

Liquid crystalline networks via living cationic polymerization of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether with 11-vinyloxyundecanyloxy methacrylate*

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SUMMARY

Living cationic copolymerization of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (**6-11**) with 11-vinyloxyundecanyloxy methacrylate (**16-11**) leads to copolymers poly[(**6-11**)-co(**16-11**)]X/Y (where X/Y is the mol ratio between the two monomers in copolymer) containing methacryloyl side groups. All copolymers are crosslinked upon annealing via the thermal induced polymerization of their methacryloyl side groups. The copolymers with X/Y = 6/4 to 9/1 lead after crosslinking to liquid crystalline networks exhibiting a S_A mesophase.

INTRODUCTION

Liquid crystalline (LC) networks obtained from side chain liquid crystalline polymers (LCPs) are of interest for the preparation of liquid crystalline elastomers,² single crystal liquid crystalline polymers,³ piezoelectric materials,⁴ for the design of novel optical display systems,⁵ etc. Most frequently, they are prepared by radical copolymerization of a bifunctional or of a mixture containing a bifunctional and a monofunctional monomer (by using either thermal- or photo-radical initiators),⁶ and by the crosslinking of a preformed liquid crystalline polysiloxane containing free Si-H groups with a divinyl compound via hydrosilylation.⁷ Both methods and variants of them lead to networks with segments of broad polydispersity and offer limited fabrication capabilities.

As a continuation of our research on the use of living cationic polymerization to tailor make side chain liquid crystalline polymers,⁸ copolymers,^{8g,h,i,9} macromonomers¹⁰ and block copolymers,¹¹ we will report a novel and general synthetic method for the preparation of side chain LCP networks. Our previous research on side chain LCPs by living cationic polymerization was reviewed.¹² This novel synthetic method consists of the living cationic copolymerization of a mesogenic vinyl ether with a bifunctional ω-vinyloxyalkyloxy methacrylate to obtain a liquid crystalline copolymer with well defined copolymer composition and molecular weight and narrow molecular weight distribution containing reactive methacryloyl side groups. Cationic polymerization of the difunctional ω-vinyloxyalkyloxy methacrylate proceeds via the vinyl ether group thus generating polymers containing reactive methacryloyl side groups. These processable thermal reactive polymers can be crosslinked as films or in other shapes by thermal heating and by other methods like photo-initiation etc., to generate networks with well defined density of crosslinking, phase transition temperatures and containing liquid crystalline segments of well defined molecular weight and narrow polydispersities.

The goal of this series of communications is to describe the synthesis of networks obtained by the living cationic polymerization of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (**6-11**) with 11-vinyloxyundecanyloxy methacrylate (**16-11**) and 2-vinyloxyethyloxy methacrylate (**16-2**) and of (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy) biphenyl-4-carboxylate (**15-8**) with **16-2**, followed by thermal

*This paper is part 26 in the series: Molecular engineering of liquid-crystalline polymers by living polymerization. Part 25: H. A. Schneider, V. Percec, Q. Zheng; Polymer, submitted

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crosslinking. The influence of copolymer composition and of the length of the alkyl group of the ω -vinyloxyalkyloxy methacrylate (16-*n*) monomer on the phase behavior of the resulted networks will be discussed. The networks obtained from the first two pairs of monomers, i.e., poly[(6-11)-co-(16-*n*)]X/Y (*n*=11 and 2) displaying a smectic (S_A) mesophase while the networks obtained from the third pair of monomers, i.e., poly[(15-8)-co-(16-2)]X/Y (where X/Y represents the mol ratio between the structural units of the two monomers) displays a chiral smectic C (S_C^*) mesophase. This first communication describes the copolymer system poly[(6-11)-co-(16-11)]X/Y.

EXPERIMENTAL

Materials

4-Hydroxybiphenyl (97%), 11-bromoundecan-1-ol (98%), *n*-butyl vinyl ether (98%), copper (I) cyanide (99%) (all from Aldrich), 1,10-phenanthroline (anhydrous, 99%), palladium (II) diacetate (both from Lancaster Synthesis) were used as received. Methacrylic acid (99%, from Aldrich) was distilled under vacuum prior to use. Methylene chloride (from Fisher) was purified by washing with concentrated sulfuric acid several times until the acid layer remained colorless, then with water, dried over anhydrous $MgSO_4$, refluxed over calcium hydride and freshly distilled under argon before each use. Dimethyl sulfide (anhydrous, 99%, from Aldrich) was first refluxed and then distilled over sodium metal under nitrogen. Trifluoromethanesulfonic acid (triflic acid, 98%, from Aldrich) was distilled under vacuum.

Techniques

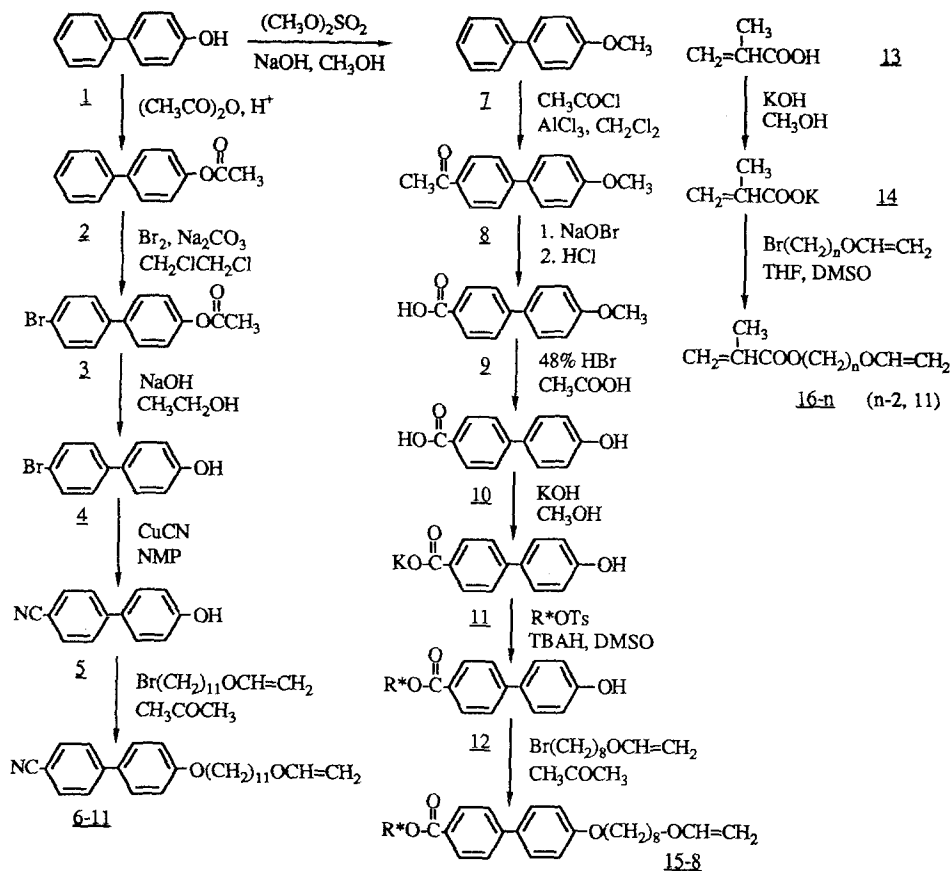
1H -NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer 1320 infrared spectrophotometer. Relative molecular weights of polymers were measured against polystyrene standards by gel permeation chromatography (GPC) with a Perkin-Elmer Series 10 LC instrument equipped with LC-100 column oven and a Nelson Analytical 900 series integrator data station. A set of two Perkin-Elmer PL gel columns of 5×10^2 and 10^4 Å with $CHCl_3$ as solvent (1ml/min) were used. The measurements were made at 40°C using the UV detector. High pressure liquid chromatography (HPLC) experiments were performed with the same instrument. A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS data station was used to determine the thermal transition temperatures which were reported as the maximum and minimum of their endothermic and exothermic peaks. In all cases, heating and cooling rates were 20°C/min. 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 11-[(4-Cyano-4'-biphenyl)oxy]undecanyl Vinyl Ether (6-11), (2*S*, 3*S*)-(+)-2-Chloro-3-methylpentyl 4'-(8-Vinyloxyoctyloxy)biphenyl-4-carboxylate (15-8) and ω -Vinyloxyalkyloxy Methacrylate (16-*n*)

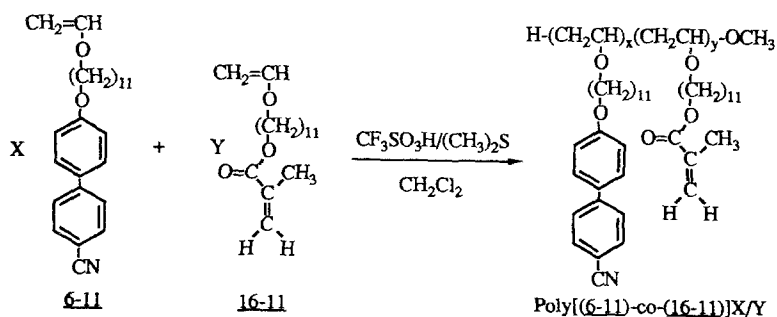
6-11^{8a}, 15-8^{8h} and 14¹³ were synthesized as described previously (Scheme 1). The synthesis of 16-11 is described below.

Synthesis of 2-Vinyloxyundecanyloxy Methacrylate (16-11)

Potassium methacrylate (14) was prepared by titrating a solution of methacrylic acid (25 ml, 0.29 mol) in methanol (400 ml) with 1.5 M KOH in methanol (216 ml, 0.32 mol) using phenolphthalein as indicator. The resulting solution was poured into diethyl ether to give a white precipitate, which was filtered and dried. 14 (4.0 g, 32 mmol) was dissolved in 15 ml dry THF and 15 ml dry DMSO. 11-Bromoundecanyl vinyl ether (8.4 g, 31 mmol) was then added to the solution and the reaction mixture was heated at 67°C for 20 hours. The reaction mixture was poured into 200 ml H_2O and the product was extracted with diethyl ether several times. After the combined ether solution was dried



Scheme 1: Synthesis of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (**6-11**), (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctoxy)biphenyl-4-carboxylate (**15-8**) and ω -vinyloxyalkyloxy methacrylate (**16-n**).



Scheme 2: Cationic copolymerization of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (**6-11**) with 11-vinyloxyundecanyloxy methacrylate (**16-11**).

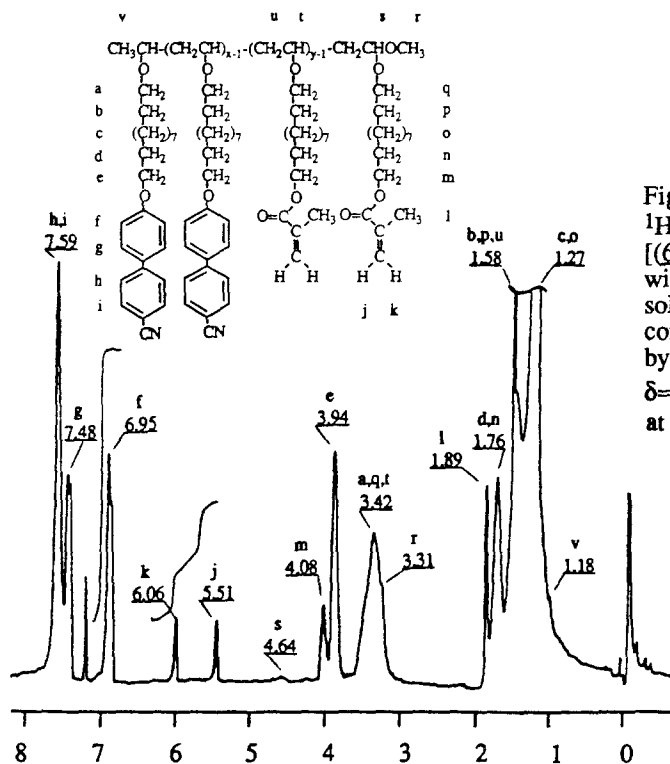


Figure 1: A representative ¹H-NMR spectrum of poly [(6-11)-co-(16-11)]X/Y with X/Y=7/3 (CDCl₃ as solvent). The copolymer composition was determined by the ratio of the singlet at $\delta=6.06$ vs. the broad singlet at $\delta=6.95$.

over anhydrous MgSO₄, diethyl ether was removed on a rotary evaporator to give a slightly yellow liquid. The crude product was purified by column chromatography (silica gel, CH₂Cl₂:C₆H₁₄=2:1 (v/v) mixture as eluent) to yield 4.6 g colorless liquid (51%). ¹H-NMR δ_{H} (CDCl₃, TMS): 1.29 (broad s, 14H, -COOCH₂CH₂(CH₂)₇-), 1.64 (broad s, 4H, -COOCH₂CH₂-, and -OCH₂CH₂-), 1.94 (s, 3H, CH₂=CH(CH₃)-), 3.66 (t, 2H, CH₂=CHOCH₂-), 3.99 (d, 1H, CH₂=CHO-, trans), 4.16 (m, 3H, CH₂=CHO-, cis and -COOCH₂-), 5.54 (s, 1H, CH₂=C(CH₃)-, trans to -CH₃), 6.09 (s, 1H, CH₂=C(CH₃)-, cis to -CH₃), 6.42-6.53 (m, 1H, CH₂=CHO-).

Cationic Polymerizations

Polymerizations were carried out in a three-necks round bottom flask equipped with Teflon stopcock and rubber septum under argon atmosphere at 0°C for 1 hour. All glassware was dried overnight at 140°C. The monomer was further dried under vacuum overnight in the polymerization flask. After the flask was filled with argon, freshly distilled dry methylene chloride was added through a syringe and the solution was cooled to 0°C. Freshly distilled dimethyl sulfide and triflic acid were then added respectively via a syringe. The monomer concentration was about 0.2 M and the dimethyl sulfide concentration was 10 times larger than that of the triflic acid initiator. The polymer molecular weight was controlled by the monomer/initiator ($[M]_0/[I]_0$) ratio. After quenching the polymerization with ammoniacal methanol, the reaction mixture was precipitated into methanol. The resulting polymers were purified by precipitation from methylene chloride solution into methanol and were collected by filtration and/or centrifugation. All polymers obtained were dried in a vacuum oven at room temperature for more than 48 hours prior to characterization.

Table I. Cationic copolymerization of 6-11 with 16-11 (polymerization temperature: 0°C; polymerization solvent: methylene chloride; $[M]_0 = [6-11] + [16-11] = 0.2M$; $[M]_0/[I]_0 = 25$; $[(CH_3)_2Si]_0/[I]_0 = 10$; 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.	[6-11]/[16-11] (mol/mol)†	Polymer yield(%)	Mnx10 ⁻³	Mw/Mn	D P	phase transitions (°C) and corresponding enthalpy changes (kcal/mru)	
						heating (20°C/min)	cooling (20°C/min)
1	3/7 (37/63)	78	5.43	1.07	17	k 44.7 (0.72) i 123 (-3.74)	i 11.1 g
						g 15.0 i	i 11.9 g
						g 19.8 i	i 14.9 i
2	4/6 (50/50)	83	6.09	1.05	19	k 44.8 (0.85) i 117 (-3.89)	i 11.0 g
						g 14.2 i	i 11.9 g
						g 17.0 i	i 14.1 g
3	5/5 (53/47)	88	6.17	1.06	18	k 49.5 (1.70) sA 120 (-2.80)	i 7.9 g
						g 12.0 i	i 9.0 g
						g 14.5 i	i 10.5 g
4	6/4 (65/35)	87	6.72	1.06	19	k 49.8 (2.08) sA 121 (-2.30)	i 89.0 (-0.11) sA 2.3 g
						g 8.8 sA 97.5 (0.13) i	i 88.0 (-0.10) sA 2.4 g
						g 9.8 sA 95.1 (0.12) i	i 87.4 (-0.10) sA 2.6 g
5	7/3 (74/26)	92	6.83	1.05	18	k 50.4 (2.14) sA 126 (-1.26)	i 101 (-0.27) sA 2.0 g
						g 5.0 sA 109 (0.33) i	i 101 (-0.27) sA 1.1 g
						g 7.8 sA 107 (0.30) i	i 99.0 (-0.25) sA 1.3 g
6	8/2 (83/17)	88	6.40	1.06	17	k 48.6 (2.27) sA 122 (0.50) i	i 97.1 (-0.51) sA 21.0 (-0.93) sX 2.0 g
						g 5.0 sX 63.2 (1.88) sA 100 (0.58) i	i 97.4 (-0.49) sA 22.4 (-0.98) sX 2.1 g
						g 6.5 sX 64.1 (1.83) sA 100 (0.57) i	i 98.3 (-0.46) sA 22.8 (-0.98) sX 2.3 g
7	9/1 (90/10)	85	6.83	1.06	18	k 51.9 (2.66) sA 139.5 (0.78) i	i 116 (-0.54) sA 9.7 (-0.054) sX 2.5 g
						g 6.5 sX 55.5 (1.82) sA 120 (0.58) i	i 114 (-0.53) sA 11.3 (-0.054) sX 3.0 g
						g 7.0 sX 56.6 (1.70) sA 118 (0.58) i	i 114 (-0.53) sA 12.5 (-0.056) sX 3.0 g
8	10/0	81	7.40	1.12	19	g 14.5 k 57.1 (3.45) sA 160 (0.90) i	i 149 (-0.89) sA 18.9 (-0.63) sX 8.8 g
						g 14.0 sX 44.2 (0.93) sA 156 (0.87) i	i 149 (-0.89) sA 18.9 (-0.63) sX 8.8 g
						g 14.0 sX 44.2 (0.93) sA 156 (0.87) i	i 149 (-0.89) sA 18.9 (-0.63) sX 8.8 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 ¹H-NMR spectroscopy.

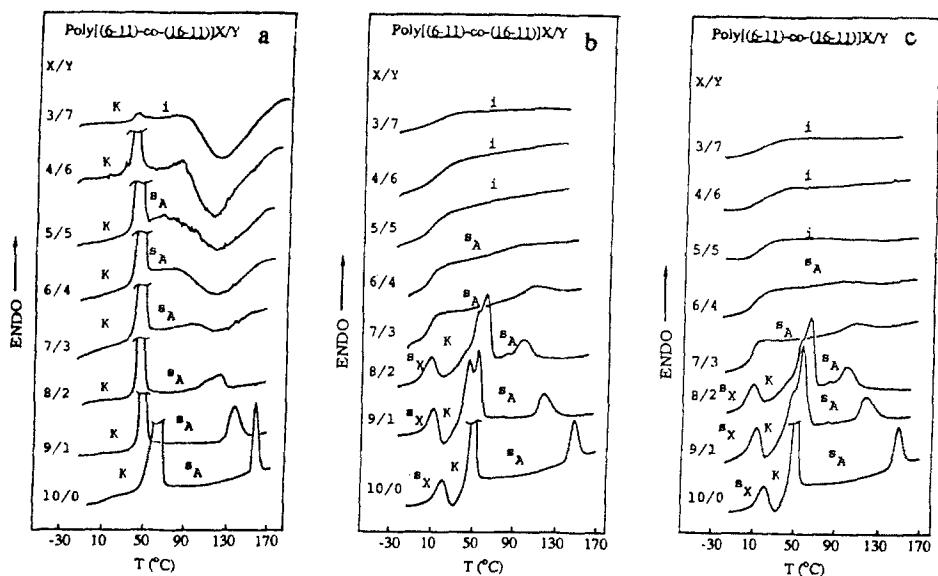


Figure 2: DSC traces of poly[(6-11)-co-(16-11)]X/Y. Copolymer composition is printed on the top of each DSC scan: (a) first heating scan; (b) second heating scan; (c) third heating scan.

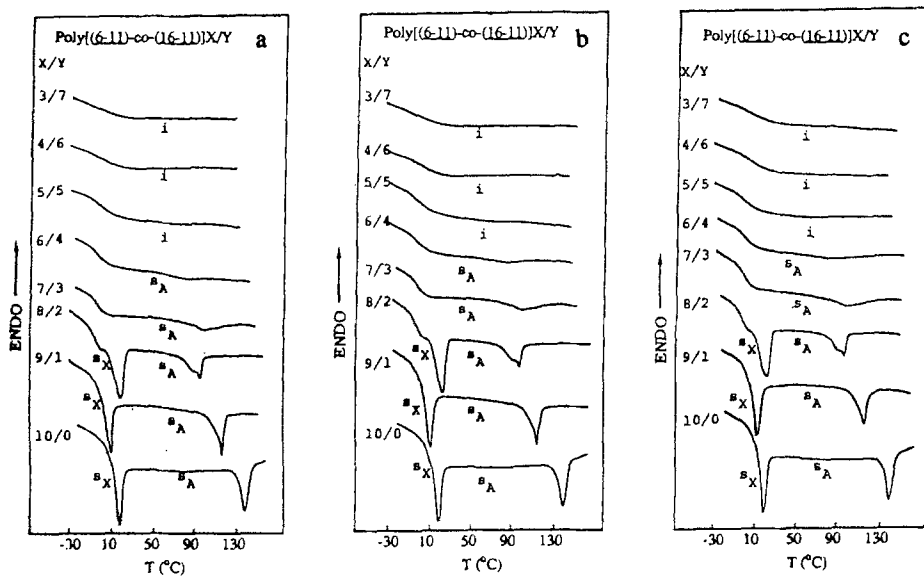


Figure 3: DSC traces of poly[(6-11)-co-(16-11)]X/Y. Copolymer composition is printed on the top of each DSC scan: (a) first cooling scan; (b) second cooling scan; (c) third cooling scan.

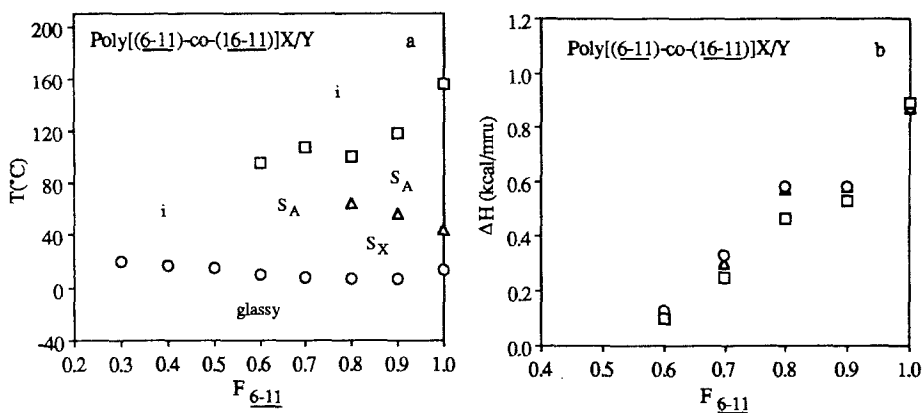


Figure 4: (a) The dependence of phase transition temperatures on copolymer composition of poly[(6-11)-co-(16-11)]X/Y; data from the third heating scan: ○ -T(g-S_A, S_X); △ -T(S_X-S_A); □ -T(S_A-i). (b) The dependence of the enthalpy change associated with the S_A-i and i-S_A phase transition on copolymer composition for poly[(6-11)-co-(16-11)]X/Y; ○ -data from the second heating scan; △ -data from the third heating scan; □ -data from the third cooling scan.

RESULTS AND DISCUSSION

Scheme 1 describes the synthesis of 16-11 while Scheme 2 the living cationic copolymerization of 6-11 with 16-11 and the structure of the resulting poly[(6-11)-co-(16-11)]X/Y copolymers. Copolymerization results and the phase behavior of the resulting copolymers are summarized in Table I. All copolymers have a degrees of polymerization (DP) of 18 ± 1 and polydispersities lower than 1.10. A representative 200 MHz ¹H-NMR spectrum of poly[(6-11)-co-(16-11)]X/Y (with X/Y=7/3) is presented in Figure 1. This spectrum demonstrates that the methacryloyl groups are tolerated by this cationic polymerization. The composition of the copolymers was calculated from their NMR spectrum and is also presented in Table I.

Figure 2 presents the first, second and third DSC heating scans of all copolymers. The corresponding cooling scans are shown in Figure 3. On the first DSC scan copolymers with X/Y=3/7 to 7/3 exhibit an exotherm which appears above the melting temperature of the copolymer. This exothermic process is due to the heat of the polymerization of the methacryloyl side groups. Due to its low value, it can not be observed for copolymers with X/Y=8/2 and 9/1. After the first heating scan all copolymers are insoluble. Subsequent heating scans increase the extent of crosslinking although no exothermic peak can be observed on their DSC traces. During the third heating scan the network obtained from copolymers with X/Y=6/4 to 9/1 exhibit a S_A phase. The networks obtained from copolymers with X/Y=8/2 and 9/1 are still exhibiting a melting transition.

Figure 4 plots the dependence of phase transition temperatures and the enthalpy changes associated with S_A-i and i-S_A transition of the networks as a function copolymer composition. The texture of the S_A phase exhibited by poly[(6-11)-co-(16-11)]X/Y resembles the one exhibited by poly(6-11)^{8a}. These results have demonstrated that liquid crystalline networks of poly[(6-11)-co-(16-11)]X/Y can incorporate up to as much as 40 mol % of 16-11 monomer. Therefore, these networks can be prepared with various degrees of crosslinking. The precursor reactive copolymer can be maintained and processed in various ways as long as it is manipulated at lower temperatures than those of the polymerization exotherms from Figure 2a.

ACKNOWLEDGMENTS

Financial support from the Office of Naval Research and a NATO traveling grant are gratefully acknowledged.

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