Polymer Bulletin 23, 463–470 (1990)

Polymer Bulletin

Synthesis and mesomorphic behavior of poly(methylsiloxane)s and poly(methylsiloxane-co-dimethylsiloxane)s containing oligooxyethylene spacers and mesogenic side groups

V. Percec and C.-S. Hsu*

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

SUMMARY

The synthesis and characterization of poly(methylsiloxanes)s and poly(methylsiloxane-co-dimethylsiloxane)s containing either bis(ethylene oxide) or tris(ethylene oxide) flexible spacers and either 4-methoxy-4'-hydroxybiphenyl a mixture containing a 1:1 ratio of 4-methoxy-4'-hydroxy-α-methylstilbene and 4-hydroxy-4'-methoxy-α-methylstilbene, or 4-[5-(4-methoxyphenyl)-1,3-dioxan-2-yl]phenol mesogenic groups, in all combinations, is presented. All polymers and copolymers display smectic mesomorphism. The dependence of phase transition temperatures on the spacer length and copolymer composition is described.

INTRODUCTION

Main chain and side chain liquid crystalline polymers containing flexible spacers which are not aliphatic are of both theoretical and practical interest (1-4). Spacers of different flexibility are useful in testing the spacer concept (5). So far, the only flexible spacer, other than paraffinic considered to some extent is based on oligooxyethylene segments (1). There are, however, a few results available on the use of oligodimethylsiloxanes (2), semifluorinated (6) and perfluorinated (7) flexible spacers.

We are presently investigating various synthetic avenues leading to host-guest liquid crystalline systems. So far, oligooxyethylenic flexible spacers (8-12) or macroheterocyclic ligands (13,14) have been used. Side chain liquid crystalline polymers containing oligooxyethylenic spacers represent a novel class of host-guest systems which is intermediate between podants and macroheterocyclics from a structural point of view, i.e., they are pseudo-crown-ethers (10).

The goal of this paper is to present the synthesis and characterization of liquid crystalline side chain poly(methylsiloxane)s and poly(methylsiloxane-co-dimethylsiloxane)s containing 4-methoxy-4'-hydroxybiphenyl, 4-methoxy-4'-hydroxy-α-methylstilbene, 4-hydroxy-4'-methoxy-α-methylstilbene and 4-[5-(4-methoxyphenyl)-1,3-dioxan-2-yl]phenol mesogenic groups and bis(ethylene oxide) and tris(ethylene oxide) based flexible spacers.

EXPERIMENTAL

Materials:

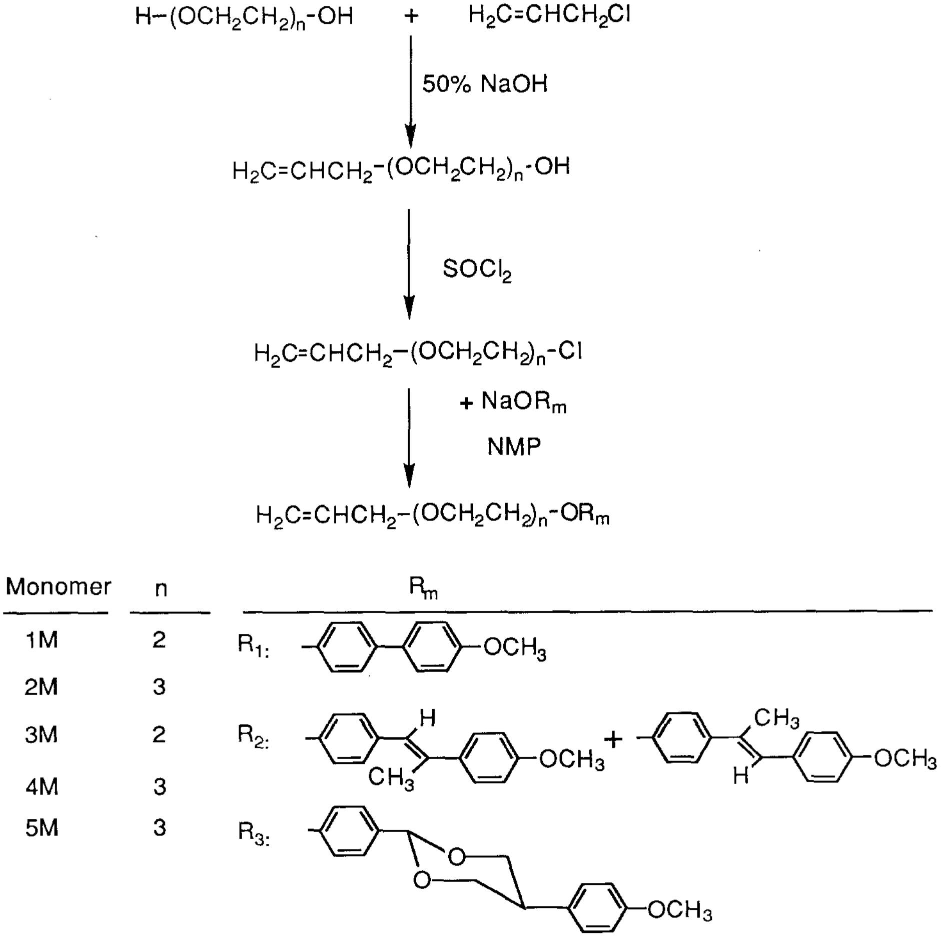
All reagents were purchased from commercial sources and were used as received or purified by standard methods. 4-Methoxy-4'-hydroxybiphenyl (8), 4-[5-(4-methoxyphenyl)-1,3-dioxan-2-yl]phenol (15) and a mixture containing a 1/1 molar ratio of 4-methoxy-4'-hydroxy-α-methylstilbene and 4-hydroxy-4'-methoxy-α-methylstilbene (16) were synthesized as described in previous publications. Poly(methylsiloxane)s and (methylsiloxane-co-dimethylsiloxane)s with different

---

*Present address: Institute of Applied Chemistry, National Ciao Tung University, 1001 Ta Hsuch Road, Hsinchu, Taiwan 300, Republic of China molecular weights were synthesized and characterized as described previously (17). Scheme I outlines the synthesis of monomers

Synthesis of 2-(2-Allyloxyethoxy)Ethanol and 2-[2-(2-Allyloxyethoxy)ethoxy]Ethanol.

Both compounds were prepared by the monoetherification of diethylene glycol and triethylene glycol with allyl chloride by a modified literature procedure (18,19). A representative example is presented below. A mixture of triethylene glycol (30 g, 200 mmol) and allyl chloride (4.07 ml, 56 mmol) in aqueous 50% sodium hydroxide (16 ml, 200 mmol NaOH) was heated at 100°C for 24 hr. The mixture was cooled, diluted with water and extracted with diethyl ether. The organic extracts were combined, dried over anhydrous magnesium sulfate, filtered and concentrated under vacuum. The remaining oil was distilled at 116-118°C/10 mm Hg, and further purified by column chromatography (silica gel, chloroform as eluent) to yield 3.5 g (37%) of monoallyl ether. ^{1}H-NMR (CDCl$_3$, TMS, δ, ppm): 3.66 (m , -C$\underline{H_2}$O, 8 protons), 4.03 (d, =CH-C$\underline{H_2}$-O-), 5.22 and 5.93 (m, C$\underline{H_2}$=C$\underline{H}$-).



Scheme I: Synthesis of Monomers

Synthesis of 2-(2-Allyloxyethoxy)Ethyl Chloride and 2-[2-(2-Allyloxyethoxy)ethoxy]Ethyl Chloride

Both compounds were synthesized by chlorination of the corresponding allyl ether alcohol with thionyl chloride. An example is presented below. 2-[2-(2-Allyloxyethoxy)ethanol] (3.5g, 18.4 mmol) was dissolved in dry methylene chloride (50 ml). Thionyl chloride (1.7 ml, 23 mmol) was added dropwise and the reaction mixture was stirred at room temperature for 2 hours. The methylene chloride and excess thionyl chloride were removed on a rotovapor and the residue was distilled at 97-99°C/12mm Hg to yield 2.8g (73%) 2-(2-allyloxyethoxy)ethyl chloride. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 3.66 (m, $-C\underline{H}_2O-$, 6 protons), 3.77 (t, $-C\underline{H}_2Cl$), 4.03 (d, $=CH-C\underline{H}_2-O-$), 5.22 and 5.93 (m, $C\underline{H}_2=C\underline{H}-$).

Synthesis of Olefinic Derivatives 1M-5M

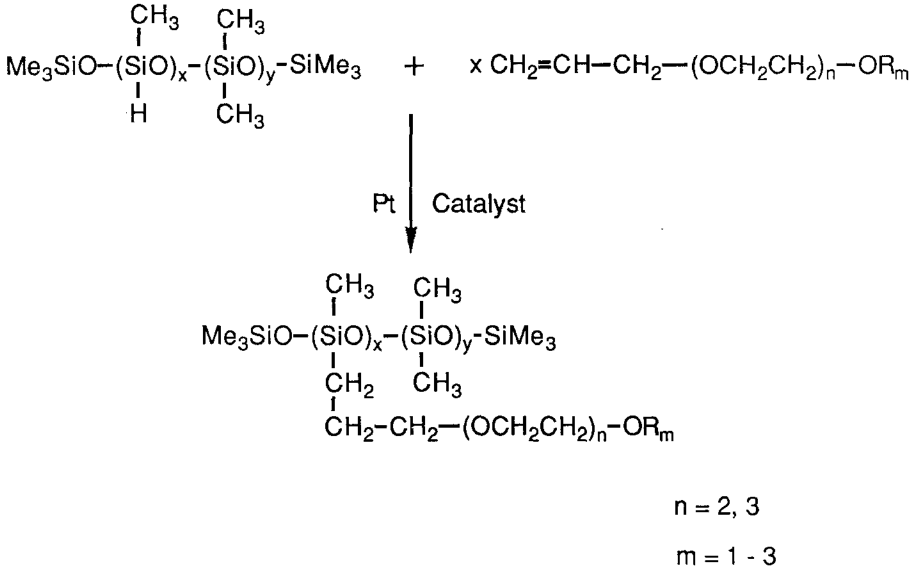
Compounds 1M to 5M were synthesized by the etherification of 4-methoxy-4'-hydroxybiphenyl (R_1), the 1/1 mixture of 4-methoxy-4'-hydroxy-α-methylstilbene and 4-hydroxy-4'-methoxy-α-methylstilbene (R_2), and 4-[5-(methoxyphenyl)-1,3-dioxan-2-yl]phenol (R_3) with either 2-(2-allyloxyethoxy)ethyl chloride or 2-[2-(2-allyloxyethoxy)ethoxy]ethyl chloride. An example is presented below. Freshly cut sodium (0.23 g, 10 mmol) was dissolved in absolute ethanol (50 ml). After the sodium was completely dissolved, 4-methoxy-4'-hydroxybiphenyl (2g, 10 mmol) was added to the reaction mixture. After ethanol was removed from the reaction mixture, dry N-methyl-2-pyrrolidinone (50 ml) was added to the residual sodium salt of 4-methoxy-4'-hydroxybiphenyl. When the sodium salt was completely dissolved, 2-[2-(2-allyloxyethoxy)ethoxy]ethyl chloride (2.29 g, 11 mmol) was added and the resulting mixture was stirred at 110 °C under a nitrogen atmosphere overnight. N-methyl-2-pyrrolidinone was removed by distillation and the residue was poured into water. The resulting precipitate was filtered, washed with dilute aqueous NaOH, water and dried under vacuum. The product was recrystallized from methanol to yield 3.0 g (81%) white crystals. Table I summarizes the melting transition(s) and ^{1}H-NMR chemical shifts of compounds 1M to 5M.

Table I: Characterization of Olefinic Derivatives 1M-5M

	m.p. (°C)		
Compound	T_1	T_2	200 MHz ^{1}H-NMR ($CDCl_3$, δ, ppm)
1M	87	-	3.62, 3.74, and 3.87 (t. 3, $-C\underline{H}_2O-$); 3.83 (s, $C\underline{H}_3O-$); 4.06 (d, $=\overset{|}{C}-C\underline{H}_2-O-$); 4.17 (t, $-C\underline{H}_2OPh$): 5.21 and 5.91 (m, $C\underline{H}_2=C\underline{H}-$); 6.94 and 7.43 (m, 8 aromatic protons)
2M	73	83	3.66 and 3.86 (m, 5 $-C\underline{H}_2O-$); 3.80 (s, $C\underline{H}_3O-$); 4.00 (d, $=\overset{|}{C}-C\underline{H}_2O-$); 4.13 (t, $-C\underline{H}_2OPh$); 5.19 and 5.89 (m, $C\underline{H}_2=C\underline{H}-$); 6.94 and 7.46 (m, 8 aromatic protons)
3M	46	-	2.26 (s, $C\underline{H}_3-\overset{|}{C}=$); 3.66, 3.76 and 3.90 (3t, 3, $-C\underline{H}_2O-$); 4.05 (d, $=C\underline{H}-C\underline{H}_2O-$); 4.17 (t, $-C\underline{H}_2OPh$); 5.25 and 5.94 (m, $C\underline{H}_2=C\underline{H}-$); 6.73 (s, $Ph-C\underline{H}=$): 6.90 to 7.48 (m, 8 aromatic protons)
4M	35	-	2.26 (s, $C\underline{H}_3-C=$); 3.66 and 3.89 (m, 5-$C\underline{H}_2O-$); 3.84 (s, $C\underline{H}_3O-$); 4.04 (d, $=C\underline{H}-C\underline{H}_2O-$); 4.15 (t,$-C\underline{H}_2OPh$); 5.25 and 5.94 (m, $C\underline{H}_2=C\underline{H}-$); 6.73 (s, $Ph-C\underline{H}=$); 6.90 to 7.48 (m, 8 aromatic protons)
5M	63	-	3.31 (m,- $\begin{smallmatrix}C\\C\end{smallmatrix}{>}C\underline{H}$-); 3.63 to 4.34 (m, 7 $-C\underline{H}_2O-$); 3.80 (s, $C\underline{H}_3O-$); 5,22 and 5.91 (m, $C\underline{H}_2=C\underline{H}-$); 5.53 (s, $-\underline{H}C\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}$ -); 6.87 to 7.46 (m, 8 aromatic protons)

Synthesis of Poly(methylsiloxane)s and of Poly(methylsiloxane-co-dimethylsiloxane)s

Both polymers and copolymers were synthesized by the hydrosilation of the poly(methylsiloxane) with the olefinic derivatives 1M to 5M in the presence of a Pt catalyst (Scheme II). Experimental details concerning the synthesis and purification of these polymers are identical to those used in the preparation of other liquid crystalline polysiloxanes (17-20).



Scheme II: Synthesis of Polymers

Characterization of Polymers and Intermediary Derivatives

All intermediary derivatives and polymers were characterized by a combination of HPLC, GPC, DSC, and thermal optical polarized microscopy according to standard procedures used in our laboratory (17,20). All purities are higher than 99% and are therefore not reported.

RESULTS AND DISCUSSION

Table II summarizes the phase behavior of all polymers and copolymers. The first column provides a notation based on the parameters n, m and R_m from Scheme I and x and y from Scheme II. Most of the homopolymers 1P to 5P present two thermal transition temperatures, T_1 and T_i. Some also display a glass transition temperature. In the case of 1P to 4P, T_1 seems to be a melting transition. Above T_1 all polymers display a smectic mesophase. Both T_g and T_i are lower for polymers based on the tris(ethylene oxide) spacer. Increasing the spacer length from bis(ethylene oxide) to tris(ethylene oxide) can decrease the T_i transition to below the T_g of the corresponding polymers (see 3P and 4P in Table II). Both T_1 and T_i of 5P are associated with liquid crystalline phase transitions (Figure 1).

Table II: Thermal Transitions and Thermodynamic Parameters of Polysiloxanes

Polymer					Thermal Transitions (^{o}C), and Enthalpy Changes, ΔH(kcal/mru)[a]				
					Heating			Cooling	
No.	x	y	n	R_m[b]	T_g	$T_1(\Delta H_1)$	$T_i(\Delta H_i)$	$T_i(\Delta H_i)$	$T_1(\Delta H_1)$
1P	80	0	2	R1	33	94(--)	114(1.05)[c]	104(1.36)[c]	92(--)
2P	80	0	3	R1	-	86(0.11)	103(2.34)	94(2.25)	79(0.10)
3P	80	0	2	R2	-	42(2.13)	52(0.03)	27(2.16)	-- (--)
4P	80	0	3	R2	-19	- (--)	30(0.72)	12(0.73)	-- (--)
5P	80	0	3	R3	-3	67(--)	76(1.60)[c]	71(1.60)[c]	60(--)
6P	10	20	2	R1	-91	- (--)	88(2.19)	80(2.21)	-- (--)
7P	10	20	3	R1	-63	- (--)	82(2.75)	72(2.73)	-- (--)

a) mru = mole of repeat units; b) x, y, n and R_m according to Schemes I and II; c) overlapped transitions, $\Delta H_i = \Delta H_j + \Delta H_1$.

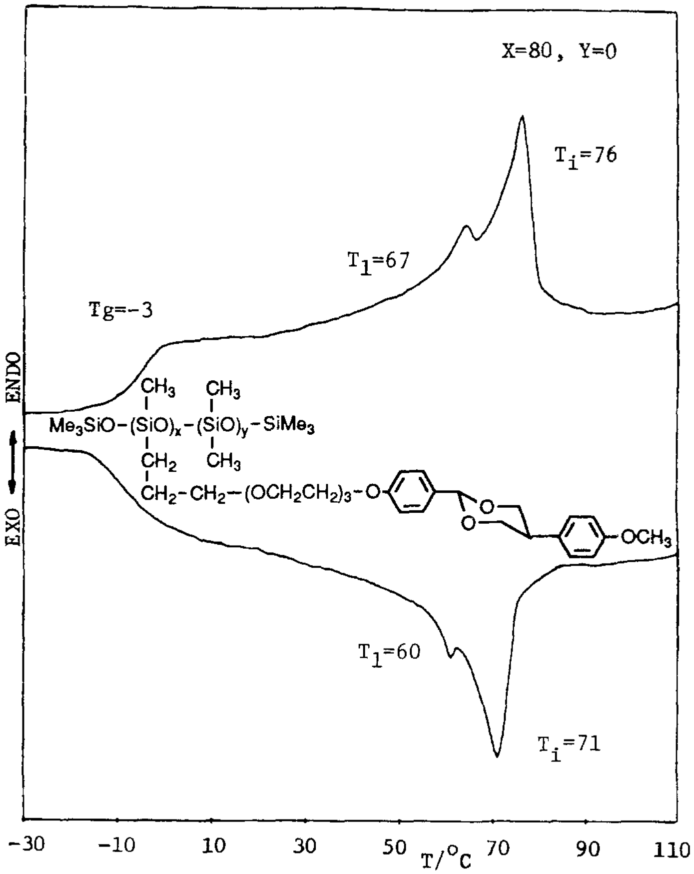


Figure 1: Second heating and cooling DSC scans (20 °C/min) of polymer 5P.

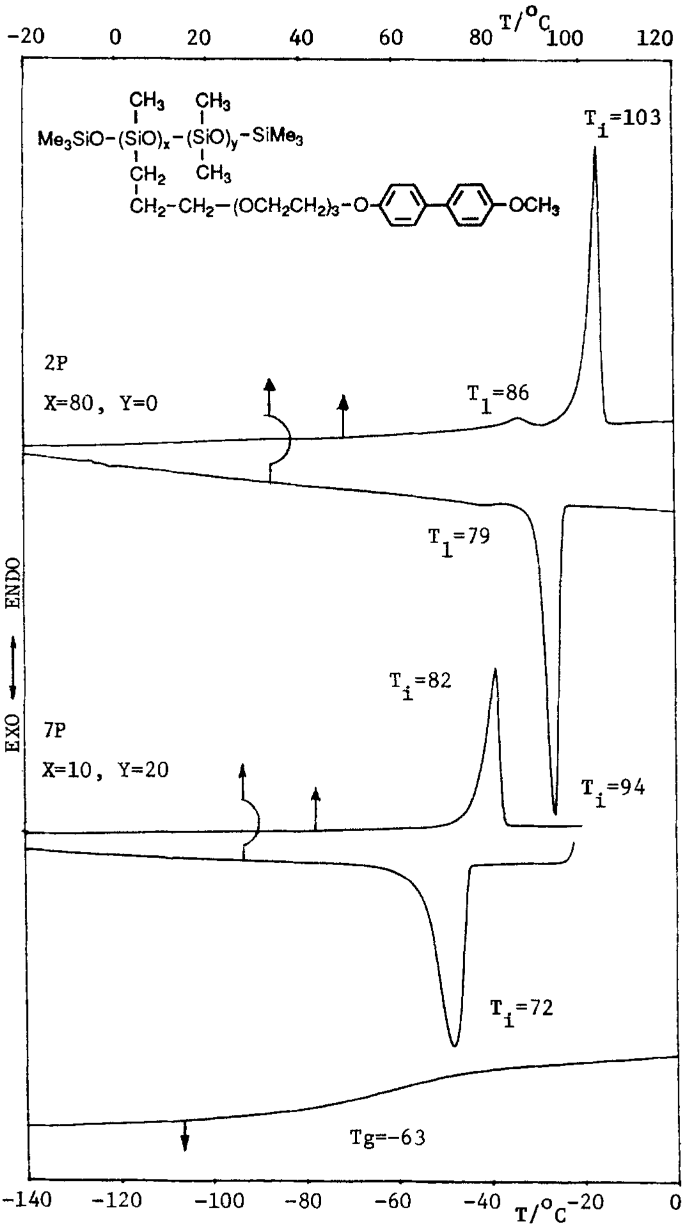


Figure 2: Second heating and cooling DSC scans (20 °C/min) of polymers 2P and 7P.

Figure 2 presents representative DSC traces of 2P and 7P. Copolymer 7P displays a lower T_i than the corresponding homopolymer 2P, and no T_1 transition. The T_g of 7P is very low. The same trend is observed by comparing homopolymer 1P and copolymer 6P (Table II). In contrast to copolysiloxanes containing aliphatic flexible spacers which display two glass transition temperatures (17,20), copolysiloxanes 6P and 7P display a single broad glass transition temperature (Table II, Figure 2). A representative smectic texture displayed by 2P is presented in Figure 3.

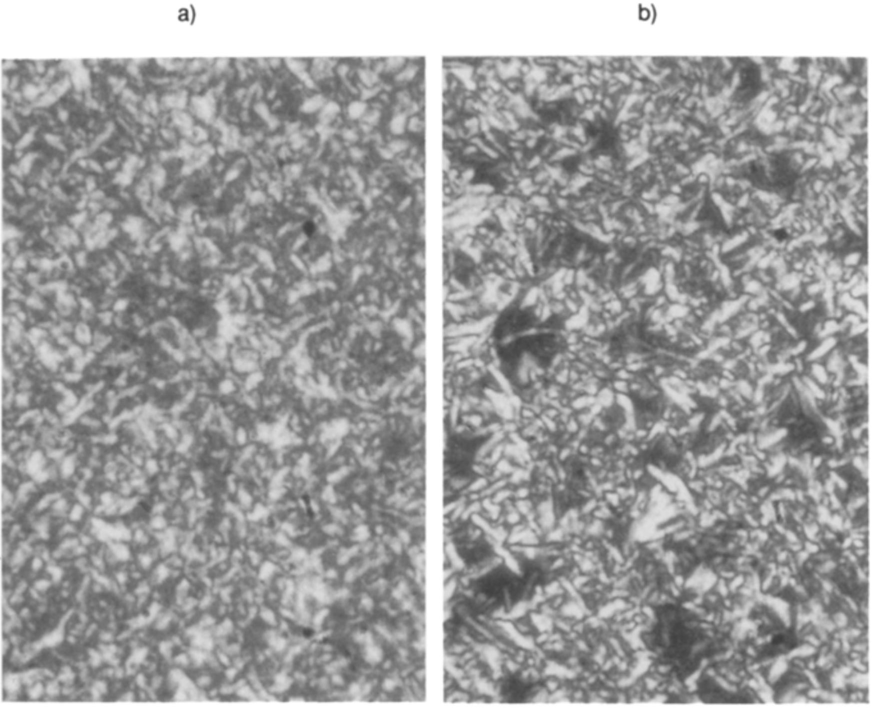


Figure 3: **Optical polarized micrographs of the textures displayed by 2P upon cooling from isotropic phase: a) 98.4 °C after 1 hour; b) 98.4 °C after 12 hours.**

ACKNOWLEDGEMENT

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

REFERENCES

1) V. Percec and C. Pugh, in "Side Chain Liquid Crystal Polymers", C.B. McArdle Ed., Chapman and Hall, New York, 1989, p. 30.
2) M. Engel, B. Hisgen, R. Keller, W. Kreuder, B. Reck, H. Ringsdorf, H.W. Schmidt and P. Tschirner, *Pure Appl. Chem.*, 57, 1009(1985).
3) H. Ringsdorf, B. Schlarb and J. Venzmer, *Angew. Chem. Int. Ed. Engl.*, 27, 113(1988).
4) C. Noel, *Makromol. Chem., Mocromol. Symp.*, 22, 95(1988).
5) W. Volksen, D. Y. Yoon and P. M. Cotts, *Macromolecules*, 22, 3846(1989).
6) V. Percec, D. Tomazos, and A.E. Feiring, *Polymer*, submitted.
7) V. Percec, Y. Tsuda and A.E. Feiring, to be published.

8) J.M. Rodriguez-Parada and V. Percec, *J. Polym. Sci. Part A: Polym. Chem.*, 24, 1363(1986).
9) V. Percec, J.M. Rodriguez-Parada and C. Ericsson, *Polym. Bull.*, 17, 347(1987).
10) V. Percec, *Makromol. Chem., Macromol. Symp.*, 13/14, 397(1988).
11) C.J. Hsieh, C.S. Hsu, G.H. Hsiue and V Percec, *J. Polym. Sci. Part A: Polym. Chem.*, 28, 425(1990).
12) T.D. Shaffer and V. Percec, *J. Polym. Sci. Part A: Polym. Chem.*, 25, 2755(1987).
13) V. Percec and R. Rodenhouse, *Macromolecules*, 22, 2043(1989).
14) V. Percec and R. Rodenhouse, *Macromolecules*, 22, 4408(1989).
15) C. S. Hsu, J. M. Rodriguez-Parada and V. Percec, *Makromol. Chem.*, 188, 1017(1987).
16) V. Percec, C.S. Hsu and D. Tomazos, *J. Polym. Sci. Part A: Polym. Chem.*, 26, 2047(1988).
17) V. Percec and B. Hahn, *Macromolecules*, 22, 1588(1989).
18) T. Gibson, *J. Org. Chem.*, 45, 1095(1980).
19) G. Coudert, M. Mpassi, G. Guillaumet and C. Selve, *Synth. Commun.*, 16, 19(1986).
20) B. Hahn and V. Percec, *Macromolecules*, 20, 2961(1987).

Accepted February 9, 1990 K