SEC in THF (polystyrene standards) (c) [I]/[M] = 6.3 mole % (8)

Thermal properties

The synthesized polymers are non crystalline in character. Their transition temperatures are listed in Table 2.

Both the glass transition and isotropization temperatures are affected by the non-mesogenic comonomer content. Clearly, an increase in the non-mesogenic monomer content causes the mesophase thermal stability to decrease. As far as comparisons can be made between polymers of different optical activity and varying in $\overline{DP}$ and polydispersity, the transition temperatures of the polymers prepared from either (R,S)-[CBO-MO] or (R)-[CBO-MO] lie on

Table 2. Thermal properties of polymers with short spacer.

Run (a)	Polymer composition M_2/M_1 (mole %)	Transition temperatures (b) (°C)	ΔT (°C)
H 1	0/100	G 80 N 161 I	81
C 2	21/79	G 76 N 108 I	32
C 1	87/13	G 32 I	
H 2	100/0	G 29 I	
C 4	7/93	G 65 Ch 128 I	63
C 3	23/77	G 71 Ch 97 I	26

(a) see Table 1 (b) G : glassy state, N : nematic, I : isotropic, Ch : cholesteric

the same curves (Fig.1). The extrapolation of the T_{NI} and Tg lines assumed almost rectilinear gives a minimum mesogenic monomer content of 60-70 mole % necessary for liquid crystal formation. This is consistent with the data previously reported for copolymers prepared by chemical modification of polyepichlorohydrin (PECH) with the sodium salt of 4-cyano-4' hydroxybiphenyl (3). In this work, it was found that PECH requires approximately 65% mesogenic group to form a mesophase.

Poly [(R,S)-[SO]-co-(R,S)-[CBO-MO]] [21:79 mol %] exhibits an enantiotropic nematic phase, the textures of which are reminiscent of those of conventional nematics (Figs.2

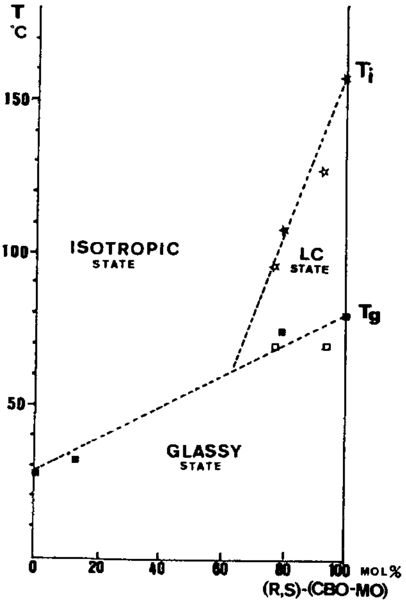


Fig. 1 - Plot of transition temperatures against mole % of mesogenic monomer for the systems (R,S)-[CBO-MO]/(R,S)-[SO] (★,■) and (R,S)-[CBO-MO]/(R)-[SO] (☆,□)

and 3). On heating, the nematic phase appears as a threaded texture (Fig.2). On cooling, the nematic phase separates from the isotropic liquid in the form of droplets which, after further cooling, grow, coalesce and give way to the formation of a stable schlieren texture with a large number of disclinations of strength $s = \pm 1/2$ (Fig.3).

Poly [(R)-[SO]-co-(R,S)-[CBO-MO]] [7:93 mol %] forms a cholesteric phase characterized by a texture with oily streaks (Fig.4). Grandjean steps can also be observed at the borders of small drops. The identification of the cholesteric phase of poly [(R)-[SO]-co-(R,S)-[CBO-MO]] [23:77 mol %] was less easy. Microscopic observations showed that this copolymer gives a birefringent phase, but no typical textures could be obtained, even after annealing for hours or days. As indicated in Table 1, this copolymer has a higher molar mass, which results in an increase in the viscosity of the liquid crystalline melt. In addition, because of the higher optically active monomer content, the helical pitch is expected to be smaller (16). A combination of these two factors might prevent the development of typical textures. It should be pointed out, however, that (i) the viscosity and the cholesteric pitch can be altered by adding a diluent, and (ii) a cholesteric liquid crystal is a modified nematic liquid crystal, i.e, in a cholesteric, a helical twist is imposed on a molecular organization which is essentially nematic in type. As a consequence, cholesteric liquid crystals are miscible (isomorphous) with nematics. Having drawn attention to this information, we used the contact method (17) to establish the cholesteric nature of the mesophase of poly [(R)-[SO]-co-(R,S)-[CBO-MO]] [23:77 mol %] through the application of miscibility rules (18). We used as reference compound p-methoxybenzylidene-p-n-butylaniline (MBBA : K 21°C N 45°C I), which exhibits a mobile nematic phase with schlieren-like texture. Contact preparation was obtained by putting at high temperature a small amount of polymer between a glass slide and a cover slip. The reference compound was then introduced by capillarity in such a way that the polymer and reference substance are in contact. Owing to the reference compound diffusion into the polymer, the composition continuously changed from one extremity of the preparation to the other one. After cooling the preparation was examined under a polarizing microscope. Uninterrupted miscibility was observed, thus establishing the isomorphy of the mesophase of poly [(R)-[SO]-co-(R,S)-[CBO-MO]] [23:77 mol %] with the nematic phase of MBBA. At certain compositions, the mixtures exhibited the typical planar texture of cholesterics with parallel lines (Fig.5) and moiré fringes.

The copolymer prepared from (R)-[SO] and the racemic oxirane with the long $-CH_2-O-(CH_2)_6$ spacer in a ratio of 24:76 exhibits a smectic phase and a nematic phase (Table 3). As yet, the smectic phase remains unidentified. The nematic phase occurs in the typical schlieren texture (Fig.6). This mesophase displays other nematic characteristics such as a tendency to form homeotropic regions, intense movement within the melt and scintillation effects due to a directly observable Brownian motion. On cooling from the isotropic state, typical droplets appear at first which after further cooling grow and coalesce to form the stable schlieren texture (Fig.7). The nematic phase persists over a broad temperature range, the smectic phase growing slowly during the cooling cycle.

It is apparent from the above results that chirality of the (R)-[SO] monomer imparts form chirality to the mesophase of the two copolymers where the mesogenic group is attached to the backbone through only one methylenic unit. The situation is different for the copolymer with long spacer. Results in Table 3 stress the effect of the length of the flexible spacer upon thermal properties.

Table 3. Thermal properties of polymers with long spacer.

Polymer	Transition temperatures °C	$\overline{Mn}$
(R,S)-[CBHO-MO] (a)	G 13 S_A 110 I	4500
(R)-[CBHO-MO] (a)	G 13 S_A 80 N 95 I	4600
(R)-[SO]-co-(R,S)-[CBHO-MO] (b,c)	G -16 S 48 N 56 I	n.d

a) prepared with CsOH as initiator (see ref. 10); (b) prepared with tBuOK/DMSO as initiator (this work); (c) the composition of the copolymer is unknown. However, the ratio of reactant monomers was 24 : 76 mol %

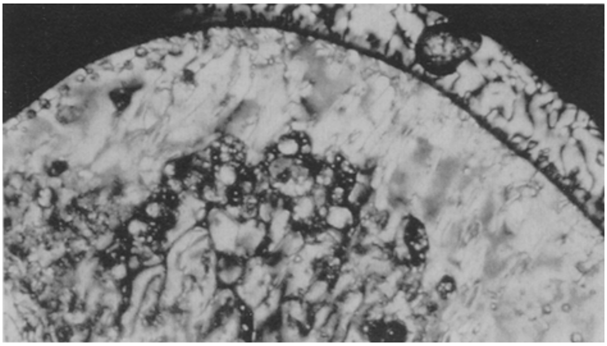


Fig. 2 - The threaded texture of the nematic phase of poly [(R,S)-[SO]-co-(R,S)-[CBO-MO]] [21: 79 mol %]

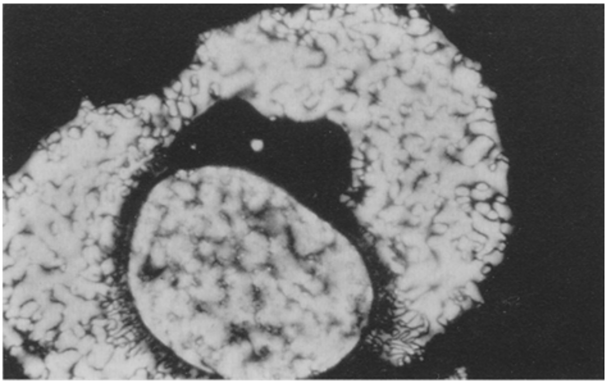


Fig. 3 - The schlieren texture of the nematic phase of poly [(R,S)-[SO]-co-(R,S)-[CBO-MO]] [21: 79 mol %] formed on cooling the isotropic liquid

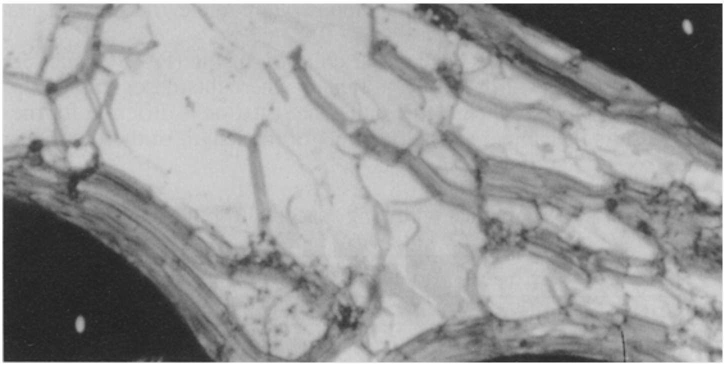


Fig. 4 - The texture of the cholesteric phase of poly [(R)-[SO]-co-(R,S)-[CBO-MO]] [7: 93 mol %]

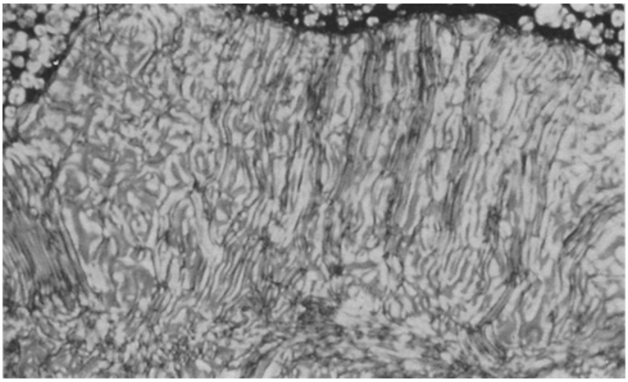


Fig. 5 - The cholesteric texture in a two-component mixture of MBBA and poly [(R)-[SO]-co-(R,S)-[CBO-MO]] [23: 77 mol %]

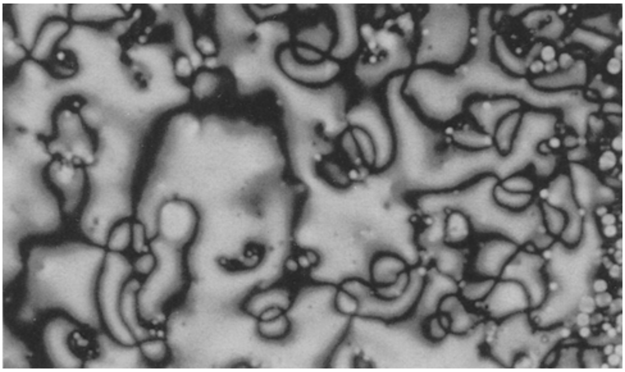


Fig. 6 - The schlieren texture of the nematic phase of the copolymer prepared from (R)-[SO] and the racemic oxirane with the -CH_2-O-$(CH_2)_6$- spacer

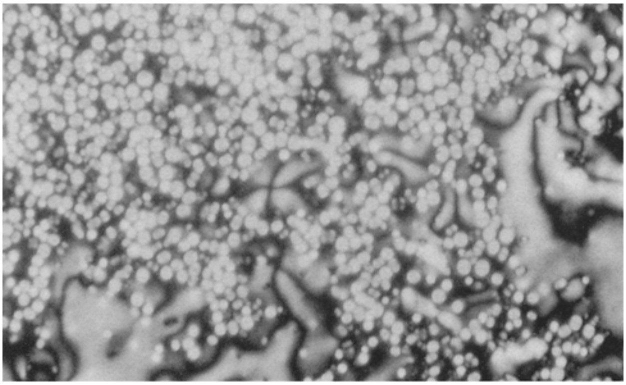


Fig. 7 - The droplets formed on cooling the isotropic liquid of the copolymer prepared from (R)-[SO] and the racemic oxirane with the -CH_2-O-$(CH_2)_6$- spacer

In the case of racemic homopolymers, increase in the length of the spacer from $-CH_2-$ to $-CH_2-O-(CH_2-)_6$ changes a purely nematic polymer to one with a S_A phase with a much lower glass transition temperature (10). As is true for low-molar-mass LCs and a number of SCLCP's (19) the tendency toward smectic mesomorphism increases with increasing spacer length. The lower Tg value reflects the plasticizing action of the longer spacer. Polymerization of the chiral monomer with spacer of only one methylenic unit yields a purely cholesteric polymer (G 81 Ch 166 I (10)) while the chiral monomer with $-CH_2-O-(CH_2)_6$ spacer gives a polymer with a S_A phase and nematic phase. Extending the length of the flexible spacer again gives way to predominantly smectic behavior. The surprising finding, however, is that the chirality of the constitutive unit is no more tranferred to the mesophase. Similar trends are observed for the copolymers prepared from (R)-[SO] and the racemic oxiranes. The short spacer of only one methylene group promotes cholesteric behavior while the $-CH_2-O-(CH_2)_6$ spacer gives a smectic and a nematic phase. Again, in the latter case no cholesteric properties are observed, thus indicating that the twisting power decreases and vanishes as decoupling increases and rotation of the side chain about their long axes becomes less hindered.

Similar results on the transfer of chirality working for short spacers, but not with long ones, were reported previously by Wulff et al. (20) for main chain, chiral vinyl polymers bearing achiral mesogens as substituents.

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