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Tailor made liquid crystalline networks exhibiting a chiral smectic C (S_C^*) mesophase via living cationic copolymerization*

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SUMMARY

Living cationic copolymerization of (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (15-8) with 2-vinyloxyethyloxy methacrylate (16-2) leads to reactive copolymers poly[(15-8)-co-(16-2)]X/Y (where X/Y is the mol ratio between the two monomers in the copolymer) containing methacryloyl side groups. The thermally crosslinked copolymers with X/Y=5/5 to 9/1 display an enantiotropic chiral smectic C (S_C^*) mesophase.

INTRODUCTION

In the previous two communications from this series we described a novel synthetic procedure for the preparation of well defined networks of side chain liquid crystalline polymers.[1,2] This procedure consists of the living cationic copolymerization of a mesogenic vinyl ether with a bifunctional monomer containing vinyl ether methacryloyl polymerizable groups i.e., ω-vinyloxyalkyloxy methacrylate (16-n, whose n represents the number of methylenic groups in the alkyl group of the bifunctional monomer). The vinyl ether group polymerizes via a cationic mechanism while the methacryloyl group polymerizes only by radical or nucleophilic (group transfer, anionic) polymerization mechanism. Therefore, the copolymers obtained from mesogenic vinyl ethers and 16-n contain reactive methacryloyl side groups and therefore, are soluble and thermally reactive. These copolymers can be prepared with well defined composition and molecular weight and narrow polydispersities. Therefore, these thermally reactive side chain liquid crystalline polymers can be processed into well defined shapes either from solution (film) or melt phase. Both processing techniques can be applied below the temperature at which the thermal induced initiation of the polymerization of the methacryloyl side groups takes place. Since the bifunctional monomers 16-n are nonmesogenic and their structures resemble that of ω-vinyloxyalkanes, the phase behavior of these two classes of copolymers is relatively similar.[1,2,3] Therefore, the 16-n with the shorter alkyl group (i.e., 2-vinyloxyethyloxy methacrylate, 16-2) can be incorporated into these copolymers with larger amounts than the 16-n with large n values and still maintain the liquid crystalline phase.[1-3] Consequently, these thermally reactive systems can be used to prepare both networks with low and with high density of crosslinking. Therefore, this novel preparative procedure can be used to tailor make side chain liquid crystalline crosslinked elastomers,[4] which are of theoretical and practical interests for the preparation of single crystal liquid crystalline polymers,[5] novel optical displaying systems,[6] novel piezoelectric materials,[7] etc. Networks of chiral side chain liquid crystalline polymers (i.e., cholesteric and chiral smectic C, S_C^*) represent a novel class of materials which exhibit piezoelectricity.[7]

The goal of this communication is to describe the synthesis of side chain liquid crystalline networks exhibiting a S_C^* mesophase via the living cationic copolymerization of

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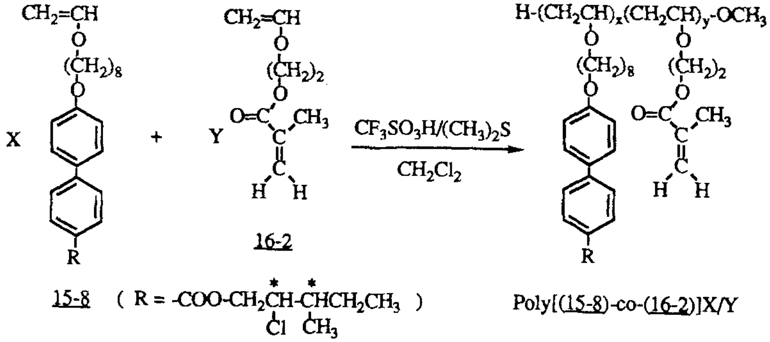

Scheme 1: Cationic copolymerization of (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctoxy) biphenyl-4-carboxylate (15-8) with 2-vinyloxyethyloxy methacrylate (16-2).

(2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (15-8) with 2-vinyloxyethyloxy methacrylate (16-2).

EXPERIMENTAL

Materials

The source and the purification of materials used in this paper were described elsewhere.[1,2,8]

Techniques

The experimental techniques used in the characterization of monomers and polymers were described previously.[1,8] ^1H-NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer 1320 infrared spectrophotometer. Relative molecular weights of polymers were measured by gel permeation chromatography (GPC) against polystyrene standards. A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS data station was used to determine the thermal transition temperatures of the resulting copolymers. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. A Carl-Zeiss optical polarized microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to observe the thermal transitions and to verify the anisotropic textures.

Synthesis of monomers

The synthesis of (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (15-8)[8] and 2-vinyloxyethyloxy methacrylate (16-2)[2] was described previously.

Cationic Polymerizations

The cationic polymerization and copolymerization as well as the characterization of the polymers were performed as described previously.[1]

RESULTS AND DISCUSSION

Scheme 1 outlines the living cationic copolymerization of 15-8 with 16-2 and the structure of the resulting poly[(15-8)-co-(16-2)]X/Y (where X/Y is the mol ratio between the two monomers in the initial reaction mixture) copolymers. The influence of molecular weight on the phase behavior of poly(15-8) was reported in a previous publication.[8] We have decided to synthesize poly[(15-8)-co-(16-2)]X/Y copolymers with degrees of

Table I. Cationic copolymerization of 15-8 with 16-2 (polymerization temperature: 0°C; polymerization solvent: methylene chloride; $[M]_0=[15\text{-}8]+[16\text{-}2]=0.2$ M; $[M]_0/[I]_0=25$; $[(CH_3)_2S]_0/[I]_0=10$; polymerization time: 1hr) and characterization of the resulting polymers. Phase transition data on first, second and third lines under both heating and cooling are from the first, second and third heating and cooling scans, respectively.

Sample No.	[15-8]/[16-2] (mol/mol)†	Polymer yield(%)	Mnx10^{-3}	Mw/Mn GPC	D P	phase transitions (°C) and corresponding enthalpy changes (kcal/mru) heating (20°C/min)	cooling (20°C/min)
1	3/7 (47/53)	60	3.52	1.22	14	g -12.0 i 117.1 (-2.46)	i -7.0 g
						g -2.0 i	i -7.0 g
						g -2.0 i	i -7.0 g
2	5/5 (62/38)	65	4.55	1.21	14	g -10.2 s_C^* 55.0-60.0 (0.15) i 133.5 (-1.40)	i 43.3 (-0.23) s_C^* -12.0 g
						g -6.0 s_C^* 53.0 (0.27) i	i 43.4 (-0.22) s_C^* -11.0 g
						g -7.5 s_C^* 54.0 (0.25) i	i 45.8 (-0.22) s_C^* -11.0 g
3	6/4 (71/29)	61	4.98	1.14	14	g -7.0 s_C^* 60.0-70.0 (0.55) i 136.0 (-1.23)	i 54.9 (-0.54) s_C^* -15.0 g
						g -5.0 s_C^* 63.2 (0.57) i	i 54.8 (-0.50) s_C^* -14.3 g
						g -5.0 s_C^* 63.4 (0.54) i	i 54.8 (-0.50) s_C^* -14.0 g
4	7/3 (75/25)	69	4.78	1.11	13	g -3.5 s_C^* 70.0-80.0 (0.61) i 139.0 (-0.73)	i 63.7 (-0.60) s_C^* -10.0 g
						g 0.2 s_C^* 67.5 (0.62) i	i 64.0 (-0.58) s_C^* -9.8 g
						g 0.5 s_C^* 67.7 (0.62) i	i 64.1 (-0.55) s_C^* -9.0 g
5	8/2 (87/13)	62	4.49	1.26	11	g 5.0 s_C^* 82.0 (0.95) i	i 78.6 (-0.76) s_C^* -3.0 g
						g 6.5 s_C^* 83.3 (0.85) i	i 78.1 (-0.74) s_C^* -2.0 g
						g 6.6 s_C^* 82.9 (0.82) i	i 78.2 (-0.74) s_C^* -2.0 g
6	9/1 (95/5)	73	4.52	1.25	10	g 8.8 s_X 20.1 (0.20) s_C^* 88.7 (††) s_A 95.9 (1.14) i	i 86.9 (-1.05) s_C^* -2.8 g
						g 9.5 s_X 20.5 (0.16) s_C^* 88.7 (††) s_A 94.4 (1.07) i	i 87.0 (-1.02) s_C^* -2.9 g
						g 9.5 s_X 20.6 (0.15) s_C^* 88.7 (††) s_A 94.7 (1.07) i	i 87.0 (-1.01) s_C^* -2.9 g
7	10/0	65	6.17	1.08	13	g 15.2 s_X 43.0 (0.04) s_C^* 92.0 (0.14) s_A 101.8 (1.04) i	i 92.6 (-0.86) s_A 86.9 (-0.16) s_C^* 35.6 (-0.46) s_X 10.3 g
						g 15.0 s_X 41.6 (0.06) s_C^* 90.9 (0.17) s_A 100.0 (0.89) i	i 92.6 (-0.86) s_A 86.9 (-0.16) s_C^* 35.6 (-0.46) s_X 10.3 g
						g 15.0 s_X 41.6 (0.06) s_C^* 90.9 (0.17) s_A 100.0 (0.89) i	i 92.6 (-0.86) s_A 86.9 (-0.16) s_C^* 35.6 (-0.46) s_X 10.3 g

†: The values on the first line are the initial molar ratio of the two monomers; The values in parenthesis are the actual copolymer compositions determined by ^{1}H-NMR spectroscopy.

††: The enthalpy of the overlaped peak is included in that of s_A-i transition peak.

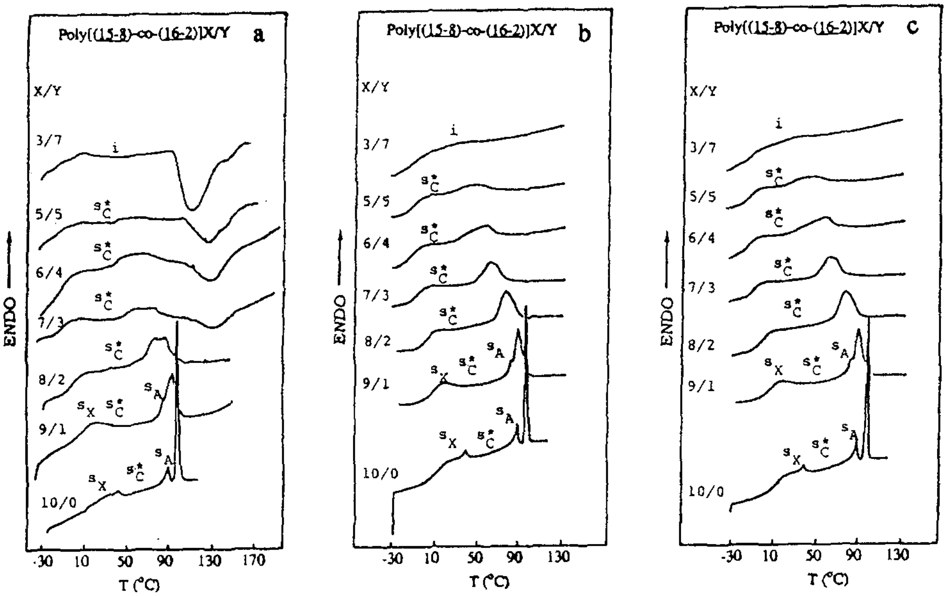

Figure 1: DSC traces of poly[(15-8)-co-(16-2)]X/Y. Copolymer composition is printed on the top of each DSC scan: (a) first heating scan; (b) second heating scan; (c) third heating scan.

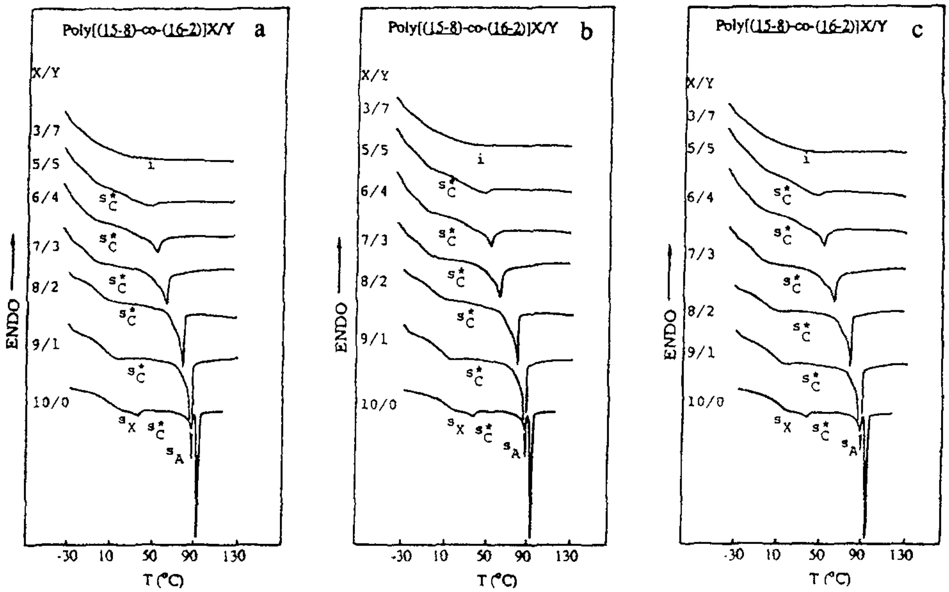

Figure 2: DSC traces of poly[(15-8)-co-(16-2)]X/Y. Copolymer composition is printed on the top of each DSC scan: (a) first cooling scan; (b) second cooling scan; (c) third cooling scan.

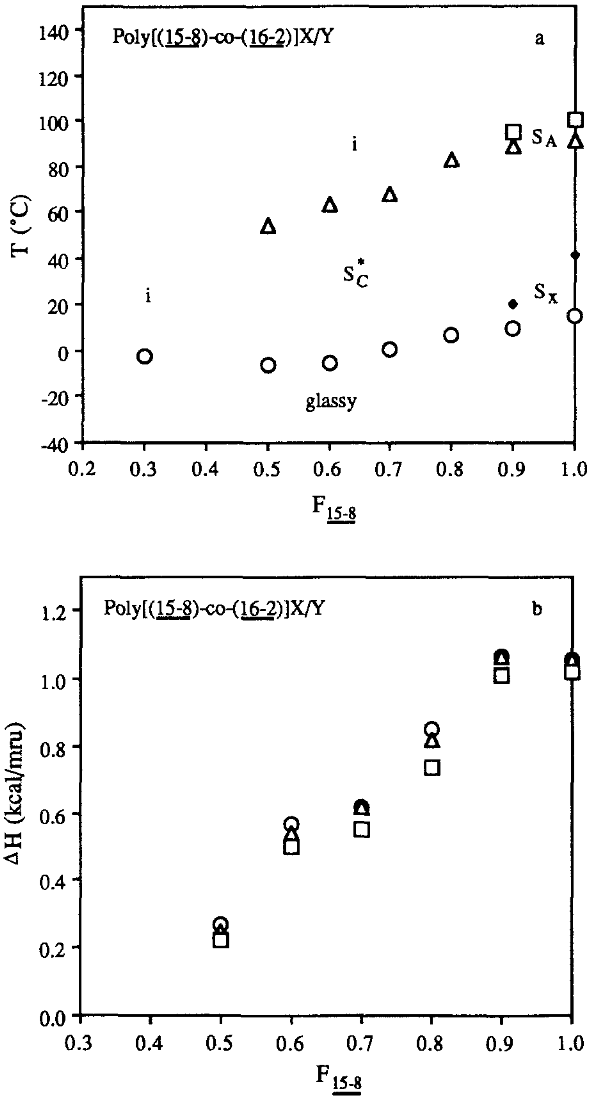

Figure 3: (a) The dependence of phase transition temperatures on copolymer composition of poly[(15-8)-co-(16-2)]X/Y, data from third heating scan: ○ -T(g-S_C^* ,S_X); ◊ -T(S_X-S_C^*); Δ -T(S_C^*-S_A,i); ☐ -T(S_A-i).

(b) The dependence of the enthalpy change associated with the S_C^*-i and i-S_C^* phase transition on copolymer composition for poly[(15-8)-co-(16-2)]X/Y: ○ -data from the second heating scan; Δ -data from the third heating scan; ☐ -data from the third cooling scan.

polymerization (DP) of 12 ± 2.0. Poly(15-8) with DP=13 displays enantiotropic S_X (i.e., an unassigned smectic mesophase), S_C^* and S_A mesophases (Table I). The copolymerization and characterization results are summarized in Table I. Data collected from the first heating DCS scan refer to the uncrosslinked polymers. Data collected from the second and third heating as well as from the first, second and third cooling scans refer to samples which were crosslinked via the thermal induced polymerization of the methacryloyl side groups of the copolymers.

The thermal induced crosslinking process and the influence of copolymer composition on the phase behavior of the polymers before and after crosslinking can be followed from the DSC traces presented in Figures 1 and 2. Poly[(15-8)-co-(16-2)]X/Y with X/Y=3/7 is only isotropic both before and after crosslinking. On its first heating scan this copolymer exhibits an exothermic peak which is due to the thermal induced polymerization of the methacryloyl side groups (Figure 1a). On the subsequent heating and cooling DSC scans (Figure 1b, c, Figure 2) the crosslinked polymer displays only a glass transition temperature. Poly[(15-8)-co-(16-2)]X/Y with X/Y=5/5 to 7/3 display on their first heating scan a S_C^* mesophase followed by the polymerization exotherm. The polymerization of the methacryloyl groups of these copolymers occurs in their isotropic phase. The polymerization exotherm can not be observed in the case of copolymers with X/Y=8/2 and 9/1. During their second and subsequent heating DSC heating scan as well as during their cooling scans the crosslinked copolymers with X/Y=5/5 to 9/1 exhibit an enantiotropic S_C^* mesophase (Figures 1, 2). A close examination of the DSC traces from Figure 1 reveals that while in poly(15-8) the endothermic peaks due to the transition from S_C^* to S_A and from S_A to isotropic are well separated, in the copolymers they merged into a single peak. Only in the case of uncrosslinked and crosslinked copolymers with X/Y=9/1 we still can observe that the peaks related to these two transitions are overlapped. In all other copolymers we can observe only the direct transition from the isotropic to the S_C^* mesophase since these two transitions are indistinguishable.

This result is rewarding since in most cases the S_C^* mesophase is generated by cooling a S_A phase, and these results demonstrate that the method elaborated in this series of communications can generate networks which exhibit only a S_C^* mesophase although the parent homopolymer exhibited the sequence of isotropic-S_A-S_C^*. Interesting to mention is that the S_X phase available in poly(15-8) also disappears in the networks prepared by the thermal crosslinking of poly[(15-8)-co-(16-2)]X/Y copolymers. Figure 3a presents the dependence of the phase transition temperatures while Figure 3b the dependence of their corresponding enthalpy changes both as a function copolymer composition. A representative texture of S_C^* exhibited by poly[(15-8)-co-(16-2)]X/Y is given in Figure 4. These phase diagrams demonstrate once again that poly[(15-8)-co-(16-2)]X/Y copolymers lead to crosslinked networks displaying a S_C^* mesophase over a broad range of composition i.e., X/Y=5/5 to 9/1. This allows the preparation of either only lightly crosslinked systems or highly crosslinked systems. Another very interesting result is that the crosslinked networks do exhibit lower glass transition temperatures than those of the parent poly(15-8). This is because the insertion of structural units derived from 16-2 lowers the glass transition of the copolymer, and although upon crosslinking the glass transition increases, it still does not increase sufficient to reach the value of poly(15-8). Therefore, this synthetic procedure is of interest for the molecular engineering of elastomeric networks exhibiting various mesophases including the S_C^* phase which was described in the present communication.

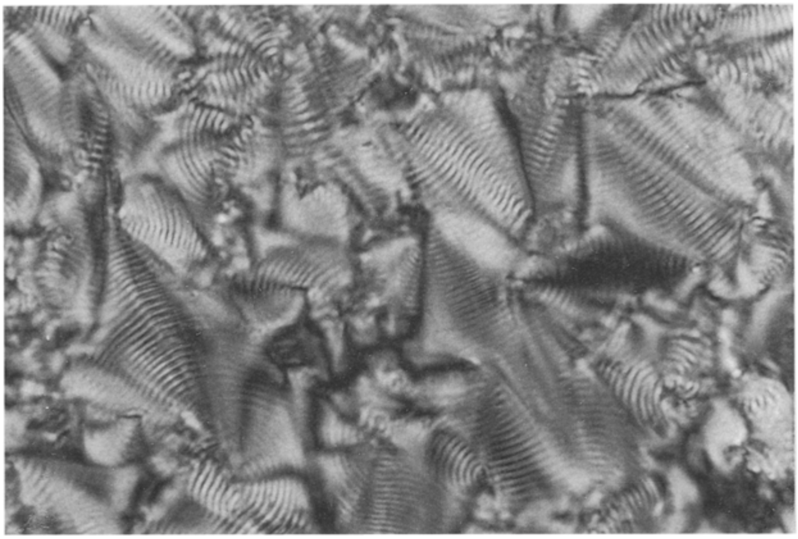

Figure 4: A representative optical polarized micrograph of S_C^* mesophase (x160) of poly[(15-8)-co-(16-2)]X/Y with X/Y=9/1 at 50°C on cooling.

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