

OFFICE OF NAVAL RESEARCH

CONTRACT N00014-89-J-1828

R&T Code 3132080

Abstract Report #1

MOLECULAR ENGINEERING OF LIQUID CRYSTALLINE POLYMERS BY "LIVING"  
POLYMERIZATION ~~39~~ SYNTHESIS AND "LIVING" CATIONIC POLYMERIZATION OF  
(2R,3S)-2-FLUORO-3-METHYLPENTYL 4'-(8-VINYLOXYOCTYLOXY)BIPHENYL-4-  
CARBOXYLATE AND ITS COPOLYMERIZATION WITH (2R,3S)-2-FLUORO-3-  
METHYLPENTYL 4'-(11-VINYLOXYUNDECANYLOXY)BIPHENYL-4-CARBOXYLATE

by

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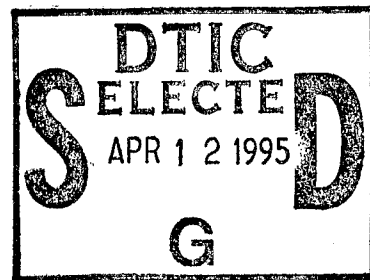
Submitted

19950410 033

to the

Journal of Materials Chemistry

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April 3, 1995

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 4-3-95	3. REPORT TYPE AND DATES COVERED Abstract Report #1
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4. TITLE AND SUBTITLE Molecular Engineering of Liquid Crystalline Polymers by "Living" Polymerization. <sup>30</sup> . Synthesis and "Living" Cationic Polymerization of (2R,3S)-...	5. FUNDING NUMBERS N00014-89-J-1828
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6. AUTHOR(S) V. Percec and H. Oda
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Macromolecular Science Case Western Reserve University Cleveland, OH 44106-7202	8. PERFORMING ORGANIZATION REPORT NUMBER N00014-89-J-1828
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000	10. SPONSORING/MONITORING AGENCY REPORT NUMBER Abstract Report #1
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Accession For
NTIS CRA&I <input checked="" type="checkbox"/>
DTIC TAB <input type="checkbox"/>
Unannounced <input type="checkbox"/>
Justification

11. SUPPLEMENTARY NOTES Submitted to J. Mater. Chem.	By _____ Distribution /
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12a. DISTRIBUTION/AVAILABILITY STATEMENT	Availability Codes	12b. DISTRIBUTION CODE
	Dist Avail and/or Special	
	A-1	

13. ABSTRACT (Maximum 200 words)

The synthesis and "living" cationic polymerization of (2R, 3S)-2-fluoro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (**11-8**) are described. Poly(**11-8**)s with degrees of polymerization from 4.3 to 15.7 and polydispersities  $\leq 1.19$  were synthesized and characterized by differential scanning calorimetry (DSC) and thermal optical polarized microscopy. All poly(**11-8**)s exhibit an enantiotropic  $S_C^*$  and an unidentified smectic ( $S_1$ ) phase. Poly(**11-8**)s with  $DP \geq 11.5$  exhibit an additional enantiotropic unidentified smectic ( $S_2$ ) phase. No  $S_A$  phase could be detected in any of poly(**11-8**)s. The nature of mesophases exhibited by poly(**11-8**) was confirmed by the investigation of the phase diagram of the copolymers prepared from **11-8** and (2R, 3S)-2-fluoro-3-methylpentyl 4'-(11-vinyloxyundecanyloxy)biphenyl-4-carboxylate (**11-11**). The  $S_C^*$  phase of these copolymers displays a continuous dependence of copolymer composition.

14. SUBJECT TERMS	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT UL
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**Molecular Engineering of Liquid Crystalline Polymers by "Living" Polymerization 30.† Synthesis and "Living" Cationic Polymerization of (2R,3S)-2-Fluoro-3-methylpentyl 4'-(8-Vinyloxyoctyloxy)biphenyl-4-carboxylate and Its Copolymerization with (2R,3S)-2-Fluoro-3-methylpentyl 4'-(11-Vinyloxyundecanyloxy)biphenyl-4-carboxylate**

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**ABSTRACT**

The synthesis and "living" cationic polymerization of (2R, 3S)-2-fluoro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (**11-8**) are described. Poly(**11-8**)s with degrees of polymerization from 4.3 to 15.7 and polydispersities  $\leq 1.19$  were synthesized and characterized by differential scanning calorimetry (DSC) and thermal optical polarized microscopy. All poly(**11-8**)s exhibit an enantiotropic  $S_C^*$  and an unidentified smectic ( $S_1$ ) phase. Poly(**11-8**)s with  $DP \geq 11.5$  exhibit an additional enantiotropic unidentified smectic ( $S_2$ ) phase. No  $S_A$  phase could be detected in any of poly(**11-8**)s. The nature of mesophases exhibited by poly(**11-8**) was confirmed by the investigation of the phase diagram of the copolymers prepared from **11-8** and (2R, 3S)-2-fluoro-3-methylpentyl 4'-(11-vinyloxyundecanyloxy)biphenyl-4-carboxylate (**11-11**). The  $S_C^*$  phase of these copolymers displays a continuous dependence of copolymer composition.

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† Part 29 in this series: Ref. 1a. The definition of "living" is presented in Ref. 1b.

## INTRODUCTION

Liquid crystalline polymers exhibiting chiral mesophases, such as cholesteric<sup>2</sup> and chiral smectic C ( $S_C^*$ )<sup>3</sup> are of both theoretical and technological interest. We have performed a series of systematic investigations aimed to derive empirical rules useful for the molecular engineering of side chain liquid crystalline polymers displaying a  $S_C^*$  mesophase.<sup>4</sup> In these investigations, we have used "living" cationic polymerization of mesogenic vinyl ethers for the synthesis of side chain liquid crystalline polymers. "Living" cationic polymerization can produce polymers with well defined molecular weight and narrow molecular weight distribution in the presence of a variety of functional groups and therefore, it provides access to the elucidation of the influence of molecular weight and spacer length on the formation of various mesophases.<sup>5</sup>

In recent years, there has been a continuing and increasing interest in the study of chiral side chain liquid crystalline polymers and a variety of polymers with new structures have been synthesized and reported.<sup>6-34</sup> Some of them show a complex phase behavior<sup>31-33</sup> including antiferroelectric<sup>33</sup> and twisted smectic A phases.<sup>34</sup>

The goal of this paper is to describe the synthesis and "living" cationic polymerization of (2R, 3S)-2-fluoro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (**11-8**) and its copolymerization with (2R, 3S)-2-fluoro-3-methylpentyl 4'-(11-vinyloxyundecanyloxy)biphenyl-4-carboxylate (**11-11**). The mesomorphic behavior of the resulting polymer poly(**11-8**) and copolymer poly[**(11-8)-co-(11-11)**] will be discussed as a function of molecular weight and copolymer composition.

## EXPERIMENTAL SECTION

### Materials

L-Isoleucine [(2S,3S)-(+)-2-amino-3-methylpentanoic acid, 99%], tetrabutylammonium fluoride hydrate ( $n\text{-Bu}_4\text{NF}\cdot x\text{H}_2\text{O}$ , 98%) and tetrabutylammonium hydrogen sulfate (TBAH, 98%) (all from Aldrich) were used as received.

NaNO<sub>2</sub> (Fisher) was dried at 140°C under vacuum for 40 hours before each use. Trifluoromethanesulfonic anhydride was prepared from CF<sub>3</sub>SO<sub>3</sub>H (Lancaster, 98+%) and P<sub>2</sub>O<sub>5</sub> according to a literature procedure.<sup>35</sup>

Pyridine was heated overnight at 100°C over KOH, distilled from KOH, and then stored over KOH. CH<sub>2</sub>Cl<sub>2</sub> was refluxed over CaH<sub>2</sub> overnight and distilled from CaH<sub>2</sub>. Dimethyl sulfoxide (DMSO) was heated overnight at 100°C over CaH<sub>2</sub>, distilled from CaH<sub>2</sub> under vacuum, and stored over molecular sieves 4Å. Tetrahydrofuran (THF) was first distilled from LiAlH<sub>4</sub> and further dried over Na/benzophenone.

CH<sub>2</sub>Cl<sub>2</sub> used as polymerization solvent was first washed with concentrated H<sub>2</sub>SO<sub>4</sub> several times until the acid layer remained colorless, then washed with water, dried over MgSO<sub>4</sub>, refluxed over CaH<sub>2</sub>, and freshly distilled under argon before each use. (CH<sub>3</sub>)<sub>2</sub>S used in these polymerizations (Aldrich, anhydrous, 99+%, packed under nitrogen in Sure/Seal bottle) was used as received. CF<sub>3</sub>SO<sub>3</sub>H used as a polymerization initiator (Aldrich, 98%) was distilled under vacuum.

All other materials were commercially available and were used as received.

## Techniques

<sup>1</sup>H-NMR spectra were recorded on a Varian XL-200 (200 MHz) spectrometer.

Relative molecular weights of polymers were determined by gel permeation chromatography (GPC). GPC analyses were carried out with a Perkin-Elmer Series 10LC instrument equipped with an LC-100 column oven and a Nelson Analytical 900 Series data station. Measurements were made by using a UV detector, THF as solvent (1ml/min, 40°C), a set of PL gel columns of 5x10<sup>2</sup> and 10<sup>4</sup>Å, and a calibration plot constructed with polystyrene standards.

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

maxima and minima of their endothermic or exothermic peaks, respectively. In all cases, heating and cooling rates were 20°C/min.

A Carl-Zeiss optical polarizing 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 analyze the anisotropic textures.

### Synthesis of monomers

Monomers **11-8** and **11-11** were synthesized from L-isoleucine according to the reaction pathway outlined in Scheme 1. The syntheses and characterization of compounds **2** through **10-n** (n=8, 11) and of monomer **11-11** were described in detail previously.<sup>4,36</sup>

#### (2R, 3S)-2-Fluoro-3-methylpentyl 4'-(8-Vinyloxyoctyloxy)biphenyl-4-carboxylate (11-8)

A mixture of **9** (3.70g, 11.7mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (4.04g, 29.2mmol) and acetone (70ml) was stirred at 60°C under a nitrogen atmosphere for 2 h. To the resulting yellow solution was added a solution of **10-8** (2.75g, 11.7mmol) in dry DMSO (3.5ml) and stirring was continued at 60°C for 20 h. The mixture was poured into water and the product was extracted into diethyl ether twice. The combined ethereal extracts were dried over anhydrous MgSO<sub>4</sub>. The solvent was evaporated and the remaining crude product was purified by column chromatography twice (silica gel; hexane-ethyl acetate 20:1 and 10:1) to yield a white solid (2.81g, 51.0%). Purity: >99% (HPLC). The transition temperatures (°C) are: K 44.4 S<sub>C</sub>\* 54.3 S<sub>A</sub> 69.1 I on heating and I 64.5 S<sub>A</sub> 50.0 S<sub>C</sub>\* 29.4 S<sub>X</sub> 21.0 K on cooling (DSC). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS): δ 0.97 (t, J=7.1Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>-), 1.04 (d, J=6.8Hz, 3H, -CH(CH<sub>3</sub>-), 1.38 (bs, 9H, CH<sub>3</sub>CH<sub>2</sub>-, CH<sub>2</sub>=CHOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>-), 1.55-1.75 (m, 3H, CH<sub>3</sub>CH<sub>2</sub>-, CH<sub>2</sub>=CHOCH<sub>2</sub>CH<sub>2</sub>-), 1.75-1.97 (m, 3H, -CH(CH<sub>3</sub>-), -CH<sub>2</sub>CH<sub>2</sub>OPh-), 3.68 (t, J=6.5Hz, 2H, CH<sub>2</sub>=CHOCH<sub>2</sub>-), 3.98 (dd, J=6.9 and 1.9Hz, 1H, CH<sub>2</sub>=CHO- trans), 4.01 (t, J=5.4Hz, 2H, -CH<sub>2</sub>OPh-), 4.18 (dd, J=14.3 and 1.9Hz, 1H, CH<sub>2</sub>=CHO- cis), 4.39-4.67, 4.79-4.93 (m, 3H, -CHFCH<sub>2</sub>O-), 6.48 (dd, J=14.3 and 6.9Hz, 1H, CH<sub>2</sub>=CHO-), 6.99 (d, J=8.8Hz, 2ArH, ortho to -(CH<sub>2</sub>)<sub>8</sub>O-), 7.57 (d, J=8.8Hz,

2ArH, meta to  $-(\text{CH}_2)_8\text{O}-$ ), 7.64 (d,  $J=8.4\text{Hz}$ , 2ArH, meta to  $-\text{COO}-$ ), 8.12 (d,  $J=8.4\text{Hz}$ , 2ArH, ortho to  $-\text{COO}-$ ).

### Cationic Polymerization

Polymerizations and copolymerizations were carried out in a three-necked round bottom flask equipped with a Teflon stopcock and rubber septa under an argon atmosphere at  $0^\circ\text{C}$  for 1 hour. All glassware was dried overnight at  $140^\circ\text{C}$ . The monomer was further dried under vacuum overnight in the polymerization flask. After the flask was filled with argon, freshly distilled dry  $\text{CH}_2\text{Cl}_2$  was added via a syringe and the solution was cooled to  $0^\circ\text{C}$ .  $(\text{CH}_3)_2\text{S}$  and  $\text{CF}_3\text{SO}_3\text{H}$  were then added carefully via a syringe. The monomer concentration was about 0.224 M and the  $(\text{CH}_3)_2\text{S}$  concentration was 10 times larger than that of  $\text{CF}_3\text{SO}_3\text{H}$ . The polymer molecular weight was controlled by the monomer/initiator ( $[\text{M}]_0/[\text{I}]_0$ ) ratio. After quenching the polymerization with a mixture of  $\text{NH}_4\text{OH}$  and methanol (1:2), the reaction mixture was poured into methanol to give a white precipitate. The obtained polymer was purified by reprecipitation by pouring its chloroform solution into methanol, and dried under vacuum.

## RESULTS AND DISCUSSION

### Polymerization of **11-8**

The optical purity of monomer **11-8** was determined as reported previously<sup>36</sup> for the C2 chiral center and is 2R 96% (92% ee). As has been demonstrated previously,<sup>36</sup> no racemization takes place during the polymerization process. The optical purity derived from the C3 chiral center was not determined.<sup>36</sup>

The homopolymerization of **11-8** is outlined in Scheme 2. All polymerizations were carried out at  $0^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$  by a "living" cationic polymerization technique using  $\text{CF}_3\text{SO}_3\text{H}/(\text{CH}_3)_2\text{S}$  as an initiating system. Previous work in our<sup>37</sup> and other<sup>38</sup> laboratories has shown that the  $\text{CF}_3\text{SO}_3\text{H}$  initiated polymerization of vinyl ethers in the presence of a Lewis base such as  $(\text{CH}_3)_2\text{S}$  gives well defined polymers with controlled molecular weights and narrow

polydispersities. The polymerization mechanism is discussed in detail in previous publications.<sup>4,5,37</sup>

The characterization of poly(**11-8**) by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) is summarized in Table I. The low polymer yields are the result of the loss of polymer during purification. Relative number-average molecular weights of polymers determined by GPC exhibit a linear dependence on the initial molar ratio of monomer to initiator ( $[M]_0/[I]_0$ ) as shown in Figure 1. All polydispersities are less than 1.19. The  $[M]_0/[I]_0$  ratio provides a good control of the polymer molecular weight. All these features support the typical characteristics of a "living" polymerization reaction. The absolute number-average molecular weights were difficult to determine by <sup>1</sup>H-NMR spectroscopy from the chain ends of the polymer owing to signal overlap.

The mesomorphic behavior of poly(**11-8**) was investigated by DSC and thermal optical polarized microscopy. Figure 2 presents the DSC thermograms of poly(**11-8**) with various degrees of polymerization (DP). The dependence between transition temperatures and DP is plotted in Figure 3. All virgin polymers except the one with DP=4.3 are crystalline and exhibit a crystalline melting peak on the first heating scan. However, on the subsequent cooling and heating scans all polymers exhibit enantiotropic  $S_C^*$  and  $S_1$  (higher order smectic) mesophases. For polymers with  $DP \geq 11.5$ , an additional enantiotropic smectic phase ( $S_2$ ) is observed in between the  $S_1$  and  $S_C^*$  phases. The formation of the  $S_2$  phase can be explained by the fact that the  $S_2$ - $S_C^*$  transition temperature has a stronger dependence on molecular weight than that of the  $S_1$ - $S_C^*$  transition temperature. It is interesting to note that poly(**11-8**)s do not show a  $S_A$  mesophase. Even when DSC experiments were performed at lower heating and cooling rates ( $<10^\circ\text{C}/\text{min}$ ), the transition peak between  $S_C^*$  and isotropic phases did not split into two peaks and therefore, no evidence for the existence of the  $S_A$  phase was obtained. In the thermal microscope analysis of poly(**11-8**) with DP=11.5, for example, a focal conic texture accompanied by equidistant lines forms directly from an isotropic liquid as shown in Figures 4a and 4b. Representative textures displayed by the  $S_C^*$  and  $S_2$  mesophases are presented in Figures 4c and

4d, respectively. The nature of the  $S_1$  and  $S_2$  phases was not identified. In a previous publication, we described the synthesis and "living" cationic polymerization of (R)- and (S)-2-fluoro-4-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (**12-8**).<sup>39</sup> The structural difference between **11-8** and **12-8** lies only in the position of the terminal methyl group as **11-8** is derived from isoleucine, while **12-8** is derived from leucine. A comparison of the phase behavior of poly(**11-8**) with that of poly(**12-8**) seems to indicate that the position of the methyl group has little effect on the phase behavior of these two polymers, since both poly(**11-8**) and poly(**12-8**) display almost identical DSC traces irrespective of their DPs. Poly(**12-8**) also did not show a  $S_A$  phase, and this was confirmed by X-ray diffraction experiments. Another similar example in which an enantiotropic  $S_C^*$  phase directly melts into and forms from an isotropic phase was reported in a previous publication from our laboratory.<sup>4d</sup>

### Copolymerization of **11-8** with **11-11**

The copolymerization of **11-8** with **11-11** is outlined in Scheme 3. Attempts were made to synthesize poly[(**11-8**)-*co*-(**11-11**)] with DP=20 over the entire range of compositions. The copolymerization results are summarized in Table II. The yields reported in Table II are lower than quantitative owing to the polymer loss during the purification process. However, all copolymerizations lead to almost quantitative conversions and therefore, the copolymer composition is identical to that of the monomer feed.<sup>5</sup> The relative number-average molecular weight of copolymers is well controlled by the  $[M]_0/[I]_0$  ratio and the molecular weight distribution of all polymers is lower than 1.13. The DSC traces of poly[(**11-8**)-*co*-(**11-11**)] are presented in Figure 5. The thermal transition temperatures determined by DSC are listed in Table II and plotted against copolymer composition in Figure 6. The mesomorphic behavior of poly(**11-11**) with various degrees of polymerization was reported in a different publication.<sup>36</sup> All poly(**11-11**)s showed enantiotropic  $S_A$ ,  $S_C^*$  and unidentified higher order smectic phases regardless of their DP. The assignment of these mesophases was confirmed by a combination of thermal polarized optical microscopy and X-ray diffraction measurements. It is clear from

Figures 5 and 6 that the  $S_C^*$  mesophase displays a continuous dependence over the entire copolymer composition range. The thermal stability of the  $S_C^*$  phase is enlarged by copolymerization. The  $S_1$  phase of poly(**11-8**) seems to be isomorphic with the higher order smectic phase of poly(**11-11**). The  $S_A$  phase in poly[(**11-8**)-*co*-(**11-11**)](X/Y) (where X/Y refers to the molar ratio of the two structural units) appears only in the range of compositions from X/Y=90/10 to 0/100 on heating and from X/Y=80/20 to 0/100 on cooling, confirming the fact that poly(**11-8**) does not exhibit a  $S_A$  mesophase. Finally, when comparing the phase behavior of poly(**11-8**) with that of poly(**11-11**), it can be concluded that a higher order mesophase is favored towards shorter spacer length. The same trend was previously reported from our laboratory in the case of polymers of (2S, 3S)-2-chloro-3-methyl 4'-( $\omega$ -vinylalkoxy)biphenyl-4-carboxylate with undecanyl, octyl and hexyl alkyl groups,<sup>4e,d</sup> whose structure is identical to that of **11-n** (n=8, 11) except that the fluorine atom of **11-n** was replaced with a chlorine atom.

#### ACKNOWLEDGMENT

Financial support by the Office of Naval Research is gratefully acknowledged.

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## SCHEME AND FIGURE CAPTIONS

Scheme 1. Synthesis of monomers **11-8** and **11-11**.

Scheme 2. Cationic polymerization of **11-8**.

Scheme 3. Cationic copolymerization of **11-8** with **11-11**.

Figure 1. Dependence of the number-average molecular weight ( $M_n$ ) and polydispersity ( $M_w/M_n$ ) of poly(**11-8**) determined by GPC on the  $[M]_0/[I]_0$  ratio.

Figure 2. DSC thermograms (20°C/min) of poly(**11-8**) with different DP: (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 3. The dependence of phase transition temperatures on the degree of polymerization of poly(**11-8**): (a) data from the first heating scans; (b) data from the second heating scans; (c) data from the first cooling scans.

Figure 4. Representative optical polarized micrographs of: (a) the  $S_C^*$  mesophase displayed by poly(**11-8**) (DP=11.5) upon cooling to 109°C; (b) the  $S_C^*$  mesophase displayed by poly(**11-8**) (DP=11.5) upon cooling to 106°C; (c) the  $S_C^*$  mesophase displayed by poly(**11-8**) (DP=4.6) upon cooling to 81°C; (d) the  $S_2$  mesophase displayed by poly(**11-8**) (DP=11.5) upon heating to 63°C.

Figure 5. DSC thermograms (20°C/min) of poly[(**11-8**)-*co*-(**11-11**)](X/Y) with different compositions: (a) first heating scans; (b) second heating scans; (c) first cooling scans.

Figure 6. The dependence of the phase transition temperatures on the composition of poly[(**11-8**)-*co*-(**11-11**)]: (a) data from the first heating scans; (b) data from the second heating scans; (c) data from the first cooling scans.

Table I. Cationic Polymerization of (2R, 3S)-2-Fluoro-3-Methylpentyl 4'-(8-Vinyloxyoctyloxy)biphenyl-4-Carboxylate (**11-8**) and Characterization of the Resulting Polymers<sup>a</sup>

[M] <sub>0</sub> /[I] <sub>0</sub>	Polymer Yield(%)	M <sub>n</sub> ×10 <sup>-3</sup>	M <sub>w</sub> /M <sub>n</sub>	DP	Phase transitions (°C) and corresponding enthalpy changes (kcal/mru) <sup>b</sup>	
					heating	cooling
2	42.3	2.0	1.05	4.3	S <sub>1</sub> 30.8 (0.20) S <sub>C</sub> * 87.1 (1.63) I S <sub>1</sub> 31.4 (0.21) S <sub>C</sub> * 87.7 (1.64) I	I 81.3 (-1.63) S <sub>C</sub> * 26.8 (-0.19) S <sub>1</sub>
3	48.9	2.2	1.19	4.6	K 43.2 (0.64) S <sub>C</sub> * 96.6 (1.71) I S <sub>1</sub> 39.5 (0.26) S <sub>C</sub> * 96.4 (1.60) I	I 87.8 (-1.64) S <sub>C</sub> * 33.4 (-0.27) S <sub>1</sub>
5	63.6	3.4	1.09	7.3	K 52.7 (1.06) S <sub>C</sub> * 105.5 (1.53) I S <sub>1</sub> 47.9 (0.33) S <sub>C</sub> * 106.0 (1.55) I	I 98.6 (-1.60) S <sub>C</sub> * 42.1 (-0.35) S <sub>1</sub>
8	71.8	4.1	1.14	8.7	K 58.9 (1.13) S <sub>C</sub> * 112.8 (1.64) I S <sub>1</sub> 57.7 (0.64) S <sub>C</sub> * 112.9 (1.55) I	I 104.2 (-1.52) S <sub>C</sub> * 49.9 (-0.55) S <sub>1</sub>
12	83.5	5.4	1.11	11.5	K 55.9 (†°) S <sub>1</sub> 63.1 (0.75) S <sub>C</sub> * 115.4 (1.59) I S <sub>X1</sub> 63.5 (0.81) S <sub>2</sub> 66.6 (†°) S <sub>C</sub> * 115.6 (1.54) I	I 109.2 (-1.54) S <sub>C</sub> * 62.0 (†°) S <sub>2</sub> 58.1 (-0.69) S <sub>1</sub>
16	76.5	5.9	1.09	12.5	K 57.3 (†°) S <sub>1</sub> 66.5 (0.60) S <sub>2</sub> 75.9 (0.02) S <sub>C</sub> * 119.6 (1.52) I S <sub>1</sub> 66.6 (0.59) S <sub>2</sub> 74.3 (0.02) S <sub>C</sub> * 119.7 (1.50) I	I 113.6 (-1.51) S <sub>C</sub> * 69.8 (-0.03) S <sub>2</sub> 61.4 (-0.52) S <sub>1</sub>
20	77.5	6.9	1.11	14.6	K 60.8 (†°) S <sub>1</sub> 68.8 (0.58) S <sub>2</sub> 82.9 (0.06) S <sub>C</sub> * 120.9 (1.53) I S <sub>1</sub> 69.5 (0.66) S <sub>2</sub> 81.9 (0.06) S <sub>C</sub> * 120.8 (1.50) I	I 113.7 (-1.51) S <sub>C</sub> * 76.6 (-0.06) S <sub>2</sub> 62.7 (-0.55) S <sub>1</sub>
25	87.5	7.4	1.11	15.7	K 56.5 (0.13) S <sub>1</sub> 68.1 (0.31) S <sub>2</sub> 81.4 (0.02) S <sub>C</sub> * 121.1 (1.53) I S <sub>1</sub> 70.0 (0.66) S <sub>2</sub> 82.9 (0.06) S <sub>C</sub> * 121.3 (1.51) I	I 115.1 (-1.52) S <sub>C</sub> * 78.3 (-0.05) S <sub>2</sub> 63.9 (-0.56) S <sub>1</sub>

<sup>a</sup> Polymerization temperature: 0°C; polymerization solvent: CH<sub>2</sub>Cl<sub>2</sub>; [M]<sub>0</sub>=0.224; [Me<sub>2</sub>S]<sub>0</sub>/[I]<sub>0</sub>=10; polymerization time: 1 h.

<sup>b</sup> Heating and cooling rates are 20°C/min.

Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.

<sup>c</sup> Overlapped peak.

Table II. Cationic Copolymerization of **11-8** with **11-11** and Characterization of the Resulting Polymers<sup>a</sup>

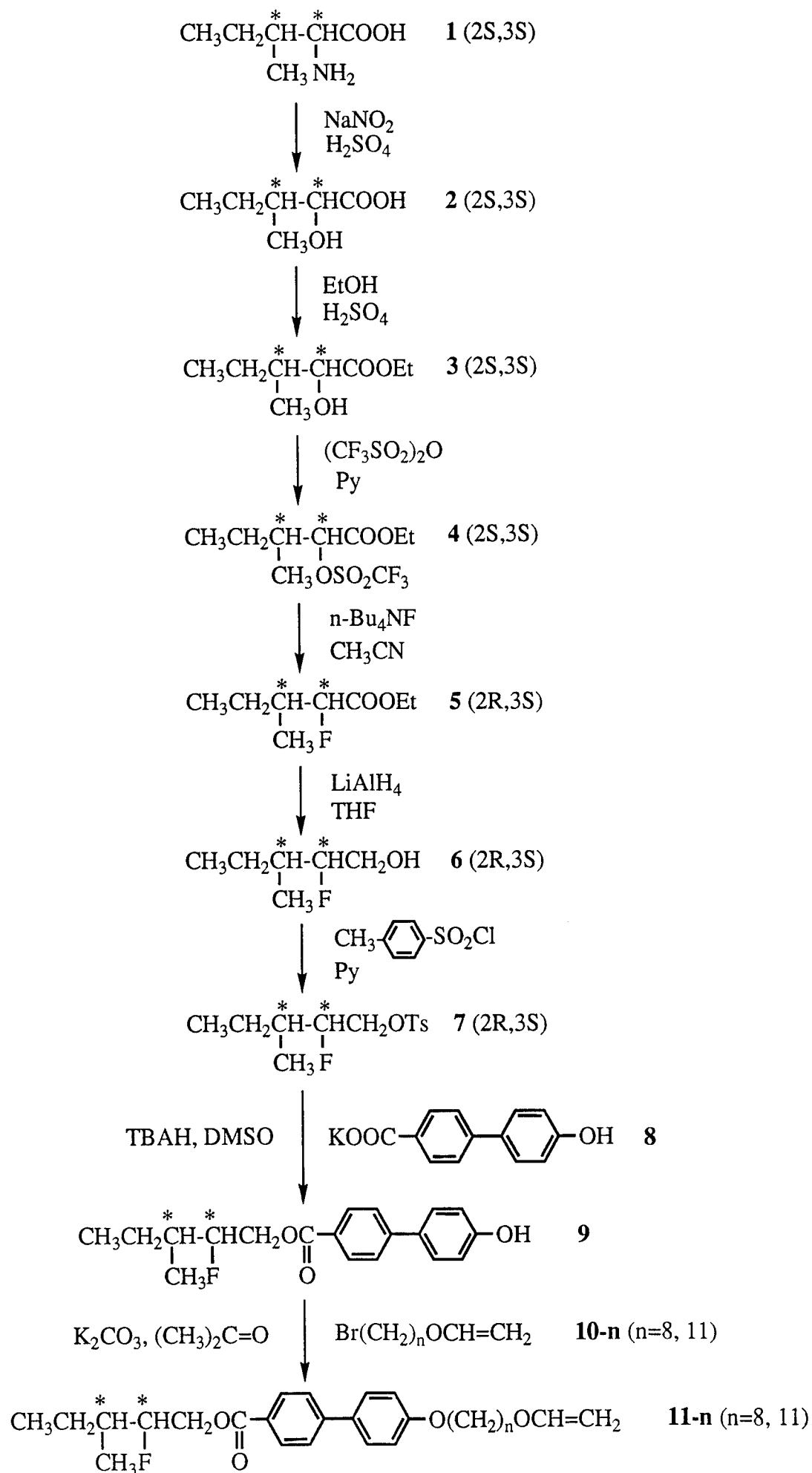
[ <b>11-8</b> ]/[ <b>11-11</b> ] (mol/mol)	Polymer Yield(%)	M <sub>n</sub> x10 <sup>-3</sup>	M <sub>w</sub> /M <sub>n</sub>	DP	Phase transitions (°C) and corresponding enthalpy changes (kcal/mru) <sup>b</sup>	
					cooling	
					heating	
100/0	77.5	6.9	1.11	14.6	K 60.8 († <sup>c</sup> ) S <sub>1</sub> 68.8 (0.58) S <sub>2</sub> 82.9 (0.06) S <sub>C</sub> * 120.9 (1.53) I S <sub>1</sub> 69.5 (0.66) S <sub>2</sub> 81.9 (0.06) S <sub>C</sub> * 120.8 (1.50) I	I 113.7 (-1.51) S <sub>C</sub> * 76.6 (-0.06) S <sub>2</sub> 62.7 (-0.55) S <sub>1</sub>
90/10	77.9	6.0	1.10	12.6	K 58.5 (0.98) S <sub>2</sub> 63.5 S <sub>C</sub> * 112.3 S <sub>A</sub> 116.4 (1.34) I S <sub>1</sub> 57.6 (0.64) S <sub>2</sub> 62.1 S <sub>C</sub> * 112.3 S <sub>A</sub> 116.2 (1.36) I	I 108.3 (-1.42) S <sub>C</sub> * 56.6 († <sup>c</sup> ) S <sub>2</sub> 51.5 (-0.63) S <sub>1</sub>
80/20	84.3	6.6	1.10	13.7	K 59.2 (0.98) S <sub>2</sub> 63.3 S <sub>C</sub> * 110.2 (0.09) S <sub>A</sub> 119.5 (1.23) I S <sub>1</sub> 57.7 (0.71) S <sub>2</sub> 64.0 S <sub>C</sub> * 109.8 (0.11) S <sub>A</sub> 119.0 (1.20) I	I 112.3 (-1.16) S <sub>A</sub> 105.5 (-0.11) S <sub>C</sub> * 58.2 S <sub>2</sub> 52.6 (-0.67) S <sub>1</sub>
70/30	85.3	6.6	1.09	13.7	K 57.2 (1.08) S <sub>C</sub> * 105.0 (0.09) S <sub>A</sub> 119.5 (1.23) I S <sub>1</sub> 55.3 (0.70) S <sub>C</sub> * 104.6 (0.09) S <sub>A</sub> 119.0 (1.24) I	I 111.9 (-1.21) S <sub>A</sub> 100.0 (-0.11) S <sub>C</sub> * 49.7 (-0.62) S <sub>1</sub>
60/40	80.5	6.2	1.10	12.6	K 53.9 (1.11) S <sub>C</sub> * 97.8 (0.06) S <sub>A</sub> 118.3 (1.30) I S <sub>1</sub> 51.3 (0.64) S <sub>C</sub> * 97.9 (0.07) S <sub>A</sub> 117.2 (1.27) I	I 110.3 (-1.24) S <sub>A</sub> 93.5 (-0.07) S <sub>C</sub> * 45.6 (-0.56) S <sub>1</sub>
50/50	81.8	6.8	1.08	13.9	K 55.4 (1.13) S <sub>C</sub> * 95.2 (0.06) S <sub>A</sub> 120.6 (1.29) I S <sub>1</sub> 53.2 (0.74) S <sub>C</sub> * 94.6 (0.05) S <sub>A</sub> 119.9 (1.28) I	I 113.0 (-1.27) S <sub>A</sub> 90.3 (-0.06) S <sub>C</sub> * 47.2 (-0.63) S <sub>1</sub>
40/60	86.3	6.3	1.13	12.8	K 54.9 (1.23) S <sub>C</sub> * 90.4 (0.04) S <sub>A</sub> 120.5 (1.33) I S <sub>1</sub> 52.8 (0.76) S <sub>C</sub> * 89.8 (0.04) S <sub>A</sub> 119.7 (1.31) I	I 112.9 (-1.30) S <sub>A</sub> 85.6 (-0.05) S <sub>C</sub> * 46.7 (-0.67) S <sub>1</sub>
30/70	78.3	6.4	1.09	12.9	K 51.5 (1.17) S <sub>C</sub> * 88.0 (0.03) S <sub>A</sub> 119.1 (1.36) I S <sub>1</sub> 50.0 (0.63) S <sub>C</sub> * 87.4 (0.04) S <sub>A</sub> 118.3 (1.36) I	I 111.6 (-1.35) S <sub>A</sub> 83.2 (-0.05) S <sub>C</sub> * 44.2 (-0.57) S <sub>1</sub>
20/80	84.8	6.8	1.09	13.4	K 53.8 (1.33) S <sub>C</sub> * 88.2 (0.03) S <sub>A</sub> 121.5 (1.38) I S <sub>1</sub> 58.2 (0.71) S <sub>C</sub> * 87.7 (0.04) S <sub>A</sub> 120.8 (1.37) I	I 113.9 (-1.36) S <sub>A</sub> 83.3 (-0.05) S <sub>C</sub> * 46.9 (-0.66) S <sub>1</sub>
10/90	87.6	8.0	1.13	15.7	K 57.2 († <sup>c</sup> ) S <sub>1</sub> 59.1 (1.49) S <sub>C</sub> * 90.0 (0.04) S <sub>A</sub> 125.4 (1.37) I S <sub>1</sub> 58.6 (0.94) S <sub>C</sub> * 89.5 (0.03) S <sub>A</sub> 124.9 (1.35) I	I 117.6 (-1.34) S <sub>A</sub> 84.7 (-0.05) S <sub>C</sub> * 52.3 (-0.82) S <sub>1</sub>
0/100	85	7.2	1.08	14.0	K 57.2 († <sup>c</sup> ) S <sub>1</sub> 60.7 (1.62) S <sub>C</sub> * 94.5 (0.05) S <sub>A</sub> 125.7 (1.37) I S <sub>1</sub> 60.8 (1.09) S <sub>C</sub> * 94.8 (0.04) S <sub>A</sub> 126.1 (1.37) I	I 117.9 (-1.40) S <sub>A</sub> 89.0 (-0.02) S <sub>C</sub> * 53.6 (-0.94) S <sub>1</sub>

<sup>a</sup> Polymerization temperature: 0°C; polymerization solvent: CH<sub>2</sub>Cl<sub>2</sub>; [M]<sub>0</sub>=[**11-8**]+[**11-11**]=0.224; [M]<sub>0</sub>/[I]<sub>0</sub>=20; [Me<sub>2</sub>S]<sub>0</sub>/[I]<sub>0</sub>=10; polymerization time: 1 h.

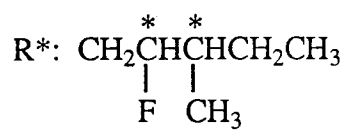
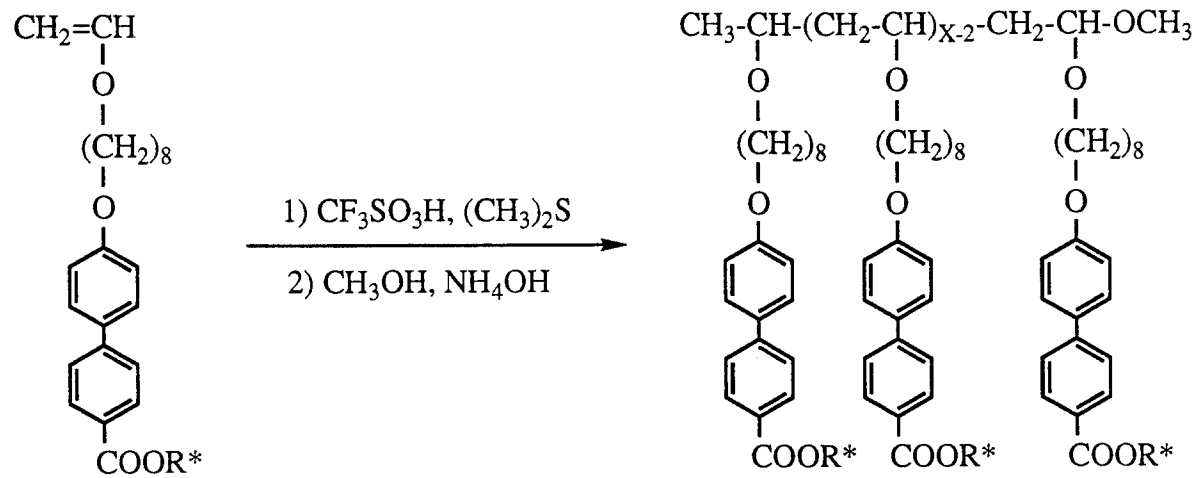
<sup>b</sup> Heating and cooling rates are 20°C/min.

Data on the first line are from first heating and cooling scans. Data on the second line are from second heating scan.

<sup>c</sup> Overlapped peak.

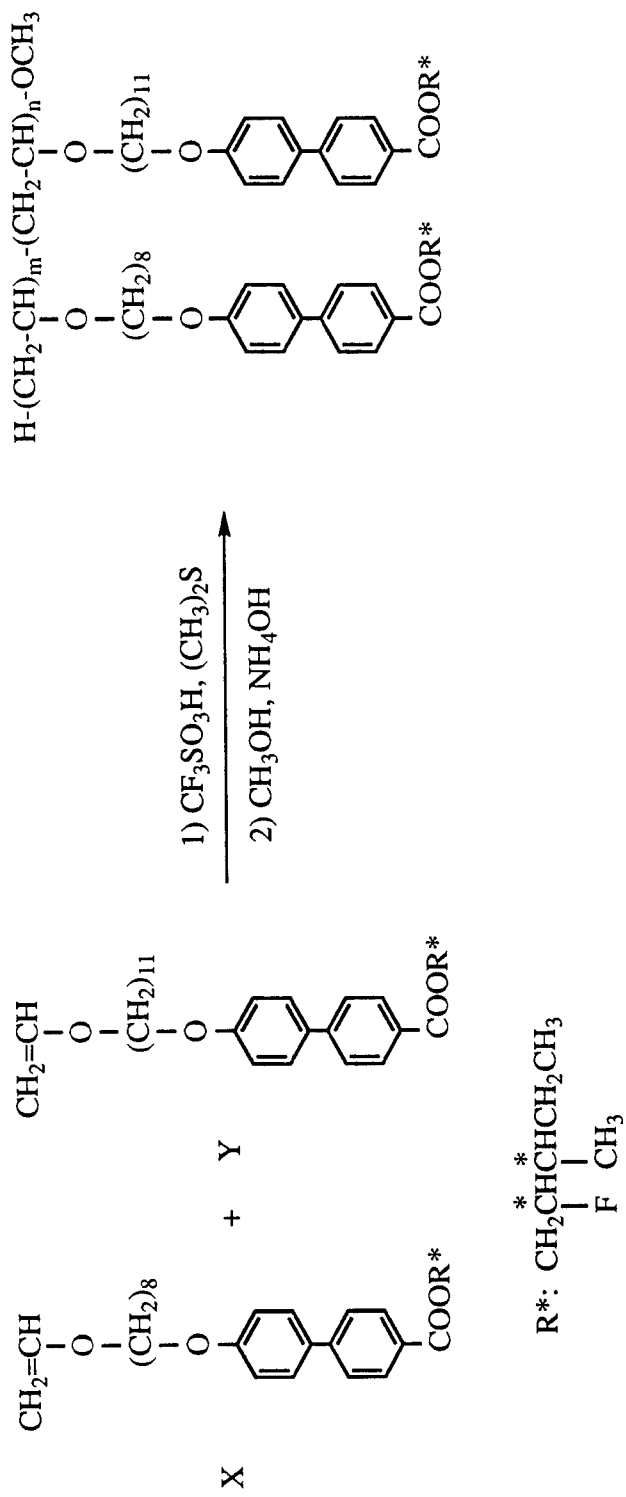


Scheme 1



11-8

Scheme 2



Scheme 3

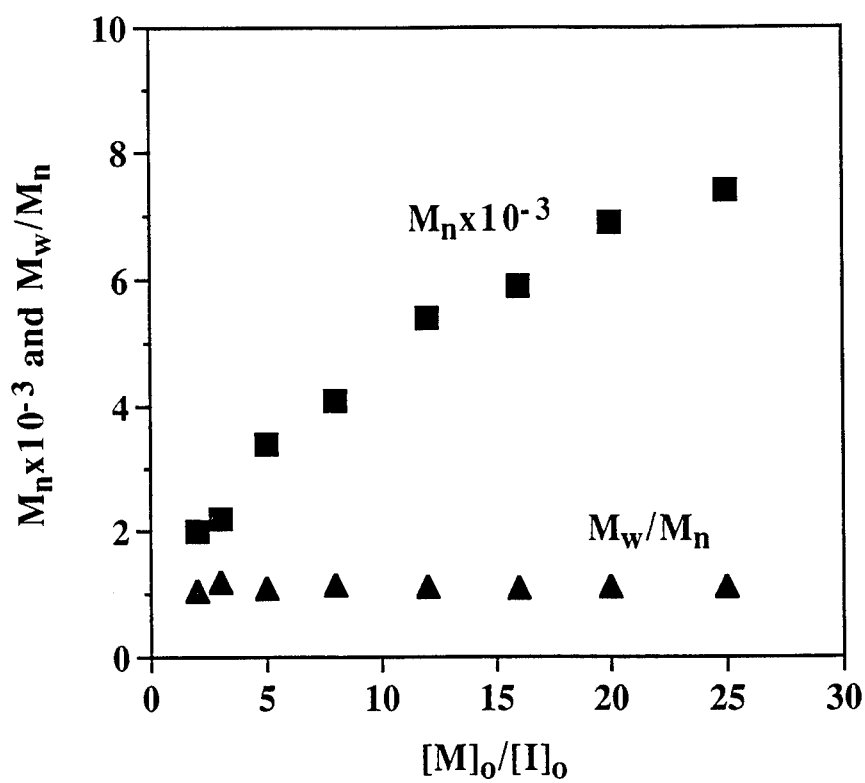


Figure 1



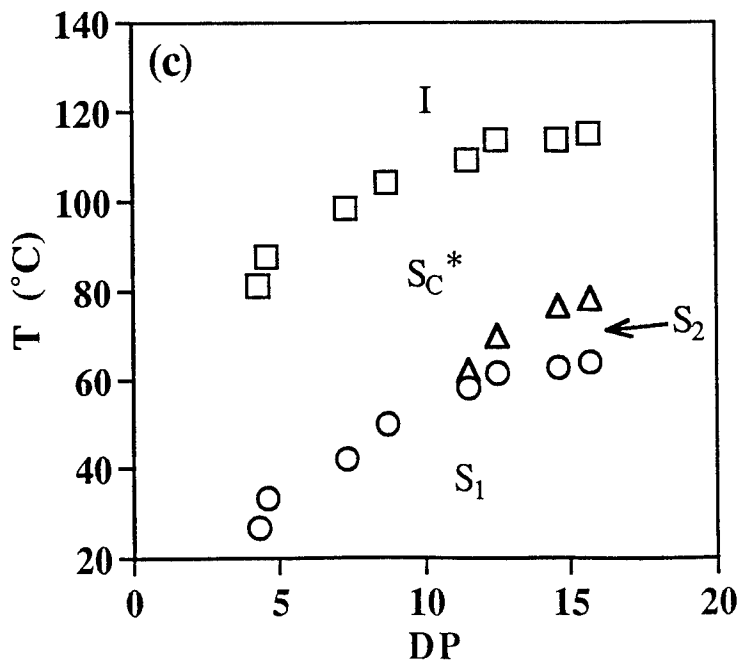
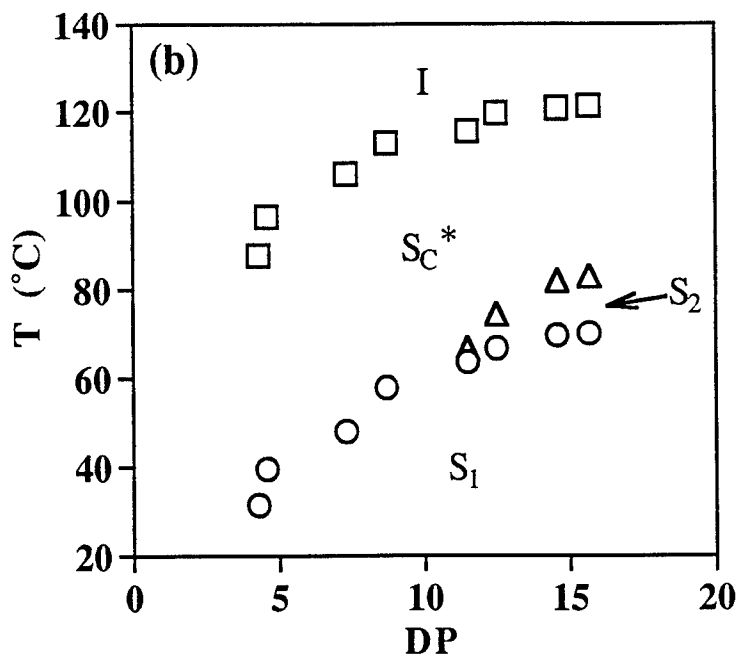
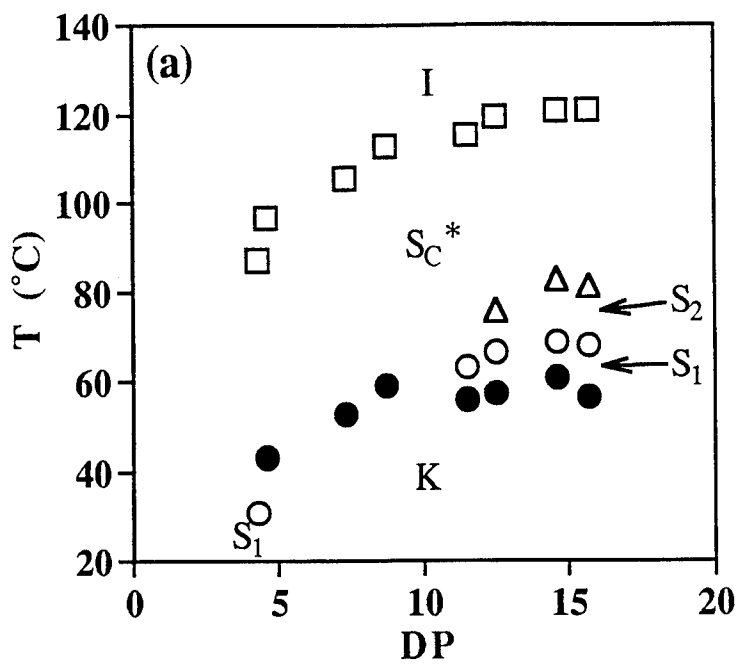
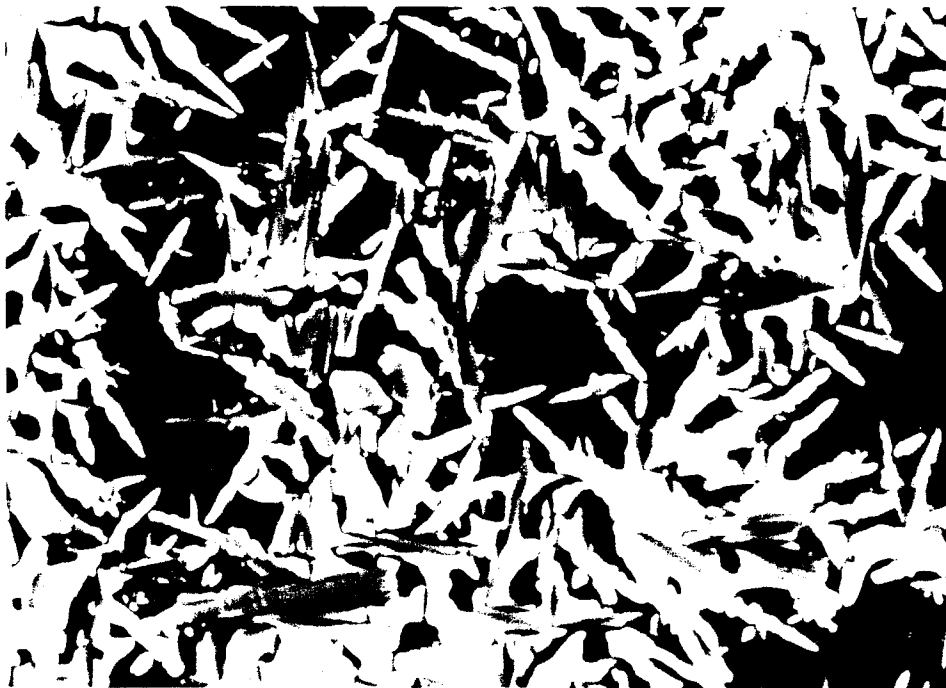


Figure 3

(a)

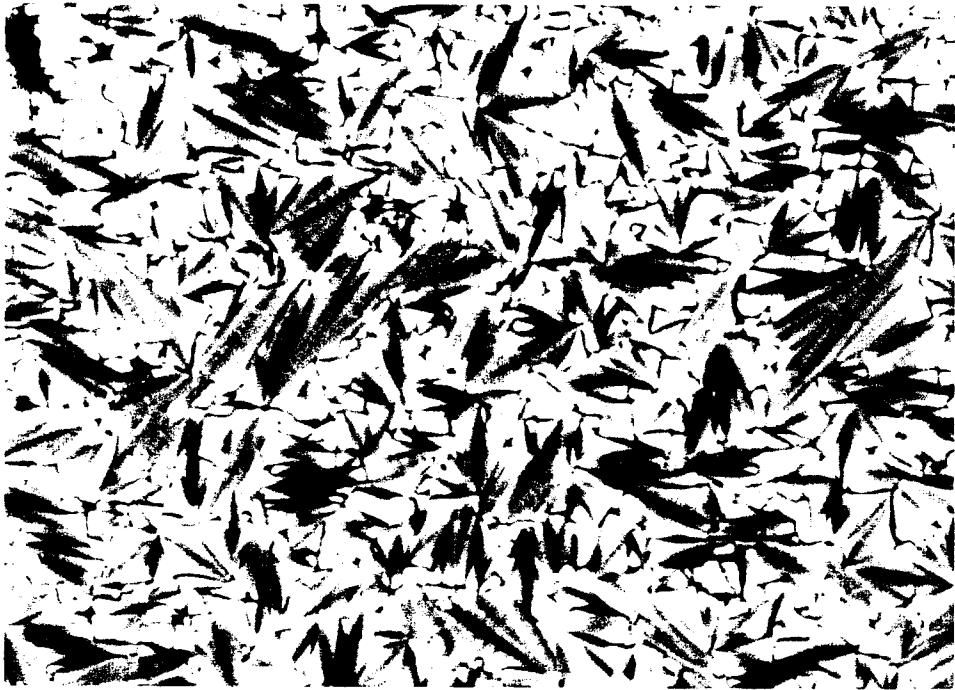


(b)



Figure 4

(c)



(d)

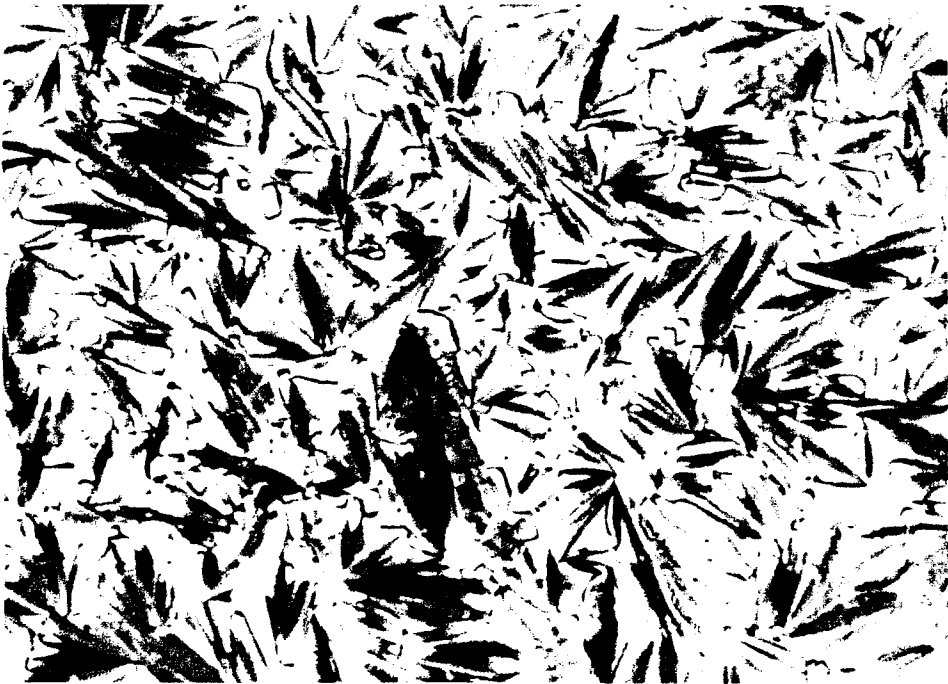


Figure 4

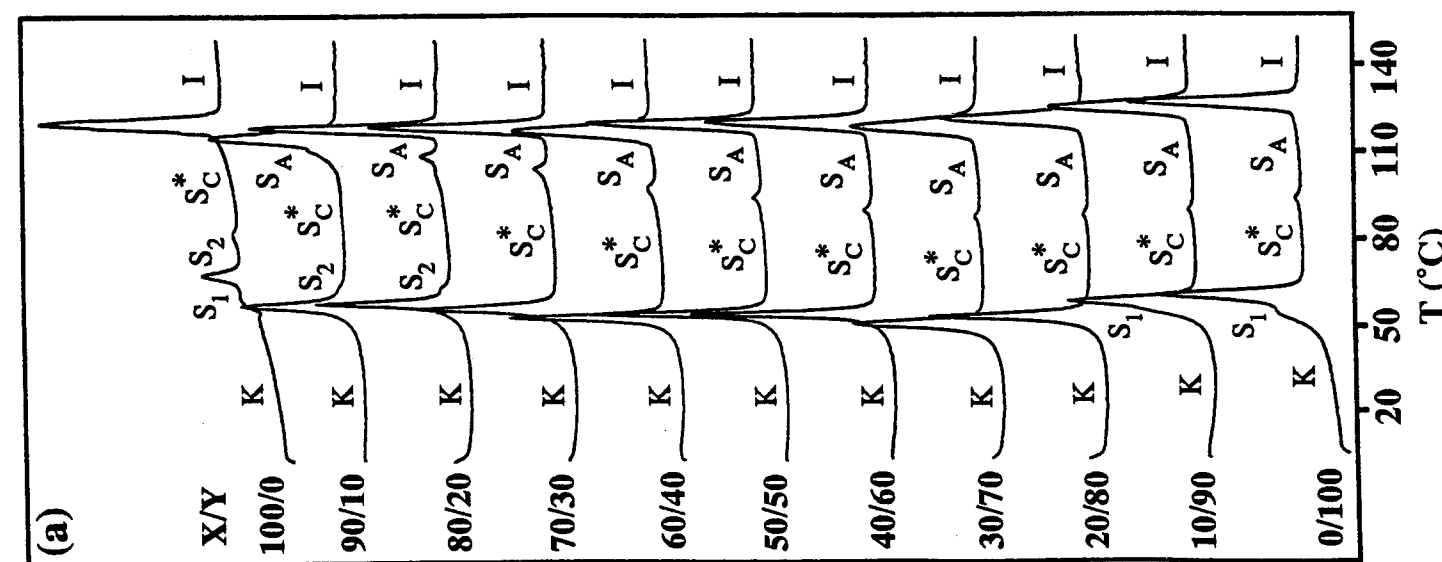
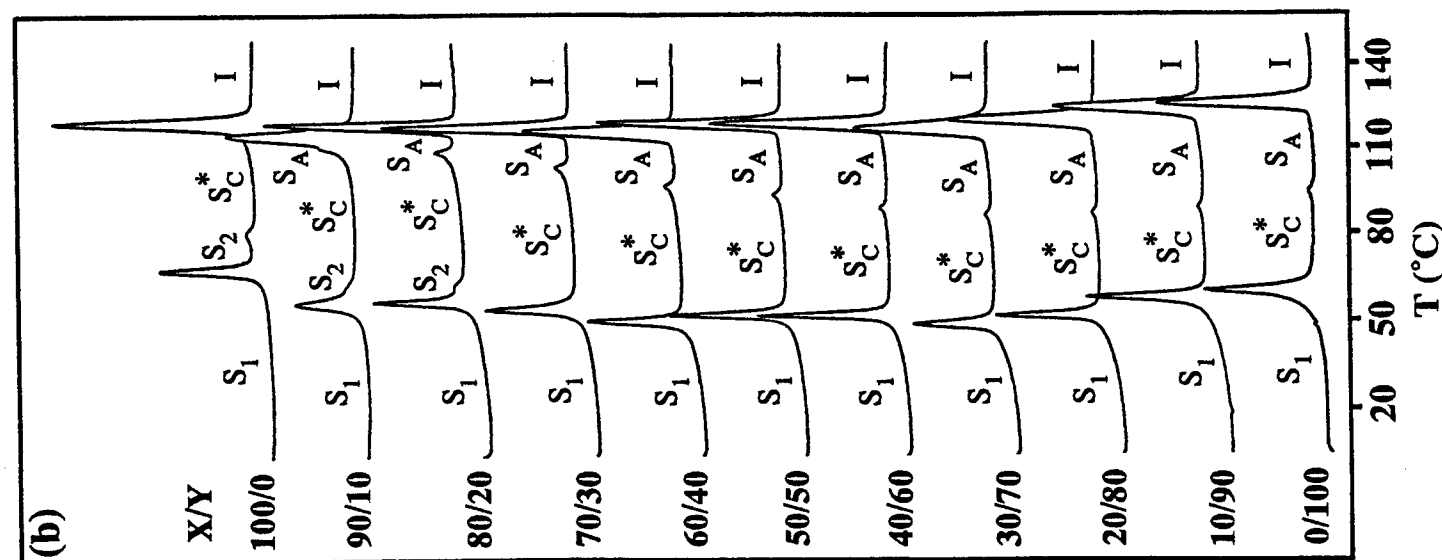
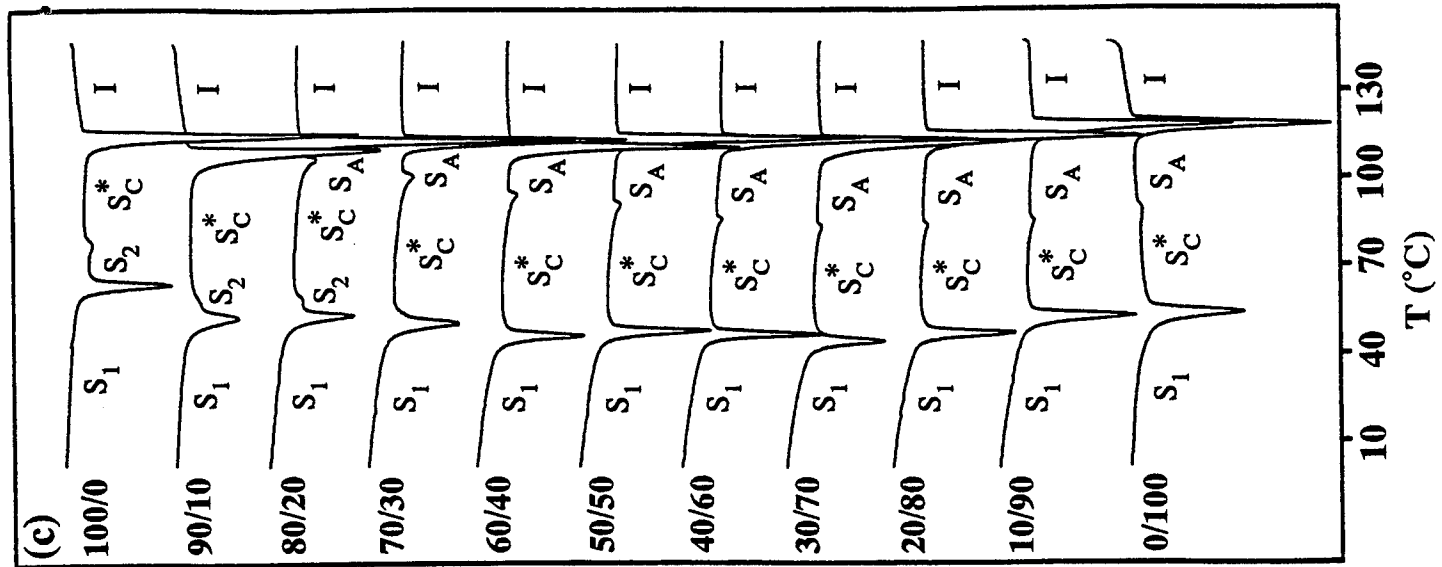


Figure 5

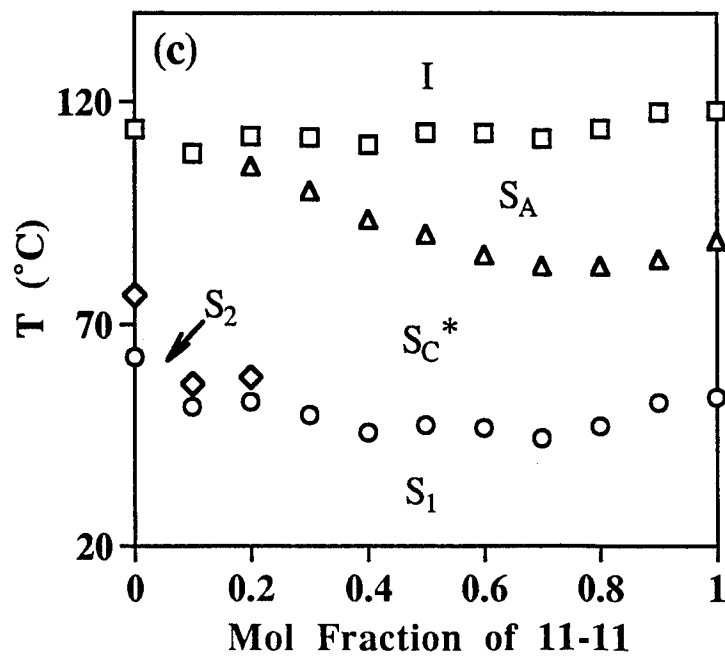
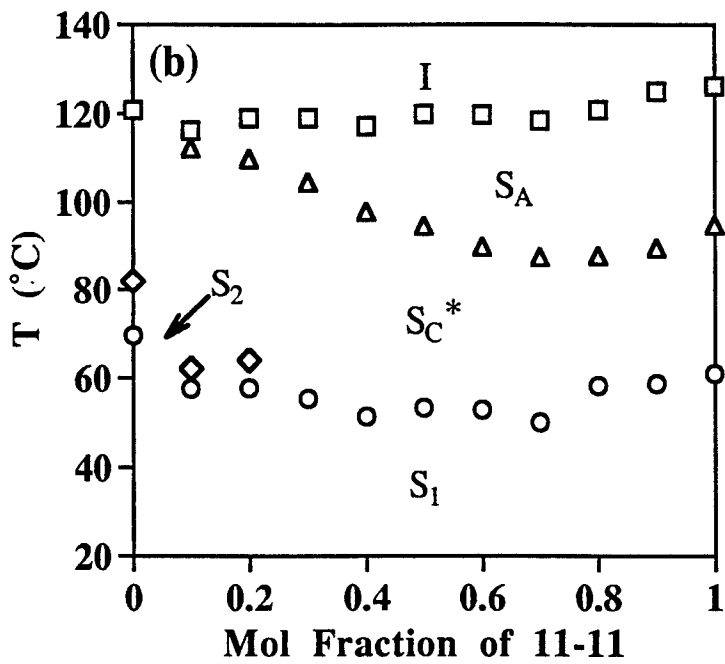
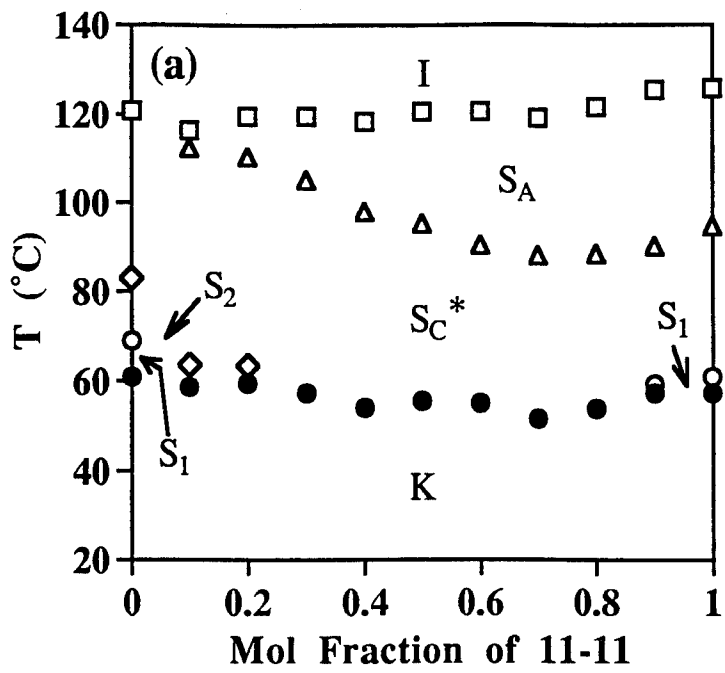


Figure 6