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Molecular engineering of liquid crystal polymers by living polymerization

12. Synthesis and living cationic polymerization of 4-[S(-)-2-methyl-1-butoxy]-4′-(ω-oxyalkyl-1-vinyl ether)-α-methylstibene with octyl and hexyl alkyl groups*

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SUMMARY

The synthesis and living cationic polymerization of 4-[S(-)-2-methyl-1-butoxy]-4'-(8-oxyoctyl-1-vinyl ether)-α-methylstilbene (6-8) and 4-[S(-)-2-methyl-1-butoxy]-4'-(6-oxyhexyl-1-vinyl ether)-α-methylstilbene (6-6) with the initiating system $CF_3SO_3H/(CH_3)_2S$ in methylene chloride at 0^oC are described. Both poly(6-8) and poly(6-6) exhibit an enantiotropic mesophase which is characterized by a focal conic texture with equidistant lines (most probable a s_C* phase).

INTRODUCTION

Presently there is continuous interest in chiral side chain liquid crystalline polymers, particularly those which exhibit a chiral smectic C (s_C*) mesophase.[1-15] The ability to control the polymer molecular weight and the molecular weight distribution represents the major parameter required to manipulate the phase transitions of side chain liquid crystalline polymers. Recently, we have elaborated synthetic procedures for a convenient synthesis of mesogenic vinyl ether monomers and for their living cationic polymerization.[16] Particularly the initiating system $CF_3SO_3H/(CH_3)_2S$[17] can be used to polymerize mosogenic vinyl ethers since it tolerates a variety of functional groups.[16] The goal of this paper is to report the synthesis and living cationic polymerization of 4-[S(-)-2-methyl-1-butoxy]-4'- (8-oxyoctyl-1-vinyl ether)-α-methylstilbene (6-8) and 4-[S(-)-2-methyl-1-butoxy]-4'-(6-oxyhexyl-1-vinyl ether)-α-methylstilbene (6-6) and the mesomorphic behavior of the resulting polymers.

EXPERIMENTAL

Materials

All materials were of commercial origin and were used as received or purified as described in previous publications.[16]

Synthesis of Monomers

The synthesis of monomers and polymers is outlined in Scheme I.

8-Bromooctyl-1-Vinyl Ether (4-8)

8-Bromo-1-octanol (10.5 g, 50 mmol) was added to a mixture of 1, 10-phenanthroline palladium (II) diacetate (1.1 g, 2.76 mmol), n-butyl vinyl ether (150 ml) and dry chloroform (140 ml). The mixture was stirred at 60^oC for 6 hr. After cooling in a refrigerator overnight to precipitate the catalyst, the reaction mixture was filtered, and the solvent was removed on a rotary evaporator. The resulting liquid was purified by column chromatography (neutral alumina, methylene chloride as eluent) to yield 9.5 g (40%) of a yellow liquid.

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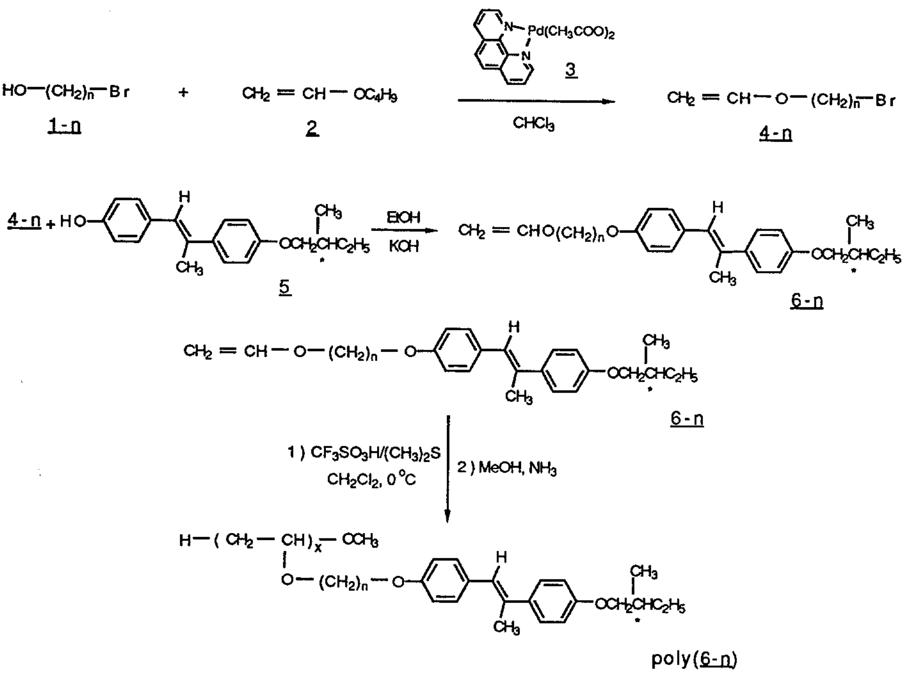


Scheme I : Synthesis and Polymerization of 6-8 and 6-6

^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.10-1.95 (m, 12H, -$(C\underline{H}_2)_6$-), 3.41 (t, 2H, Br-$C\underline{H}_2$-), 3.67 (t, 2H, -$C\underline{H}_2O$-), 3.96 and 4.00 (2d, 1H, -O-CH=$C\underline{H}_2$, trans), 4.13 and 4.20 (2d, 1H, -O-CH=$C\underline{H}_2$,cis), 6.45 (q, 1H, -O-$C\underline{H}$=CH_2)

6-Chlorohexyl-1-Vinyl Ether (4-6)

6-Chloro-1-hexanol (8.7 g, 63.7 mmol), n-butyl vinyl ether (160 ml) and 1, 10-phenanthroline palladium (II) diacetate (0,85 g, 2.1 mmol) were reacted as in the case of 8-bromooctyl-1-vinyl ether to yield 7.8 g of a colorless liquid. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.20-1.95 (m, 8H, -$(C\underline{H}_2)_4$-), 3.54 (t, 2H, Cl-$C\underline{H}_2$-), 3.68 (t, 2H, -$C\underline{H}_2O$-), 3.96 and 4.00 (2d, 1H, -O-CH=$C\underline{H}_2$, trans), 4.13 and 4.21 (2d, 1H, -O-CH=$C\underline{H}_2$,cis), 6.45 (q, 1H, -O-$C\underline{H}$=CH_2)

4-[S(-)-2-Methyl-1-Butoxy]-4'-(8-Oxyoctyl-1-Vinyl Ether)-α-Methylstilbene (6-8)

4-[S(-)-2-Methyl-1-butoxy]-4'-(hydroxy)-α-methylstilbene (15) (1.89 g, 6.38 mmol) was added to a mixture containing 0.43 g (7.66 mmol) of KOH and 25 ml of 95% EtOH. The reaction was stirred for 30 min, after which 1.5 g (6.38 mmol) of 8-bromooctyl-1-vinyl ether was added and the mixture was heated to reflux temperature overnight. The ethanol was removed on a rotary evaporator and the residue was dissolved in diethyl ether. The ether solution was washed with 2N aqueous KOH, water, dried over $MgSO_4$, filtered and the ether was removed on a rotary evaporator. The resulting solid was recrystallized twice from MeOH to yield 1.0 g (35%) of white crystals. Purity: 99%. m.p., 66.5°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.9-1.1 (m, 6H, $C\underline{H}_3$-), 1.1-2.0 (m, 12H, -$(C\underline{H}_2)_6$-), 2.24 (s, 3H, $C\underline{H}_3$-C=C-Ph), 3.68 (t, 2H, -$C\underline{H}_2$-O-CH=CH_2), 3.78 (m, 2H, $C_2H_5(CH_3)CH$-$C\underline{H}_2$-O), 3.97 (m, 3H, -$C\underline{H}_2$-OPh, -O-CH=$C\underline{H}_2$, trans), 4.14 and 4.21 (2d, 1H, -O-CH=$C\underline{H}_2$, cis), 6.50 (q, 1H, -O-$C\underline{H}$=CH_2), 6.72 (s, 1H, -$\underline{H}$C=C-Ph), 6.89-7.44 (3d, 8H, ArH)

4-[S(-)-2-Methyl-1-Butoxy]-4'-(6-Oxyhexyl-1-Vinyl Ether)-α-Methylstilbene (6-6)

4-[S(-)-2-Methyl-1-butoxy]-4'-(hydroxy)-α-methylstilbene (3.0 g, 10.2 mmol) and potassium carbonate (4.57 g, 27.66 mmol) were added to a flask containing 50 ml of DMSO/acetone 5/95 (v/v). After stirring for 30 min, 1.5 g (9.22 mmol) of 6-chlorohexyl-1-vinyl ether was added and the reaction mixture was heated to reflux overnight. The solvent was removed on a rotary evaporator and the residue was mixed with water and extracted with chloroform. The chloroform layer was separated, dried over $MgSO_4$ and the chloroform was removed on a rotary evaporator. The resulting solid was recrystallized twice from methanol to yield 0.8 g (21%) of white crystals. Purity: 99 %. m.p., 63.1°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.9-1.1 (m, 6H, $C\underline{H}_3$-), 1.1-2.0 (m, 8H, -$(C\underline{H}_2)_4$-), 2.24 (s, 3H, $C\underline{H}_3$-C=C-Ph), 3.69 (t, 2H, -$C\underline{H}_2$-O-CH=CH_2), 3.80 (m, 2H, $C_2H_5(CH_3)CH$-$C\underline{H}_2$-O), 3.97 (m, 3H, -$C\underline{H}_2$-OPh, -O-CH=$C\underline{H}_2$, trans), 4.14 and 4.21 (2d, 1H, -O-CH=$C\underline{H}_2$, cis), 6.50 (q, 1H, -O-C$\underline{H}$=CH_2), 6.71 (s, 1H, -$\underline{H}$C=C-Ph), 6.89-7.43 (3d, 8H, ArH)

Cationic Polymerization

All polymerization were initiated with the $CF_3SO_3H/(CH_3)_2S$[17] system and were performed in methylene chloride solution at 0°C. Experimental details were described previously.[16]

Techniques

All monomers and polymers were characterized by a combination of techniques consisting of 200 MHz ^{1}H-NMR, gel permeation chromatography (GPC, polystyrene standards), high pressure liquid chromatography (HPLC), differential scanning calorimetry (DSC, 20°C/min) and thermal optical polarized microscopy. Experimental details were presented elsewhere.[16]

RESULTS AND DISCUSSIONS

Scheme I outlines the synthesis of 6-8 and 6-6 and their cationic polymerization by using the initiating system $CF_3SO_3H/(CH_3)_2S$.[17] 5 was synthesized as was reported previously.[14,15] The synthesis of the vinyl ethers 6-n was performed according to a general procedure developed in our laboratory.[16] This procedure can be applied only with minor modifications to the synthesis of any mesogenic vinyl ether. The polymerization results of both 6-8 and 6-6, and the characterization of the resulting polymers are summarized in Table I. Both monomers are only crystalline. We have synthesized an entire series of poly(6-8)s with degrees of polymerization ranging from 4 to 25 and a poly(6-6) with degree of polymerization of 18. Although the molecular weights of these polymers are only relative to polystyrene standards they show a very good agreement with the calculated ones. In addition, all polymers exhibit molecular weight distributions equal or lower than 1.10. Figure 1 plots the dependence of M_n and M_n/M_w versus $[M]_0/[I]_0$ for the polymerization of 6-8. This plot demonstrates a living polymerization character for this polymerization.

Figure 2a, b and c exhibits the first and second heating and the cooling DSC traces of poly(6-8)s with various degrees of polymerization. The degrees of polymerization (DP) are presented on the figure. Poly(6-8) with DP = 4 exhibits an enantiotropic smectic mesophase which overlaps the resulting peaks and is well separated only on the cooling scan. However, this mesophase can be only observed on the optical polarized microscope. By increasing the degree of polymerization, the peaks of the melting, crystallization and isotropization transitions get a better separation (Figure 2). In the first heating DSC traces of all poly(6-8) exhibit two melting transitions (Figure 2a), while in the second heating scan only one melting transition (Figure 2b). Thermal transition temperatures collected from first and second heating and from cooling scans are presented in Figure 3. On the optical polarized microscope all poly(6-8) exhibit a focal conic type texture which at the first sight would be assigned to a s_A phase. However, the focal conic texture contains equidistant lines which suggest that the texture of poly(6-8) may be due to a chiral smectic C (s_C*) mesophase (Figure 4). Additional experiments are required to provide a definitive assignment of this phase.

Table I Cationic Polymerization of 6-8 and 6-6 (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_0 = 0.226$; $[(CH_3)_2S]/[CF_3SO_3H] = 10$; polymerization time, 1hr) and Characterization of the Resulting Polymers. Data from the first heating and cooling scans are on the first line, and from second heating scan are on the second line.

Sample	$[M]_0/[I]_0$	Polymer	GPC			Transition Temperatures (°C) and Corresponding	
No.		Yield(%)	M_n	M_w/M_n	DP	Enthalpy (Kcal/mru^b) and Entropy (cal/°K·mru) Changes	
(6-8)1	4	82	1740	1.10	4	k 44 k 74^a s 75^a (5.73) i k 74^a s 75^a (5.17) i	i 67 (0.66) s 55 (4.20) k
(6-8)2	7	91	3210	1.08	7	k 48 k 79 (4.20) s 88 (0.66) i k 80 (4.15) s 88 (0.56) i	i 79 (0.64) s 57 (3.38) k
(6-8)3	12	87	6090	1.07	14	k 50 k 83 (3.04) s 96 (0.66) i k 84 (2.77) s 97 (0.61) i	i 89 (0.73) s 62 (2.94) k
(6-8)4	18	92	7610	1.08	17	k 49 k 83 (2.82) s 100 (0.61) i k 83 (2.76) s 100 (0.71) i	i 91 (0.57) s 61 (2.83) k
(6-8)5	28	95	10810	1.10	24	k 49 k 85 (2.66) s 102 (0.57) i k 85 (2.57) s 102 (0.62) i	i 91 (0.55) s 61 (2.50) k
(6-6)1	20	94	8030	1.12	18	k 53 (0.08) k 84 (3.19) s 92 i g 22 k 77 k 85^a s 94^a (3.08) i	i 83 (0.48) s 62 (1.23) k 16 g

[a] overlapped transitions, enthalpy change corresponds to the sum of both transitions; [b] mru = mole repeat unit.

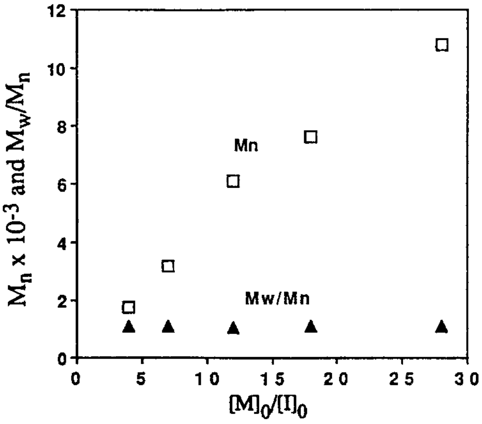
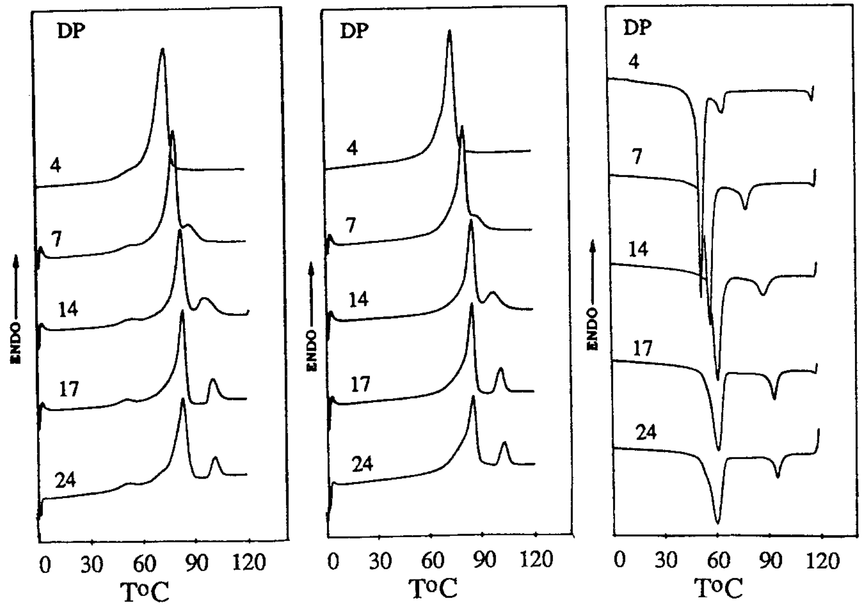


Figure 1 :
The dependence of the number average molecular weight (M_n) and of the polydispersity (M_w/M_n) of poly(6-8) on the $[M]_0/[I]_0$ ratio.

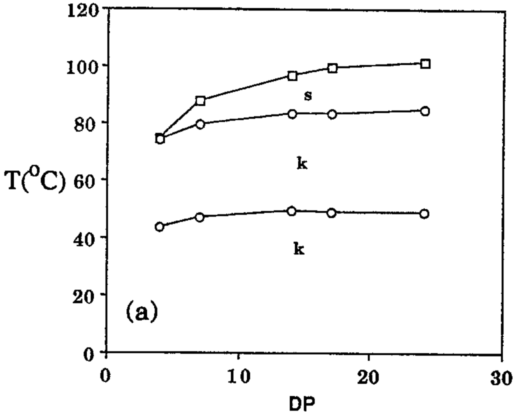


(a)

(b)

(c)

Figure 2 : DSC traces displayed during the first (a) and second (b) heating and the cooling (c) scans by poly(6-8) with different degrees of polymerization (DP). DP is shown on the top of each DSC scan.



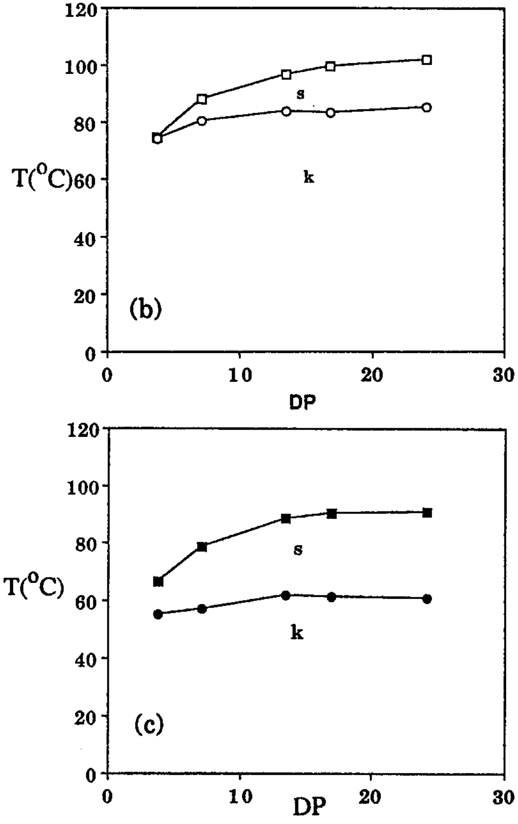


Figure 3 : The dependence of phase transition temperatures on the degree of polymerization of poly(6-8). a) data from first heating scan : ○ - Tk-k and Tk-s; □ - Ts-i; b) data from second heating scan : ○ - Tk-k and Tk-s; □ - Ts-i; c) data from cooling scan : ■ - Ti-s; ● -Ts-k.

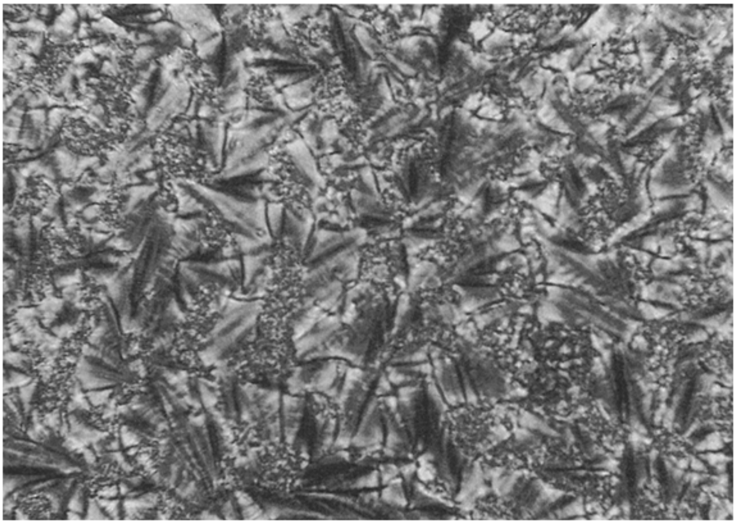


Figure 4; Focal-conic fan shape texture with equidistant lines of poly(6-8) with DP=24 obtained at 69 °C upon cooling from the isotropic phase.

Only one polymer was synthesized from the monomer 6-6. Although its degree of polymerization was 18, poly(6-6) exhibited a smectic mesophase with a much narrower thermal stability than the corresponding poly(6-8) with the same degree of polymerization (Table I). The texture of poly(6-6) resembles that of poly(6-8) and therefore poly(6-6) exhibits either a s_A or a s_C* mesophase.

From the preparative point of view these experiments are very rewarding since they have demonstrated that the initiating system $CF_3SO_3H/(CH_3)_2S$ can be used to induce the living cationic polymerization of vinyl ether monomers containing both double bonds and nucleophilic alkyloxy aryl groups in their mesogen.

ACKNOWLEDGEMENTS

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REFERENCES

1. For a review on side chain liquid crystalline polymers exhibiting s_C* phases see: P. LeBarny and J. C. Dubois in "Side Chain Liquid Crystalline Polymers", C. B. McArdle Ed., Chapman and Hall, New York, 1989, p. 130
2. a) V. P. Shibaev, M. V. Kozlovsky, L. A. Beresnev, L. M. Blinov and N. A. Plate, *Polym. Bull.*, **12**, 299(1984); b) V. P. Shibaev, M. V. Kozlovsky, N. A. Plate, L. A. Beresnev and L. M. Blinov, *Polym. Sci. USSR*, **29**, 1616(1987); c) L. M. Blinov, V. A. Baikalov, M. J. Barnik, L. A. Beresnev, E. P. Pozhidayev and S. V. Yablonsky, *Liq. Cryst.*, **2**, 121(1987)

3 a) G. Decobert, F. Soyer and J. C. Dubois, *Polym. Bull.*, **14**, 179(1985); b) J. M. Guglielminetti, G. Decobert and J. C. Dubois, *Polym. Bull.*, **16**, 411(1986); c) J. C. Dubois, G. Decobert, P. LeBarny, S. Esselin, C. Friedrich and C. Noel, *Mol. Cryst. Liq. Cryst.*, **137**, 349(1986); d) G. Decobert, J. C. Dubois, S. Esselin and C. Noel, *Liq. Cryst.*, **1**, 307(1986); e) S. Esselin, L. Bosios, C. Noel, G. Decobert and J. C. Dubois, *Liq. Cryst.*, **2**, 505(1987); f) S. Esselin, C. Noel, G. Decobert and J. C. Dubois, *Mol. Cryst. Liq. Cryst.*, **155**, 371(1988)

4. a) R. Zentel, G. Reckert and B. Reck, *Liq. Cryst.*, **2**, 83(1987); b) S. Bualek and R. Zentel, *Makromol. Chem.*, **169**, 797(1988); c) H. Kapitza and R. Zentel, *Makromol. Chem.*, **189**, 1793(1988); d) S. Bualek, H. Kapitza, J. Meyer, G. F. Schmidt and R. Zentel, *Mol. Cryst. Liq. Cryst.*, **155**, 47(1988); e) S. U. Vallerien, R. Zentel, F. Kremer, H. Kapitza and E. W. Fisher, *Makrormol. Chem., Rapid Commun.*, **10**, 333(1989); f) R. Zentel, H. Kapitza, F. Kremer and S. U. Vallerien, in "Liquid Crystalline Polymers", R. A. Weiss and C. K. Ober Eds., ACS Symposium Series 435, Washington DC., 1990, p. 207

5. S. Uchida, K. Morita, K. Miyoshi, K. Hashimoto and K. Kawasaki, *Mol. Cryst. Liq. Cryst.*, **155**, 93(1988)

6. N. Koide, K. Uehara and K. Iimura, *Mol. Cryst. Liq. Cryst.*, **157**, 151(1988)

7. T. Suzuki, T. Okawa, T. Ohnuma and Y. Sakon, *Makromol. Chem., Rapid Commun.*, **9**, 755(1988)

8. M. Dumon, H. T. Nguyen, M. Mauzac, C. Destrade, M. F. Achard and H. Gasparoux, *Macromolecules*, **23**, 355(1990)

9. D. M. Walba, P. Keller, D. S. Parmar, N. A. Clark and M. D. Wand, *J. Am. Chem. Soc.*, **111**, 8273(1989)

10. H. Kapitza, R. Zentel, R. J. Twieg, C. Nguyen, S. U. Vallerien, F. Kremer and C. G. Willson, *Adv. Mater.*, **2**, 539(1990)

11. T. Kitazume, T. Ohnogi and K. Ito, *J. Am. Chem. Soc.*, **112**, 6608(1990)

12. H. M. Colquhoun, C. C. Dudman, C. A. O'Makoney, G. C. Robinson and D. J. Williams, *Adv. Mater.*, **2**, 139(1990)

13. a) B. Hahn and V. Percec, *Macromolecules*, **20**, 2961(1987); b) V. Percec and B. Hahn, *Macromolecules*, **22**, 1588(1989); c) B. Hahn and V. Percec, *Mol. Cryst. Liq. Cryst.*, **157**, 125(1988); d) V. Percec and B. Hahn, M. Ebert and J. H. Wendorff, *Macromolecules*, **23**, 2092(1990)

14. V. Percec and B. Hahn, *J. Polym. Sci., Part A: Polym. Chem.*, **27**, 2367(1989)

15. V. Percec and C.-S. Wang, *J. Macromol. Sci. Macromol. Chem.*, submitted

16. R. Rodenhouse, V. Percec and A. E. Feiring, *J. Polym. Sci. Polym. Lett. Ed.*, **28**, 345(1990); V. Percec, M. Lee and H. Jonsson, *J. Polym. Sci. Part A: Polym. Chem.*, **29**, 000(1991); H. Jonsson, V. Percec and A. Hult, *Polym. Bull.*, in press; V. Percec and M. Lee, *Macromolecules*, in press

17. C. G. Cho, B. A. Feit and O. W. Webster, *Macromolecules*, **23**, 1918(1990)

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