

Molecular design of ferroelectric liquid crystalline polymers

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Abstract :The synthesis and characterization of several series of ferroelectric side-chain polymers were presented. Differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction measurement were used to determine their thermal transitions and analyze their anisotropic textures. The influence of polymer backbones, flexible spacers, mesogenic cores as well as chiral end groups on the mesomorphic properties of the polymers was discussed.

INTRODUCTION

The chiral smectic C(S_C^*) mesophase was theoretically presented and experimentally proven to be ferroelectric by Meyer in 1975.^[1] A bistable, fast switching, electrooptical device which uses the ferroelectric liquid crystals (FLCs) was demonstrated a few years later by Clark and Lagerwell.^[2] An increasing interest in the synthesis of low molar mass S_C^* liquid crystals has since then developed. Numerous FLC compounds and room-temperature mixtures have so far been prepared for fast electrooptical applications. Besides low molar mass FLCs, several side-chain liquid crystalline polymers (LCPs) exhibiting a S_C^* mesophase have recently been reported. Ferroelectric properties, e.g. spontaneous polarization in these polymers, have also been provided in some cases. This field has been reviewed by LeBarny and Dubois.^[3] However the detailed structure-property relationship of S_C^* LCPs, has still remained unclear. This has been due to the limited experimental data available in previous literature. Several series of S_C^* LCPs that have been performed in our laboratory are reviewed in this study.^[4-11]

RESULTS AND DISCUSSION

The first S_C^* side-chain LCP was prepared by Shibaev et. al. in 1984.^[12] Since then several structural modifications have been attempted for a S_C^* side-chain LCP.^[3] A S_C^* side-chain LCP is generally comprised of four constituents: (i) spacer (ii) polymer backbone (iii) mesogenic core and (iv) chiral end group. In this work, a more systematic investigation is presented regarding the influence of these four components on the possibility of obtaining a ferroelectric side-chain LCP

Influence of spacer on phase transitions

Table 1 summarizes the thermal transitions of a series of polysiloxanes containing 4-[(S)-2-methyl-1-butoxy]phenyl 4-hydroxybiphenyl-4'-carboxylate moieties as mesogenic units and aliphatic spacers containing three to eleven methylene units respectively.^[4] This series of polymers represent the illustrative examples used here which display the influence of the spacer length on the formation of a S_C^* phase. These examples indicate that short spacers are not favorable for realization of the S_C^* phase. Both PS4 and PS5 which contain six and eleven methylene units in the spacers respectively reveal enantiotropic S_A , S_B and S_C^* phases. These phase assignments have been conducted by both optical polarizing microscopy and temperature-dependent X-ray diffractions.^[4] These results demonstrate that the tendency toward S_C^* mesomorphism increases with increasing spacer length.

Besides polymethylene, oligooxyethylene spacers have usually been used as flexible spacers for side chain LCPs.^[5] Side-chain LCPs containing oligooxyethylene spacers represent a new class of pseudo-crown ethers and have potential application in the field of solvent-free polymer electrolytes^[13,14]. Studying the influence of oligooxyethylene spacer on the formation of a S_C^* phase will be very interesting. Table 2 presents the thermal transition of a series of S_C^* LC polysiloxanes containing oligooxyethylene spacers and 4-(S)-2-methyl-1-butyl [[(4-hydroxybiphenyl-4'-yl)carbonyl]oxy]benzoate mesogens. All three polysiloxanes PS6-PS8 exhibit enantiotropic smectic A and chiral smectic C phases. The chiral smectic C phase covers a rather broad temperature range (about 200°C). These results reveal that the oligooxyethylene spacer can increase dramatically the thermal stability of the chiral smectic C phase.

Table 1 : Thermal Transitions and Phases Transition Enthalpies for Polymers PS1-PS5.

polymer	m	n	phase transition, °C (corresponding enthalpy change, Kcal/mru ^a)
PS1	40	3	heating: G 25 S_A 117 (1.82) I cooling: I 99 (1.80) S_A
PS2	40	4	heating: G 18 S_A 84 (0.78) I cooling: I 80 (0.42) S_A
PS3	40	5	heating: G 22 S_B 99 (0.89) S_A 212 (0.86) I cooling: I 204 (0.68) S_A 89 (0.82) S_B
PS4	40	6	heating: G 16 S_B 120 (1.73) S_C^* 166 (-) ^b S_A 244 (1.24) I cooling: I 236 (0.98) S_A 164 (-) ^b S_C^* 109 (1.47) S_B
PS5	40	11	heating: G 20 S_B 109 (0.78) S_C^* 143 (-) ^b S_A 218 (0.86) I cooling: I 210 (0.89) S_A 142 (-) ^b S_C^* 103 (0.74) S_B

a) mru = mol repeating unit. b) Enthalpy is very small.

c) G = glassy, S_A = smectic A, S_B = smectic B, S_C^* = chiral smectic C.

Table 2 : Phase Transitions and Phase Transition Enthalpies for Polymers PS6- PS8.

$$\text{Me}_3\text{Si}-\text{O}-\left(\text{Si}\begin{array}{c} \text{CH}_3 \\ | \\ \text{---} \\ | \\ \text{CH}_2 \\ | \\ \text{CH}_2-\text{CH}_2-(\text{OCH}_2\text{CH}_2)_n-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{C}_2\text{H}_5 \end{array}\right)_m-\text{SiMe}_3$$

polymer	m	n	phase transition, °C (corresponding enthalpy change, Kcal/mru ^a)
PS6	40	1	<u>heating</u> G 9.8 S _C * 215.2 (0.07) S _A 234.6 (0.80) I <u>cooling</u> I 229.2 (0.73) S _A 211.7 (0.03) S _C *
PS7	40	2	<u>heating</u> G - 11.2 S _C * 208 (-) ^b S _A 211.8 (0.85) I <u>cooling</u> I 212.0 (0.49) S _A 206 (-) ^b S _C *
PS8	40	3	<u>heating</u> G - 25.1 S _C * 168 (-) ^b S _A 190.3 (0.94) I <u>cooling</u> I 184.2 (0.98) S _A 161 (-) ^b S _C *

a) mru = mol repeating unit. b) Enthalpy is very small

c) G = glassy, S_A= smectic A, S_B= smectic B, S_C*= chiral smectic C.

Influence of polymer backbone on phase transitions

The influence of polymer backbone on the formation of a S_C* phase is next studied. Two series of side chain LC polymethacrylates were prepared. Their thermal transitions and corresponding enthalpy changes are listed in Tables 3 and 4. A comparison is made of their thermal behavior with that of their corresponding polymers listed in Table 1 and 2. This comparison indicates that the polymer backbone can affect not only the thermal stability of the

Table 3 : Molecular Weights, Phase Transitions, and Phase Transition Enthalpies for Polymers PM1-PM3.

$$\left(\text{CH}_2-\text{C}\begin{array}{c} \text{CH}_3 \\ | \\ \text{---} \\ | \\ \text{COO}-(\text{CH}_2)_n-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{C}_2\text{H}_5 \end{array}\right)_m$$

n = 3, 6, 11

polymer	n	\bar{M}_w	\bar{M}_n	\bar{M}_w / \bar{M}_n	phase transition, °C (corresponding enthalpy change, Kcal/mru ^a)
PM1	3	22030	17994	1.22	<u>heating</u> G 33 S _B 84 (0.33) S _A 196 (0.97) I <u>cooling</u> I 193 (0.88) S _A 81 (0.42) S _B
PM2	6	19889	11814	1.68	<u>heating</u> G 31 S _B 131 (0.75) S _A 181 (1.73) I <u>cooling</u> I 176 (1.70) S _A 127 (0.72) S _B
PM3	11	20632	15442	1.34	<u>heating</u> G 30.5 K 101(0.83) S _C * 132(-) ^b S _A 197(0.39) I <u>cooling</u> I 207 (0.50) S _A 130 (-) ^b S _C * 96 (0.75) K

a) mru = mol repeating unit

b) Enthalpy is very small

c) G = glassy, S_A = smectic A, S_B = smectic B, S_C* = chiral smectic C, K = crystalline.

Table 4 : Phase Transitions, and Phase Transition Enthalpies for Polymers PM4-PM6.

$$\left(\text{CH}_2 - \underset{\text{C}}{\overset{\text{CH}_3}{\text{C}}} \right)_m - \text{C}(=\text{O}) - (\text{O}-\text{CH}_2-\text{CH}_2)_n - \text{O} - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{O} - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{O} - \text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{C}_2\text{H}_5$$

polymer	n	\overline{M}_w	\overline{M}_n	$\overline{M}_w / \overline{M}_n$	phase transition, °C (corresponding enthalpy change, Kcal/mru ^a)	
					heating	cooling
PM4	1	10386	16872	1.62	G 35.3 S _A 159.4 (0.26) I I 139.2 (0.25) S _A	
PM5	2	12382	19083	1.54	G 17.8 S _A 130.6 (0.39) I I 127.8 (0.51) S _A	
PM6	3	11957	19480	1.63	G -7.7 S _C [*] 120 (-) ^b S _A 154.8 (1.15) I I 133.1 (0.78) S _A 114 (-) ^b S _C [*]	

a) mru = mol repeating unit
 b) Enthalpy is very small
 c) G = glassy, S_A = smectic A, S_C^{*} = chiral smectic C, I = isotropic.

mesophases but also the nature of the mesophases formed. Furthermore, a flexible polymer backbone is observed to have a tendency toward having a lower glass transition and a wider mesomorphic temperature range. The most important tendency is that the flexible polymer backbone also leads to a wider temperature range of a S_C^{*} phase.

Table 5 : Phase Transitions and Phase Transition Enthalpies for Polymers PS9-PS11.

$$\text{Me}_3\text{SiO} - \left(\underset{\text{CH}_2}{\overset{\text{Me}}{\text{Si}}} - \text{O} \right)_{35} - \text{Si}(\text{Me})_3$$

$$\text{CH}_2 - \text{CH}_2 - (\text{OCH}_2\text{CH}_2)_n - \text{O} - \text{C}_6\text{H}_4 - \text{COO} - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{COO} - \text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{C}_2\text{H}_5$$

polymer	n	phase transition, °C (corresponding enthalpy change, Kcal/mru ^a)	
		heating	cooling
PS9	1	G 5.2 S _F [*] - (-) ^b S _C [*] 190(-) ^c S _A 199(0.40) N [*] 205.6(-) ^d I I 204.2(-) ^d N [*] 198.9(0.64) S _A 189 - (-) ^c S _C [*] 40(-) ^c S _F [*]	
PS10	2	G 3.1 S _F [*] 40.4(0.14) S _C [*] 181(-) ^c S _A 196.5(0.78) N [*] 201.4(-) ^d I 197.7(-) ^d N [*] 190.5(0.46) S _A 180 - (-) ^c S _C [*] 50(-) ^c S _F [*]	
PS11	3	G 3.5 S _C [*] - (-) ^b S _A 170.7(0.76) I I 166.6(0.50) S _A 163.4 - (-) ^c S _C [*]	

a) mru = mole repeating unit. G = glassy, S_F^{*} = chiral smectic F
 S_C^{*} = chiral smectic C, S_A^{*} = chiral smectic A, N^{*} = cholesteric, I = isotropic
 b) The transition temperature was difficult to detect
 c) The transition temperature was determined by optical microscopy.
 d) Overlapped transition.

Influence of mesogenic core on phase transitions

In order to study the influence of mesogenic core on the formation of a S_C^* phase, we prepared a new series of polysiloxanes containing the same oligooxyethylene spacers and different mesogenic cores (see the Table 5).^[10] Polymers PS9 and PS10 shows a cholesteric phase and a S_F^* phase besides the S_A and S_C^* phases. Polymer PS11 reveals only enantiotropic S_A and S_C^* phases. A comparison of chemical structure of PS6-PS8 with that of PS9 -PS11 shows that their only difference is the position of the phenyl and biphenyl groups. The former contains a biphenyl group near the polymer backbone while the latter contains a biphenyl group near the chiral end group. The results indicate that both series of polymers display a rather broad temperature range of S_C^* phase. However, the former shows a wider temperature range of S_C^* phase than that of the latter. Polymer PS9 reveals N^* , S_A , S_C^* and S_F^* phases while its corresponding polymer PS6 exhibits only S_A and S_C^* phases.

Table 6 : Phase Transitions and Phase Transition Enthalpies for Polymers PS12-PS14.

n = 3, 6, 11 PS12 - PS14

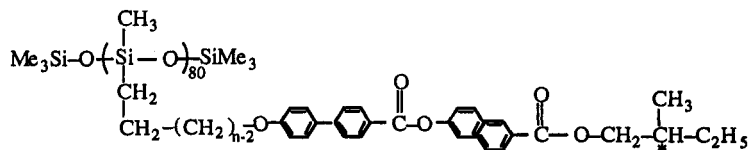
polymer	m	n	phase transition, °C (corresponding enthalpy change, Kcal/mru ^a)	
PS12	40	3	heating cooling	G 24 I -
PS13	40	6	heating cooling	G16 S _A 132 (0.28) I I 129.6 (0.31) S _A
PS14	40	11	heating cooling	G 14.4 S _A 202.2 (1.33) I I 198.6 (1.24) S _A 32.8 (0.17) S _B

a) mru = mol repeating unit b) Overlapped transition
 c) G = glassy, S_A = smectic A, S_C^{*} = chiral smectic C, I = isotropic

Table 6 lists the thermal transitions and phase transition enthalpies for polymers PS12-PS14. This series of polymers represent a system that contain a trans-1,3-dioxane ring instead of a phenyl ring if they are compared with polymers PS1, PS4 and PS5 (see Table 1). The conformational isomers of the trans-1,3-dioxane-based mesogens are in dynamic equilibrium. Mesogenic units based on the trans-1,3-dioxane ring can be used to synthesize noncrystallizable side-chain LCPs as has been demonstrated in our previous work^[15-18]. Experimental results in this study indicate that PS12 show no mesophase, PS13 reveal an enantiotropic S_A phase while PS14 display an enantiotropic S_A phase and a monotropic S_B phase. The reason could be due to the presence of several conformers for their mesogenic side groups. Their presence would impede the formation of a tilted S_C^* phase.^[6]

Table 7 lists the thermal transitions and phase transition enthalpies for polymer PS15-PS17. This series of polymers represent a system that contains a

Table 7 : Phase Transitions and Phase Transition Enthalpies for polymers PS15-PS17



Polymer	n	(corresponding enthalpy changes, Kcal / mru ^a)
PS15	3	heating: G 15.1 S _A 151.3 (0.29) I
		cooling: I 150.4 (0.39) S _A
PS16	6	heating: G 6.9 S _A 285.6 (1.51) I
		cooling: I 283.2 (2.51) S _A
PS17	11	heating: G 1.0 S _A 326.7 (0.99) I
		cooling: I 311.5 (0.62) S _A

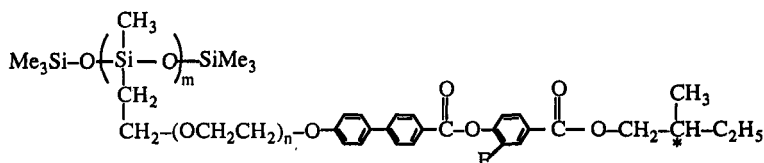
a) mru = mol repeating unit, G = glassy, S_A = smectic A, I = isotropic.

naphthalene ring instead of a phenyl ring if they are compared with polymers PS1, PS4 and PS5 (see Table 1). All of polymers PS15-PS17 reveal respectively only an enantiotropic S_A phase. The result indicates that introducing a naphthalene ring into the mesogenic core decreases dramatically the formation of a chiral smectic C phase.

Influence of lateral substituent on phase transitions

Polymers PS18-PS20 represents a system that contains a lateral fluoro-substituent if they are compared with polymers PS6-PS8 (see Tables 2 and 8). The former display a quite similar mesomorphic behavior with that of the latter. However, their mesomorphic temperature ranges are much narrower than those of polymers PS6-PS8. The experimental results indicate that incorporating a lateral fluoro-substituent into the mesogenic core can decrease the thermal stability of the mesophases including the S_C* phase.

Table 8 : Phase Transitions and Phase Transition Enthalpies for Polymers PS18-PS20.



polymer	m	n	phase transition, °C (corresponding enthalpy change, Kcal/mru ^a)
PS18	80	1	heating: G 0.9 S _c * 153.4(-) ^b S _A 168.5 (0.66) I
			cooling: I 164.6 (0.57) S _A 150.4(-) ^b S _c *
PS19	80	2	heating: G - 8.0 S _c * 157.9 - (-) ^b S _A 160.0 (0.87) I
			cooling: I 157.3 (0.71) S _A 155.3 - (-) ^b S _c *
PS20	80	3	heating: G - 12.5 S _c * 142.1(-) ^b S _A 148.0 (0.87) I
			cooling: I 144.8 (0.77) S _A 139.8(-) ^b S _c *

a) mru = mol repeating unit b) Overlapped transition
 c) G= glassy, S_A= smectic A, S_C* = chiral smectic C, I = isotropic.

Influence of chiral end group on phase transitions

In order to study the influence of chiral end group on the formation of a S_C^* phase, we prepared two new series of polysiloxanes containing the same oligooxyethylene spacer and mesogenic core, and different chiral end groups (see the Tables 9 and 10).^[10] A comparison of chemical structure of polymers PS21-PS23 and PS24-PS26 with that of PS9-PS11 (see Table 5) shows that their only difference is the chiral end groups. For polymers PS18-PS20, (R)-1-methyl-1-heptyl is used to replace (S)-2-methyl-1-butyl as the chiral end group.

Table 9. Phase Transitions and Phase Transition Enthalpies for Polymers PS21-PS23.

Polymer	n	heating cooling	phase transitions, °C (corresponding enthalpy changes; Kcal/mru ^a)
PS21	1	heating cooling	G 10.2 S _A 150 (0.457) I I 132 (0.5) S _A
PS22	2	heating cooling	G -5.0 TGB _A 122.7 (0.526) I I 117.5 (0.625) TGB _A
PS23	3	heating cooling	G -0.4 TGB _A 100(-) ^b N* 112 (0.737) I I 101.7 (-) ^c N* 94.6 (0.649) TGB _A

a) mru = mole repeating unit, G= glassy, S_A= smectic A, TGB_A=twist grain boundary A, N*= cholesteric. I = isotropic. b) The transition was determined by optical microscopy, c) Overlapped transition.

Table 10. Phase Transitions and Phase Transition Enthalpies for Polymers PS24-PS26.

Polymer	n	heating cooling	phase transitions, °C (corresponding enthalpy changes; Kcal/mru ^a)
PS24	1	heating cooling	G 20.1 S _F * -(-) ^b S _C * 204.4(-) ^c N* 218 (0.457) I I 202(0.554) N* 195.1(-) ^c S _C * 55(-) ^c S _F *
PS25	2	heating cooling	G 7.6 S _F * -(-) ^b S _C * 197.6(-) ^c N* 204(0.533) I I 190(0.518) N* 182.2(-) ^c S _C * 65(-) ^c S _F *
PS26	3	heating cooling	G 12.4 S _C * 171.3(-) ^c N* 173(0.867) I I 160.5(0.808) N* 150(-) ^c S _C *

a) mru = mole repeating unit, G = glassy, S_F*= chiral smectic F, S_A= smectic A, S_C*= chiral smectic C, N*=cholesteric. I = isotropic. b) The transition was difficult to detect. c) Overlapped transition.

Polymers PS21-PS23 do not reveal the chiral smectic C phase, while polymers PS9-PS11 show very wide temperature ranges of chiral smectic C phase. For polymers PS24-PS26, a (2S,3S)-2-chloro-3-methylpentoxy group is used as the chiral end group. Both polymers PS20 and PS25 reveal enantiotropic N*, S_C* and S_F* phases while polymer PS26 presents only enantiotropic N* and S_C* phases. The mesomorphic property of PS24-PS26 are also different from that of PS9-PS11. All these results demonstrate that the chiral end group can affect not only the thermal stability of the mesophases but also the nature of the mesophases.

CONCLUSION

Several series of S_C* side-chain LCPs were prepared in this work so as to examine the influence of flexible spacer, mesogenic core, chiral end group and polymer backbone in regards to the formation of a S_C* phase. The following conclusions could be drawn on the basis of data obtained in this work :

- (i) The tendency toward chiral smectic C mesomorphism increases by increasing the length of flexible spacer;
- (ii) The oligooxyethylene spacer plays a rather crucial role in the thermal stability of the chiral smectic C phase. It can be used to prepare a side-chain LCP containing a very wide temperature range of the chiral smectic C phase;
- (iii) The flexibility of the polymer backbone would affect the thermal stability of the chiral smectic C phase. Flexible polymer backbones enhance the decoupling of the motions of the side chain and main chain, thereby tending to give rise to a higher thermal stability of the mesophase, including the chiral smectic C phase;
- (iv) The mesogenic core plays the most important role on the formation of a chiral smectic C phase;
- (v) Incorporation of a flexible 1,3-dioxane ring or a naphthalene ring into the mesogenic core would decrease the tendency to form a chiral smectic C phase;
- (vi) Incorporation of a lateral fluoro-substituent into a mesogenic core will decrease the thermal stability of the mesophases, including the chiral smectic C phase; and
- (vii) The chiral end group would affect not only the nature of the mesophases formed but also the thermal stability of the chiral smectic C phases.

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REFERENCES

1. R. B. Meyer, L. Liebert, L. Strezelecki, and L. Lellier, *J. Phys. Lett.* **36**, L-69 (1975).
2. N. A. Clark and S. T. Lagerwell, *Appl. Phys. Lett.* **36**, 899 (1980).
3. P. LeBarny and J. C. Dubois, In "Side Chain Liquid Crystals Polymers", C. B. McArdle Eds., Blackie : Glasgow and London, p. 130 (1989).
4. C. S. Hsu, J. H. Lin, L. R. Chou and G. H. Hsiue, *Macromolecules*, **25**, 7126 (1992).
5. C. S. Hsu, L. J. Shih and G. H. Hsiue, *Macromolecules*, **26**, 3161 (1993).
6. T. M. Junang, Y. J. Leu and C. S. Hsu, *Mol. Cryst. Liq. Cryst.*, **237**, 223 (1993).
7. J. H. Chen, R. C. Chang, and G. H. Hsiue, *Ferroelectrics*, **147**, 241 (1994).
8. J. H. Chen, R. C. Chang, G. H. Hsiue and F. W. Guu, *Liq. Cryst.*, **18**, 291 (1995).
9. G. H. Hsiue, P. J. Hsieh, C. S. Hsu and S. L. Wu, *Polym. Bull.*, **33**, 159 (1994).
10. J. H. Chen and G. H. Hsiue, *Macromolecules*, accepted (1995).
11. G. R. Jee, J. H. Chen and G. H. Hsiue, *Macromolecular Chem. Phys.*, accepted (1995).
12. V. P. Shibaev, M. V. Kozlovsky, L. A. Beresnev, L. M. Blinov and N. A. Plate, *Polym. Bull.* **12**, 299 (1984).
13. C. J. Hsieh, C. S. Hsu and G. H. Hsiue, *J. Polym. Sci., Polym. Chem.*, **28**, 425 (1990).
14. C. J. Hsieh, G. H. Hsiue and C. S. Hsu, *Makromol. Chem.*, **191**, 2195 (1990).
15. C. S. Hsu, J. M. Rodriguez-Parada and V. Percec, *Makromol. Chem.*, **188**, 1017 (1987).
16. C. S. Hsu, J. M. Rodriguez-Parada and V. Percec, *J. Polym. Sci. Polym. Chem.*, **25**, 2425 (1987).
17. C. S. Hsu and V. Percec, *Makromol. Chem. Rapid Commun.*, **8**, 331 (1987).
18. C. S. Hsu and V. Percec, *Polym. Bull.*, **8**, 331 (1987).