Polymer Bulletin 29, 493–500 (1992)

**Polymer Bulletin**

# Thermally reactive liquid crystalline copolymers based on 11-[(4-cyano-4′-biphenyl)oxy]undecanyl vinyl ether and 2-vinyloxyethyloxy methacrylate*

**V. Percec** and Q. Zheng**

Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA

## SUMMARY

Living cationic copolymerization of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11) with 2-vinyloxyethyloxy methacrylate (16-2) leads to reactive copolymers poly[(6-11)-co-(16-2)]X/Y (where X/Y is the mol ratio between the two monomers in copolymer) containing methacryloyl side groups. Upon thermal crosslinking via the polymerization of their methacryloyl side groups, the copolymers with X/Y=5/5 to 9/1 lead to liquid crystalline networks displaying a $S_A$ mesophase. These results have demonstrated that a shorter spacer in the reactive bifunctional monomer 16-2 than in the mesogenic 6-11 monomer leads to networks with broader range of mesomorphism than those derived from a reactive monomer containing a spacer length equal to that of the mesogenic monomer.

## INTRODUCTION

In the previous publication from this series[1] we described the elaboration of a novel synthetic procedure for the preparation of thermally reactive side chain liquid crystalline polymers. It consist of the living cationic copolymerization of a mesogenic vinyl ether[2,3,4] with ω-vinyloxyalkyloxy methacrylate. The resulted copolymers contain reactive methacryloyl side group. These reactive polymers have well defined molecular weights, narrow polydispersities and well defined composition. They can be crosslinked either by direct heating as films or other shapes or by UV initiation polymerization methods.

Previous results from our laboratory on the cationic copolymerization of mesogenic vinyl ethers with unreactive ω-vinylalkyloxy ethers have shown that the range of the mesophase of these copolymers is much broader for the copolymers with short alkyl groups in the ω-vinylalkyloxy ethers used.[5] Based on these results we can speculate that the same should be the case for the range of the mesophase obtained with ω-vinylalkyloxy ethers and mesogenic vinyl ethers. In the previous paper from this series we reported the synthesis and characterization of the thermally reactive copolymers prepared from 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11) and 11-vinyloxyundecanyloxy methacrylate (16-11). The resulted networks displayed a $S_A$ mesophase up to amounts of 16-11 in the reactive copolymer as high as 40 mol %.

The goal of this communication is to report our results on the synthesis and characterization of thermally reactive copolymers based on 6-11 and 2-vinyloxyethyloxy methacrylate (16-2).

## EXPERIMENTAL

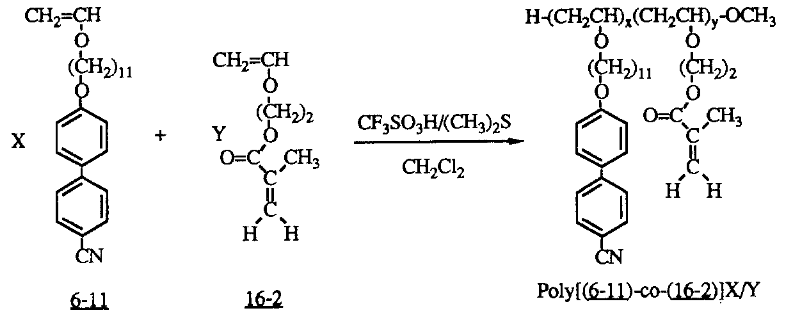
### Materials

2-Chloroethyl vinyl ether (99%, from Aldrich) was used as received. Other materials used were described in the previous publication.[1]

---

*This paper is part 27 in the series: Molecular engineering of liquid-crystalline polymers by living polymerization. Part 26: V. Percec, Q. Zheng: Polym. Bull., previous paper in the issue

**Corresponding author



6-11 16-2 Poly[(6-11)-co-(16-2)]X/Y

Scheme 1: Cationic copolymerization of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11) with 2-vinyloxyethyloxy methacrylate (16-2).

### Techniques

The instruments and conditions used in the characterization of the resulting copolymers were described previously.[1]

### Synthesis of monomers

The synthesis of 6-11 was described previously.[2a] The synthesis of 16-2 is described below.

### Synthesis of 2-Vinyloxyethyloxy Methacrylate (16-2)

Monomer 16-2 was synthesized by the method described previously[1] for 16-11. Starting with 9.0 g (72.5 mmol) potassium meacrylate and 7.3 g (68.9 mmol) 2-chloroethyl vinyl ether, 5.1 g of a colorless liquid was produced (47%). $^1$H-NMR $\delta_H$ ($CDCl_3$, TMS): 1.96 (s, 3H, $CH2=CH(C\underline{H}_3)$-), 3.94 (t, 2H, $CH_2=CHOC\underline{H}_2$-), 4.05 (d, 1H, $C\underline{H}_2=CHO$-, trans), 4.22 (d, 1H, $C\underline{H}_2=CHO$-, cis), 4.39 (t, 2H, $-COOC\underline{H}_2$-), 5.60 (s, 1H, $C\underline{H}_2=C(CH_3)$-, trans to $-CH_3$), 6.16 (s, 1H, $C\underline{H}_2=C(CH_3)$-, cis to $-CH_3$), 6.44-6.54 (m, 1H, $CH_2=C\underline{H}O$-).

### Cationic Polymerizations

The cationic copolymerizations were performed as described previously.[1]

## RESULTS AND DISCUSSION

Scheme 1 outlines the living cationic copolymerization of 6-11 with 16-2 and the structure of the resulting poly[(6-11)-co-(16-2)]X/Y (where X/Y is the mol ratio between the two monomers in the initial reaction mixture) copolymers. The copolymerization results and the characterization of all copolymers resulted from the first, second and third heating and cooling DSC scans are summarized in Table I. The number average degrees of polymerization (DP) of all copolymers are 18 ± 2 and their polydispersities are less than 1.20.

Figure 1 presents the DSC traces of the first, second and third heating scan, while Figure 2 those of the corresponding cooling scans. Copolymers with X/Y=2/8 to 5/5 exhibit a polymerization exotherm after the melting point. Above this polymerization exotherm the polymers are isotropic. However on cooling and reheating the crosslinked poly[(6-11)-co-(16-2)]X/Y with X/Y=4/6 and 5/5 exhibit the $S_A$ mesophase displayed by poly(6-11). The networks obtained from copolymers with X/Y=3/7 and 2/8 are isotropic. In the case of copolymers with X/Y=5/5 the polymerization exotherm starts on top of the endothermic peak which was due to the isotropization of the $S_A$ phase (Fig. 1a).

Table I. Cationic copolymerization of 6-11 with 16-2 (polymerization temperature: 0°C; polymerization solvent: methylene chloride; $[M]_0=[6\text{-}11]+[16\text{-}2]=0.2M$; $[M]_0/[I]_0=25$; $[(CH_3)_2S]_0/[I]_0=10$; 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. | [6-11]/[16-2] (mol/mol)† | Polymer yield(%) | $Mn\times10^{-3}$ | Mw/Mn | D P | phase transitions (°C) and corresponding enthalpy changes (kcal/mru) | |
|---|---|---|---|---|---|---|---|
| | | | GPC | GPC | | heating (20°C/min) | cooling (20°C/min) |
| 1 | 2/8 | 65 | 4.12 | 1.10 | 20 | g -5.5 k 49.5 (0.59) i 104 (-5.22) | i 9.5 g |
| | (46/54) | | | | | g 12.5 i | i 11.5 g |
| | | | | | | g 14.0 i | i 13.0 g |
| 2 | 3/7 | 53 | 3.97 | 1.15 | 18 | g -3.0 k 50.7 (1.11) $s_A$ 100 (-2.73) | i 6.6 g |
| | (53/47) | | | | | g 10.2 i | i 7.5 g |
| | | | | | | g 10.5 i | i 7.5 g |
| 3 | 4/6 | 58 | 4.42 | 1.17 | 18 | g 1.0 k 53.9 (1.72) $s_A$ 110 (-1.97) | i 86.9 (-0.20) $s_A$ 4.5 g |
| | (60/40) | | | | | g 9.5 $s_A$ 96. 3 (0.27) i | i 88.8 (-0.19) $s_A$ 5.0 g |
| | | | | | | g 10.0 $s_A$ 97.3 (0.27) i | i 88.6 (-0.17) $s_A$ 5.5 g |
| 4 | 5/5 | 65 | 4.29 | 1.19 | 16 | g 4.2 k 50.9 (1.90) $s_A$ 126 (-1.09) | i 120 (-0.38) $s_A$ 4.1 g |
| | (72/28) | | | | | g 9.2 $s_A$ 128, 151 (0.43) i | i 120 (-0.30) $s_A$ 4.7 g |
| | | | | | | g 9.8 $s_A$ 128, 150 (0.42) i | i 120 (-0.26) $s_A$ 5.1 g |
| 5 | 6/4 | 70 | 4.96 | 1.14 | 17 | g 5.1 k 51.8 (1.83) $s_A$ 119 (0.62) i | i 116 (-0.54) $s_A$ 1.2 g |
| | (78/22) | | | | | g 6.8 $s_A$ 121, 136 (0.58) i | i 116 (-0.53) $s_A$ 1.5 g |
| | | | | | | g 7.1 $s_A$ 122 (0.58) i | i 116 (-0.53) $s_A$ 1.8 g |
| 6 | 7/3 | 76 | 5.43 | 1.13 | 17 | g 6.8 k 51.7 (1.87) $s_A$ 132 (0.76) i | i 127 (-0.64) $s_A$ 2.2 g |
| | (82/18) | | | | | g 7.5 $s_A$ 130, 142 (0.65) i | i 127 (-0.64) $s_A$ 2.7 g |
| | | | | | | g 8.0 $s_A$ 130, 141 (0.64) i | i 127 (-0.64) $s_A$ 3.0 g |
| 7 | 8/2 | 80 | 5.94 | 1.10 | 17 | g 9.3 k 53.5 (2.19) $s_A$ 141 (0.83) i | i 135 (-0.73) $s_A$ 5.5 g |
| | (89/11) | | | | | g 9.7 $s_A$ 139 (0.79) i | i 135 (-0.72) $s_A$ 6.2 g |
| | | | | | | g 10.1 $s_A$ 139 (0.77) i | i 135 (-0.69) $s_A$ 6.5 g |
| 8 | 9/1 | 88 | 6.12 | 1.12 | 17 | g 11.0 k 55.8 (2.39) $s_A$ 150 (0.86) i | i 144 (-0.78) $s_A$ 6.4 g |
| | (93/7) | | | | | g 11.9 $s_A$ 150 (0.81) i | i 143 (-0.78) $s_A$ 6.9 g |
| | | | | | | g 12.1 $s_A$ 151 (0.79) i | i 142 (-0.78) $s_A$ 7.0 g |
| 9 | 10/0 | 81 | 7.40 | 1.12 | 19 | g 14.5 k 57.1 (3.45) $s_A$ 160 (0.90) i | i 149 (-0.89) $s_A$ 18.9 (-0.63) $s_X$ 8.8 g |
| | | | | | | g 14.0 $s_X$ 44.2 (0.93) $s_A$ 156 (0.87) i | i 149 (-0.89) $s_A$ 18.9 (-0.63) $s_X$ 8.8 g |
| | | | | | | g 14.0 $s_X$ 44.2 (0.93) $s_A$ 156 (0.87) i | i 149 (-0.89) $s_A$ 18.9 (-0.63) $s_X$ 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 $^1$H-NMR spectroscopy.

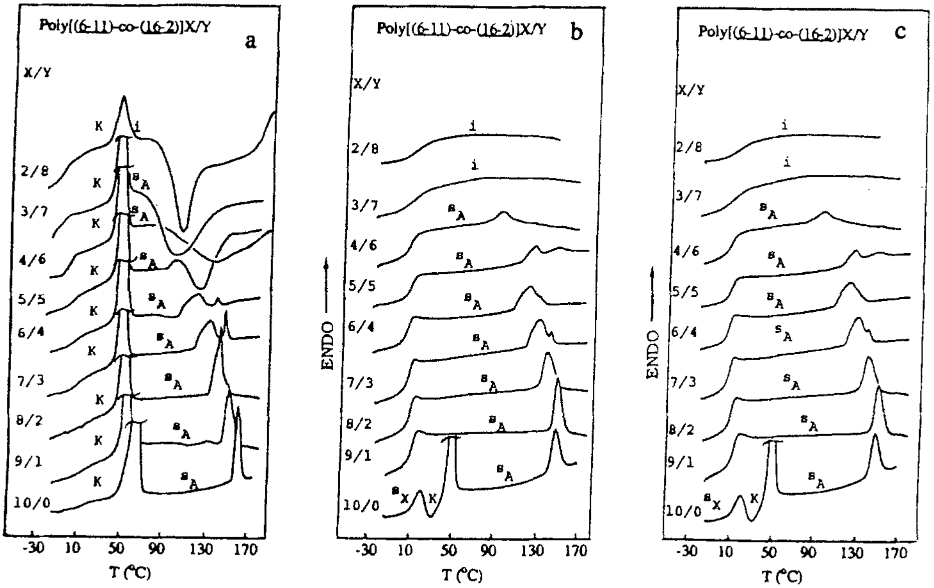


Figure 1: DSC traces of poly[(6-11)-co-(16-2)]X/Y. Copolymer composition is printed on the top of each DSC scan: (a) first heating scan; (b) second heating scan; (c) third heating scan.

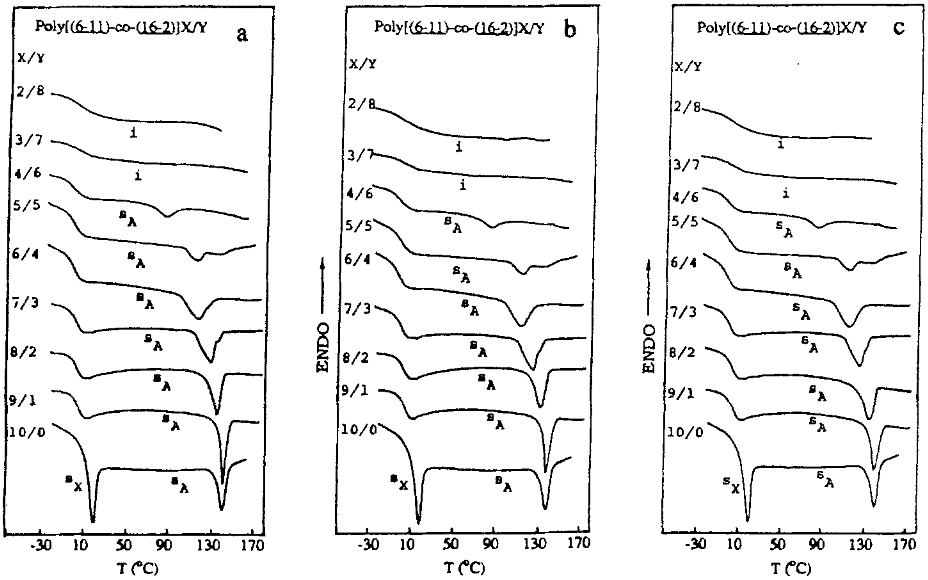


Figure 2: DSC traces of poly[(6-11)-co-(16-2)]X/Y. Copolymer composition is printed on the top of each DSC scan: (a) first cooling scan; (b) second cooling scan; (c) third cooling scan.

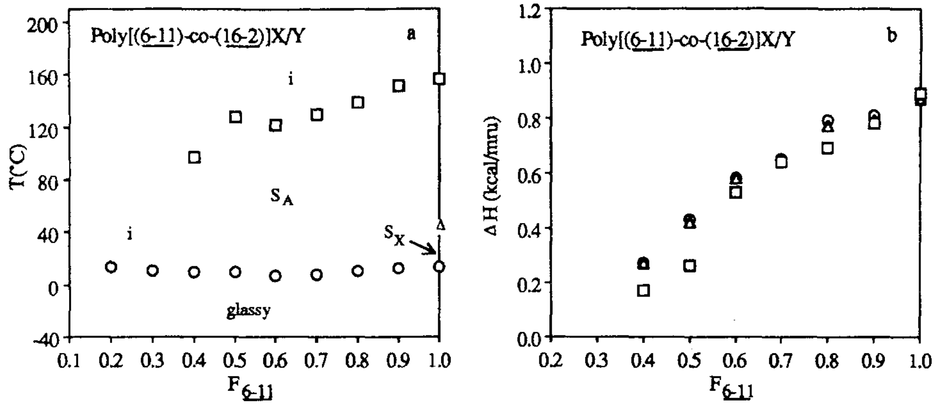


Figure 3: (a) The dependence of phase transition temperatures on copolymer composition of poly[(6-11)-co-(16-2)]X/Y; data from the third heating scan: ○ -T(g-$S_A$, $S_X$); Δ -T($S_X$-$S_A$); ❑ -T($S_A$-i).
(b) The dependence of the enthalpy change associated with the $S_A$-i and i-$S_A$ phase transition on copolymer composition for poly[(6-11)-co-(16-2)]X/Y: ○ -data from the second heating scan; Δ -data from the third heating scan; ❑ -data from the third cooling scan.

Presently it is difficult to observe an exothermic peak related to the polymerization of the methacryloyl side groups of the copolymers with X/Y=6/4 to 9/1. After crosslinking all copolymers lost their ability to crystallize (Fig. 1, 2). The most rewarding result is that the crosslinked networks obtained from poly[(6-11)-co-(16-2)]X/Y exhibit a $S_A$ mesophase for a very broad range of composition, i.e., X/Y=4/6 to 9/1. The networks obtained from poly[(6-11)-co-(16-11)]X/Y displayed a $S_A$ mesophase only for the range X/Y = 6/4 to 9/1.[1] In addition, poly[(6-11)-co-(16-11)]X/Y copolymers with X/Y=8/2 and 9/1 were still crystallizable.[1] These results demonstrate that these networks behave analogously with conventional copolymers obtained from mesogenic and nonmesogenic monomers. That is, in both cases, the shorter the alkyl groups in the nonmesogenic monomer the larger its amounts which can be accommodated in the mesomorphic phase of the copolymer.

Figure 3 plots the dependence of the phase transition temperature and their associated enthalpy changes of the crosslinked poly[(6-11)-co-(16-2)]X/Y copolymers as a function of composition. A representative texture of $S_A$ of poly[(6-11)-co-(16-2)]X/Y is given in Figure 4.

Poly[(6-11)-co-(16-2)]X/Y with X/Y=5/5 to 7/3 exhibit an isotropization peak which is splitted into two peaks both on heating and cooling. We suspected that this may be due to incomplete crosslinking during the period of the DSC scan, and that these two peaks are responsible for the transition of $S_A \leftrightarrow i$ generated from crosslinked and uncrosslinked copolymer segments. After suitable annealing experiments which eventually increase the extent of crosslinking close to completion, these two peaks merge into a single one. Representative annealing experiment results are presented in Table II and Figure 5. Each of the three copolymers labeled as A, B and C, which represent poly[(6-11)-co-(16-2)]X/Y with X/Y in the order of 5/5 6/4 and 7/3, were annealed at a temperature below the isotropization temperature for 1 hour. Then their heating and cooling DSC traces were scanned. As observed in Figure 5, the $S_A \leftrightarrow i$ transition of copolymers A and B merged into one peak, indicating that the crosslinking was completed. However, copolymer C still showed a splitted peak. Therefore, poly[(6-11)-co-(16-2)]X/Y with X/Y=7/3 labeled as D was annealed at the same temperature for two hours. The $S_A \leftrightarrow i$ peak was still splitted but the crosslinking is closer to completion compared with

Table II. Annealing effect on the mesomorphic behavior of poly[(6-11)-co-(16-2)]X/Y

| Polymer samples | Annealing temperature (°C) | Annealing time (hour) | phase transition temperatures (°C) and corresponding enthalpy changes (kcal/mru) | |
|---|---|---|---|---|
| | | | heating (20°C/min) | cooling (20°C/min) |
| A: Poly[(6-11)-co-(16-2)]5/5 | 93 | 1 | g 12.4 $s_A$ 146 (0.36) i<br>g 12.6 $s_A$ 140 (0.36) i | i 133 (-0.32) $s_A$ 6.4 g<br>i 132 (-0.32) $s_A$ 6.6 g |
| B: Poly[(6-11)-co-(16-2)]6/4 | 100 | 1 | g 11.6 $s_A$ 137 (0.51) i<br>g 11.6 $s_A$ 131 (0.51) i | i 122 (-0.48) $s_A$ 3.7 g<br>i 121 (-0.48) $s_A$ 3.7 g |
| C: Poly[(6-11)-co-(16-2)]7/3 | 100 | 1 | g 10.9 $s_A$ 135, 148 (0.67) i | i 126 (-0.58) $s_A$ 1.9 g |
| D: Poly[(6-11)-co-(16-2)]7/3 | 120 | 1 | g 12.2 $s_A$ 139, 148 (0.58) i | i 127 (-0.58) $s_A$ 3.0 g |
| E: Poly[(6-11)-co-(16-2)]7/3† | 120 | 2 | g 11.1 $s_A$ 133 (0.58) i<br>g 11.1 $s_A$ 133 (0.58) i | i 127 (-0.56) $s_A$ 3.4 g<br>i 127 (-0.56) $s_A$ 3.4 g |
| F: Poly[(6-11)-co-(16-2)]7/3 | 120 | 2 | g 11.1 $s_A$ 142 (0.57) i<br>g 11.1 $s_A$ 135 (0.57) i | i 127 (-0.57) $s_A$ 3.4 g<br>i 127 (-0.57) $s_A$ 3.4 g |
| G: Poly[(6-11)-co-(16-2)]7/3 | 165 | 1 | g 5.3 $s_A$ 127 (0.64) i<br>g 5.3 $s_A$ 128 (0.64) i | i 121 (-0.55) $s_A$ 0.9 g<br>i 119 (-0.55) $s_A$ 0.9 g |

†: Sample E is the same one used as sample C after annealed at 100°C for 1 hour

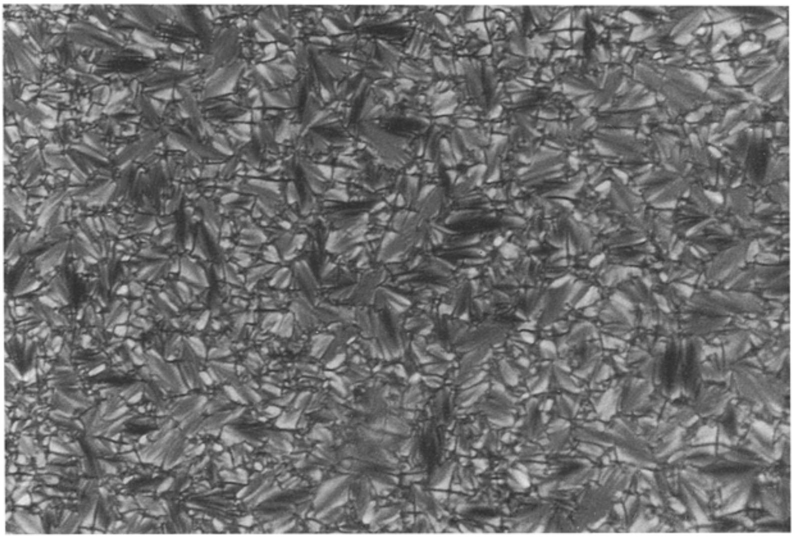


Figure 4: A representative optical polarized micrograph of the $S_A$ mesophase (x100) of poly[(6-11)-co-(16-2)]X/Y with X/Y=9/1 at 116°C on cooling.

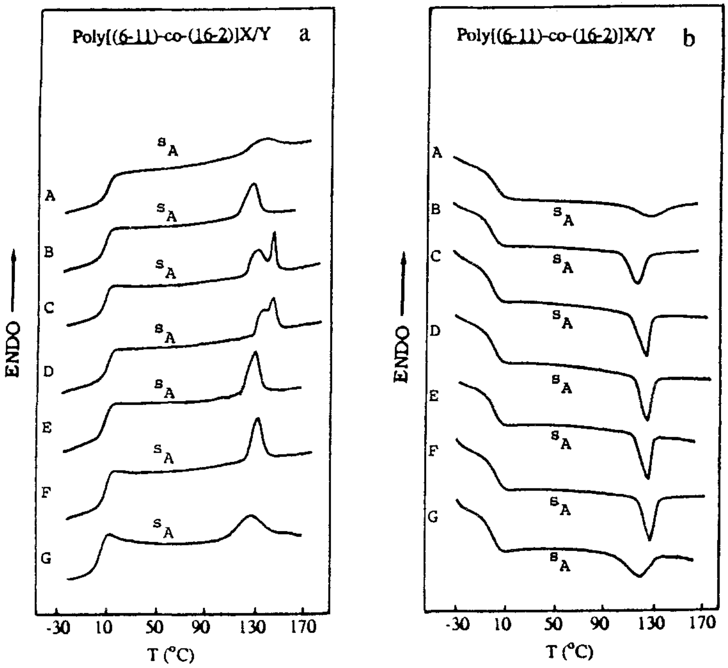


Figure 5: DSC traces of poly[(6-11)-co-(16-2)]X/Y after annealing under different thermal conditions: (a) heating scan; (b) cooling scan.

copolymer C (the sharper peak in copolymer C is larger than that of copolymer D). The copolymer C was then annealed at a higher temperature but still below the $T_i$ for 2 hours and the splitting of its isotropization peak disappeared (labeled as copolymer E) (Fig. 5). Compared with the copolymer G (also poly[(6-11)-co-(16-2)]X/Y with X/Y=7/3) which was annealed above the $T_i$, the $S_A \leftrightarrow i$ transition peak is higher and narrower when the copolymer was crosslinked below the isotropization temperature.

If we compare the crosslinking behavior of poly[(6-11)-co-(16-11)]X/Y with that of poly[(6-11)-co-(16-2)]X/Y, the former is faster. This is probably due the fact that during the crosslinking reaction the mobility of poly[(6-11)-co-(16-11)]X/Y is higher than that of poly[(6-11)-co-(16-2)]X/Y since the $S_A \leftrightarrow i$ transition temperature of poly[(6-11)-co-(16-11)]X/Y is lower than that of the corresponding poly[(6-11)-co-(16-2)]X/Y.

## ACKNOWLEDGMENTS

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

## REFERENCES

1. V. Percec and Q. Zheng, *Polym. Bull.*, submitted.
2. a) V. Percec, M. Lee and H. Jonsson, *Polym. Sci. Polym. Chem. Ed.*, **29**, 327(1991); (b) V. Percec and M. Lee, *Macromolecules*, **24**, 1017(1991); (c) V. Percec and M. Lee, *J. Macromol. Sci.-Chem.*, **A28**, 651(1991); (d) V. Percec, M. Lee and C. Ackerman, *Polymer*, **33**, 703(1992); (e) V. Percec and M. Lee, *Macromolecules*, **24**, 2780(1991); (f) V. Percec, Q. Zheng and M. Lee, *J. Mater. Chem.*, **1**, 611(1991); (g) V. Percec, Q. Zheng and M. Lee, *J. Mater. Chem.*, **1**, 1015(1991); (h) V. Percec and Q. Zheng, *J. Mater. Chem.*, **2**, 475(1992); (i) V. Percec and Q. Zheng, *J. Mater. Chem.*, in press.
3. (a) V. Percec and M. Lee, *Polymer*, **32**, 2862(1991); (b) V. Percec and M. Lee, *Polym. Bull.*, **25**, 123(1991); (c) V. Percec and M. Lee, *Polym. Bull.*, **25**, 131(1991); (d) V. Percec and M. Lee, *Macromolecules*, **24**, 4963(1991); (e) V. Percec and M. Lee, *J. Mater. Chem.*, **1**, 1007(1991); (f) V. Percec, M. Lee and Q. Zheng, *Liq. Cryst.*, in press.
4. (a) V. Percec and D. Tomazos, Adv. Mater., in press. (b)V. Percec and D. Tomazos, "Molecular Engineering of Liquid Crystalline Polymers" in "*Comprehensive Polymer Science*", Supplement Vol. 1, G. Allen and J. C. Bevington Eds., Pergamon Press, Oxford, 1992, in press.
5. V. Percec and M. Lee, *J. Mater. Chem.*, **2**, 617(1992).

Accepted September 3, 1992 K