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Coleen Pugh; Stephen Arehart; Hui Liu; Ramasubramanian Narayanan

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NEW ARCHITECTURES FOR SIDE CHAIN LIQUID CRYSTALLINE POLYMERS WITH CHIRAL SMECTIC C MESOPHASES

COLEEN PUGH,* STEPHEN AREHART, HUI LIU, and RAMASUBRAMANIAN NARAYANAN

Department of Chemistry
The University of Michigan
Ann Arbor, Michigan 48109-1055

ABSTRACT

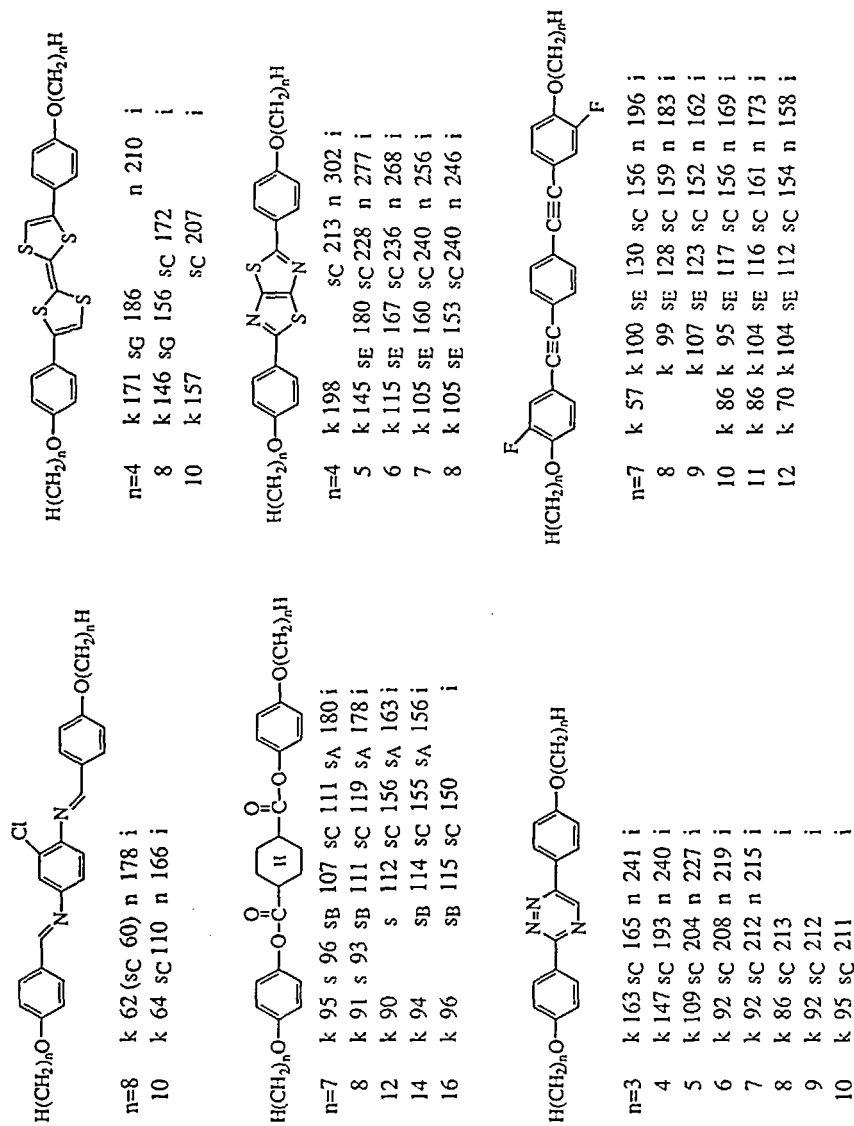
All attempts at synthesizing side chain liquid crystalline polymers (SCLCPs) with chiral smectic C (s_C^*) mesophases simply functionalize one terminal group of the mesogen with a chiral substituent and attach the other terminus to the polymer backbone through a spacer. If a s_C^* mesophase is observed, it is usually in the less desirable $s_C^*-s_A$ phase sequence. We propose that SCLCPs with laterally attached (vs terminally attached) mesogens offer an ideal architecture for obtaining s_C^* mesophases. This is because *extended* mesogens *symmetrically* disubstituted with *long n*-alkoxy groups can be attached to the polymer backbone through a *chiral* spacer. Thus, mesogens which typically form the desirable s_C^*-n phase sequence can be used, and the chiral group can be introduced at the center of the mesogen which should result in high values of spontaneous polarization. We are not only using mesogens which exhibit s_C^*-n phase sequences, but are also attempting to induce smectic layering into laterally attached systems which typically form nematic mesophases by electron-donor-acceptor interactions and immiscible hydrocarbon/fluorocarbon components. Smectic layering was successfully induced in 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes when the *n*-alkoxy substituents were terminated with perfluorinated segments.

INTRODUCTION

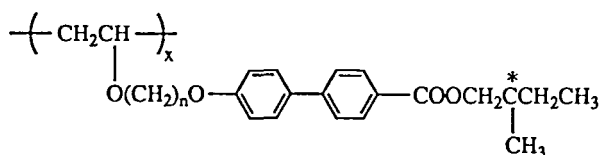
The elementary structural principles of side chain liquid crystalline polymers (SCLCPs) are beginning to be elucidated [1]. Nevertheless, it is still difficult to design polymers with predetermined mesophases, although most SCLCPs exhibit either nematic (n) or smectic A (s_A) mesophases. There is theoretical interest in SCLCPs which form uncommon and more ordered mesophases, such as s_F , s_G , and s_H . In addition, materials which form chiral smectic C (s_C^*) mesophases are highly sought after because s_C^* mesophases are ferroelectric and spontaneously polarize if the helix is unwound [2]. The potential applications of SCLCPs take advantage of their ability to freeze an anisotropic alignment below the glass transition coupled with the fluidity of the mesophase. While SCLCPs generally cannot compete with low molar mass liquid crystals (LMMLCs) for the same applications due to their higher viscosities, ferroelectric mesophases of polymers are fluid and therefore have fast switching times comparable to those of LMMLCs.

Although the correlation of the structure of SCLCPs to their thermotropic behavior is limited, there is important information from the structure/property relationships of LMMLCs which can be used in designing polymers with s_C^* mesophases. The following structure/property relationships should be considered. First, the highest absolute values of the spontaneous polarization are obtained the closer the chiral center is to the mesogenic core, the closer the chiral carbon is to the center of the molecule, and the stronger the dipole is at a given chiral carbon [2]. Second, materials having the s_C^* -n phase sequence possess much larger absolute values of spontaneous polarization compared to materials having the s_C^* - s_A sequence [2]. In addition, a review of the literature on LMMLCs demonstrates that s_C mesophases are common for extended mesogens which are symmetrically disubstituted with long *n*-alkoxy substituents. Some examples of LMMLCs which form s_C mesophases are shown in Scheme 1, and they include 2-chloro-*N,N'*-bis[4''-*n*-alkoxybenzylidene]phenylene-1,4-diamines [3], *trans*-1,4-bis[4'-*n*-alkoxyphenyl]cyclohexane dicarboxylates [3], 3,6-bis[4'-*n*-alkoxyphenyl]-1,2,4-triazines [3], 2,6-bis[4'-*n*-alkoxyphenyl]-1,4,5,8-tetrathiafulvalenes [3], 2,5-bis[4'-*n*-alkoxyphenyl]thiazolo-[5,4-*d*]thiazoles [3], and 1,4-bis[(3',3''-difluoro-4',4''-di-*n*-alkoxyphenyl)ethynyl]benzenes [4].

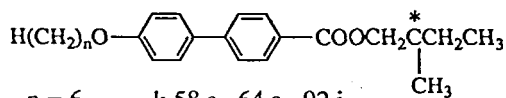
Nevertheless, almost all SCLCPs containing chiral substituents are prepared with the chiral center in the terminal group of the mesogen, with the other terminus attached to the polymer backbone through various spacer lengths. If a s_C^* mesophase is observed, it is usually in the less desirable s_C^* - s_A phase sequence. This is not surprising considering that the mesogens used have not corresponded to LMMLCs with s_C phases or the desired s_C -n-i phase sequence. For example, the low molar mass analogues of the poly(vinyl ether)s [5] containing (*S*)-(-)-2-methylbutyl-4-*n*-alkoxybiphenyl-4'-carboxylate display s_B - s_A -i and monotropic (s_C)- s_A -i phase sequences as shown in Scheme 2 [3]. The low molar mass analogues of the polymethacrylates [6] containing chiral cinnamic acid phenylesters exhibit n-i and s_C - s_A -i phase sequences [3]. Perhaps the most successful architecture so far for obtaining the s_C -n-i sequence is that of combined liquid crystalline polymers with both main-chain and side-chain mesogenic components (Scheme 3) [7]. However, it is impossible to obtain well-defined polymers approaching Poisson distributions of molecular weight ($M_w/M_n \sim 1.0$) since this architecture is prepared by step polymerizations.



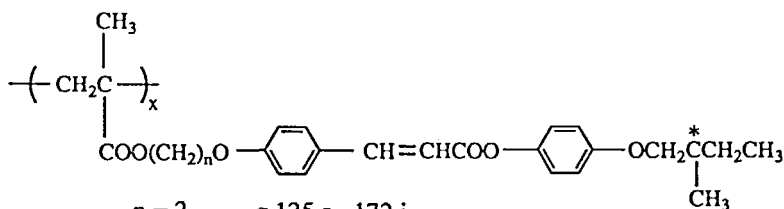
SCHEME 1.



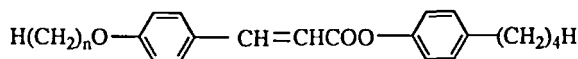
n = 6 g 30 s 58 s_A 110 i
 n = 11 g 11 k 62 (s 26 s_C* 53) s_A 123 i



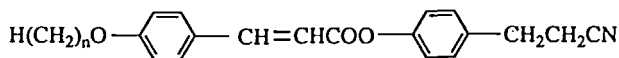
n = 6 k 58 s_B 64 s_A 92 i
 n = 7 k 62 (s_C* 59) s_A 89 i
 n = 10 k 54 (s_C* 49) s_A 82 i



n = 2 g 125 s_A 172 i
 n = 6 g 50 k 92 s_A 172 i
 n = 11 g 35 k 65 s_C* 115 s_A 142 i

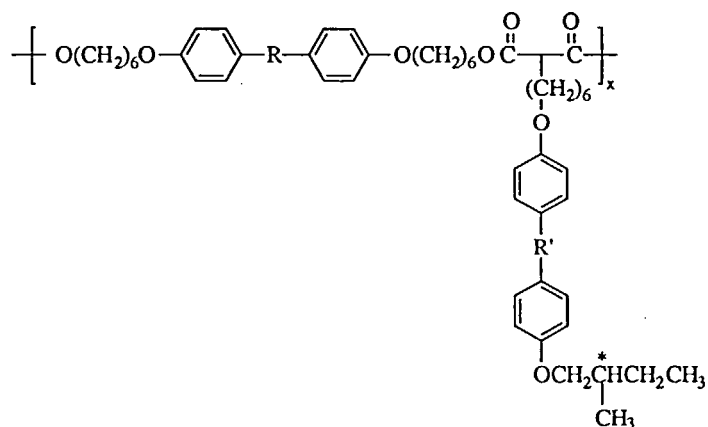


n = 1 k 82 n 93 i
 n = 5 k 96 n 102 i
 n = 7 k 65 s 86 n 111 i



n = 2 k 114 n 124 i
 n = 6 k 72 n 109 i
 n = 10 k 72 (s_C 58) s_A 109 n 109.5 i
 n = 12 k 82 (s_C 58) s_A 107 i

SCHEME 2.



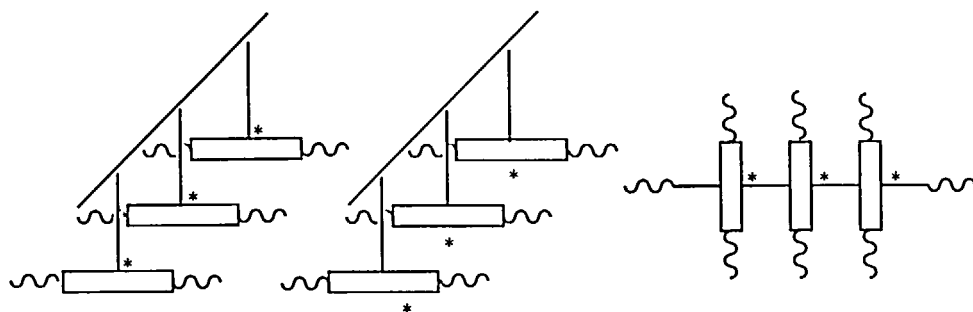
R	R'	
-N=N-	--	k 108 s _C * 115 n* 128 i
--	-N=N-	k 130 s _C * 136 i
-N=N-	-N=N-	k 107 s _C * 111 n* 133 i
-N=N-, O	--	g 20 s _C * 100 n* 128 i

SCHEME 3.

In addition, the combined LCPs have high viscosities and tend to crystallize rather than form a glass which can freeze in the mesophase alignment.

NEW ARCHITECTURES

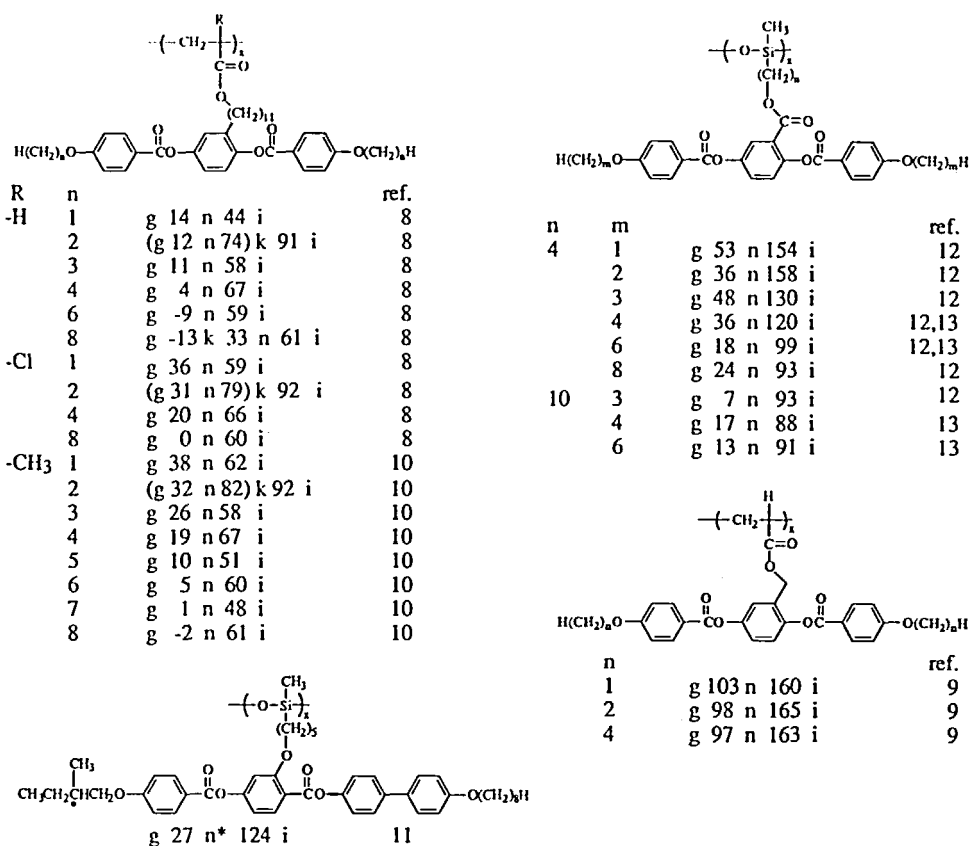
Since s_C mesophases are common for symmetrically disubstituted extended mesogens with long *n*-alkoxy substituents, a more rational design for polymers exhibiting s_C mesophases would be to incorporate this type of mesogen using either of the two architectures shown in Scheme 4, in which the chiral group is either in



SCHEME 4.

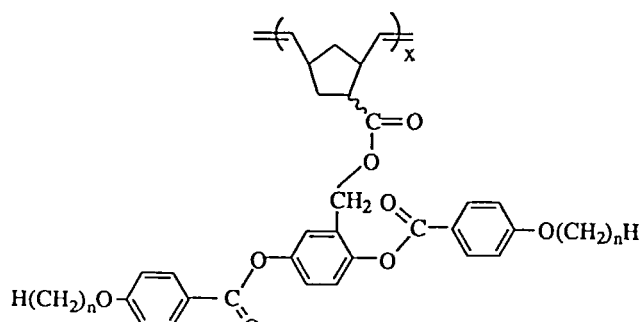
the spacer or laterally attached at the center of the mesogen. This paper will concentrate on SCLCPs with laterally attached mesogens. However, it is commonly believed that SCLCPs with laterally attached mesogens are capable of forming only nematic mesophases. Although almost all laterally attached SCLCPs prepared to date exhibit only nematic mesophases, their mesogens correspond to LMMLCs which show little tendency to organize into layers. For example, the poly(acrylate)s [8, 9], poly(chloroacrylate)s [8], poly(methacrylate)s [10], and poly(methylsiloxane)s [12, 13] shown in Scheme 5, and the polynorbornenes shown in Table 1 [14], are based on 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]-1-alkylbenzene mesogens. Table 2 demonstrates that both 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes and 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]undecylbenzenes do not exhibit smectic mesophases [3].

Two polymers with laterally attached mesogens which do exhibit a smectic mesophase are shown in Table 3 [15]. Leube and Finkelmann were successful in inducing smectic A mesophase formation in polymethacrylates containing laterally attached bis[(4'-*n*-alkylcyclohexylcarboxyl)oxy]naphthyl mesogens by increasing the anisotropy of polarizability perpendicular to the long axis of the mesogen. These polymers therefore resemble conventional SCLCPs with terminally attached mesogens, but with bulky nonpolar lateral substituents. In contrast, we are taking



SCHEME 5.

TABLE 1. Molecular Weight and Phase Transitions of Polynorbornenes with Laterally Attached 2,5-Bis[(4'-*n*-alkoxybenzoyl)oxy]benzyl Mesogens [14]



<i>n</i>	X_n	$M_n \times 10^{-3}$	PDI	Phase transitions, °C
1	5.1	2.7	1.16	g 79 n 131 i
1	8.2	4.3	1.20	g 90 n 146 i
1	14	7.2	1.12	g 91 n 155 i
1	39	21	1.13	g 97 n 163 i
1	45	24	1.13	g 98 n 164 i
1	100	53	1.16	g 97 n 163 i
2	32	18	1.19	g 92 n 172 i
3	44	26	1.24	g 83 n 140 i
4	23	14	1.17	g 73 n 138 i
5	45	29	1.18	g 60 n 123 i
6	66	44	1.24	g 56 n 126 i

the three approaches shown in Scheme 6 to induce smectic layering in SCLCPs with laterally attached mesogens. First, we are using mesogens which exhibit the desired s_C - n - i phase sequence such as the 1,4-bis[(3',3''-difluoro-4',4''-di-*n*-alkoxyphenyl)ethynyl]benzenes [4]. Alternatively, the mesogens may be forced into a layer alignment by incorporating *n*-alkoxy substituents terminated with perfluorinated segments. This is based on the observation that chain molecules containing hydrocarbon and fluorocarbon segments of at least 6 to 8 carbons tend to organize in layered structures due to the incompatibility of the two segments [16]. As exemplified by the compounds shown in Scheme 7, diblock $H(CH_2)_n(CF_2)_mF$ and triblock $F(CF_2)_m(CH_2)_n(CF_2)_mF$ molecules with $4 \leq n \leq 14$ and $m \geq 6$ undergo solid-solid transitions into a smectic mesophase before melting into an isotropic state.

Since there is greater interaction between the mesogens in a smectic vs nematic alignment, the third approach toward inducing smectic layering will be to copolymerize one monomer containing an electron-rich mesogen with a second monomer containing an electron-poor mesogen. Although the donating and accepting groups are not conjugated to the polymerizable double bond and therefore do not affect their frontier orbitals, the resulting copolymers may tend toward alternation if

TABLE 2. Thermotropic Behavior of Laterally Substituted 1,4-Bis[(4'-*n*-alkoxybenzoyl)oxy]benzenes [3]

R	<i>n</i>	
-H	1	k 217 (s 178) n 301 i
-CH ₃	1	k 166 n 252 i
	2	k 187 n 248 i
	3	k 138 n 209 i
	4	k 115 n 206 i
	5	k 90 n 178 i
	6	k 88 n 173 i
-(CH ₂) ₁₁ H	1	k 82 (n 58) i
	2	k 121 (n 81) i
	3	k 89 (n 56) i
	4	k 79 (n 71) i
	5	k 76 (n 62) i
	6	k 71 (n 69) i
	7	k 68 n 68 i
	8	k 52 n 72 i
	9	k 54 n 68 i

propagation involves an electron-donor-acceptor (EDA) complex in addition to the individual monomers [17]. Mesogenic comonomer pairs capable of forming EDA interactions have not been copolymerized previously; however, low molar mass electron acceptors have been added to polymers containing disc-like mesogens in order to induce a discotic mesophase or to stabilize the mesophase and increase its order [18]. In addition, smectic mesophases have been induced in mixtures of low molar mass nematic donors and acceptors [19]. EDA interactions also induce increased order and even miscibility in polymer blends [20].

MODEL SYSTEMS

Ideally, any new SCLCP will be synthesized by a living technique in which the molecular weight dependence of the thermal transitions can be reliably established, and in which the influence of polydispersity is minimized. In this case the effect of a single structural variable on the polymer's thermotropic behavior can be determined. The polynorbornenes shown in Table 1 are the most well-defined SCLCPs prepared to date with laterally attached mesogens. Both the molecular weight depen-

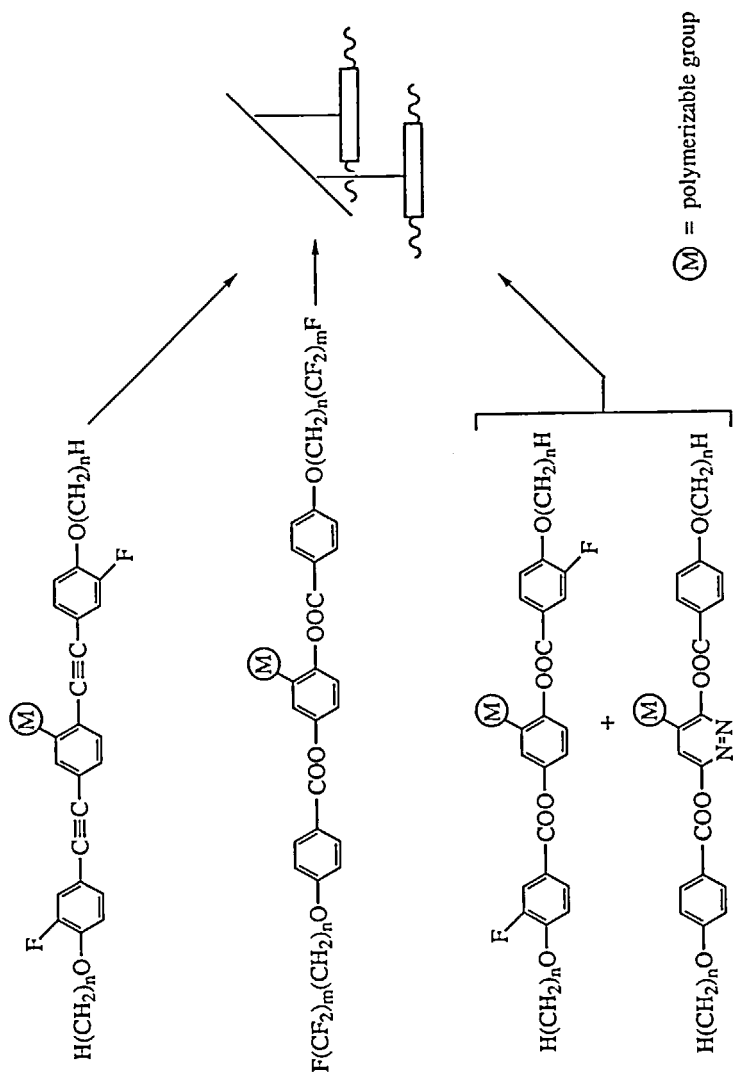
TABLE 3. Thermotropic Behavior of Poly(methacrylate)s Containing Bis[(4'-*n*-alkylcyclohexylcarboxyl)oxy]naphthyl Mesogens [15]

<i>n</i>		
2	g 29	n 49 i
4	g 30	<i>s</i> _A 45 n 50 i
6	g 30	<i>s</i> _A 47 n 53 i

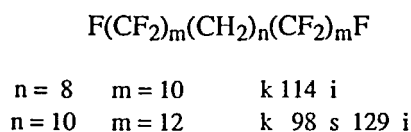
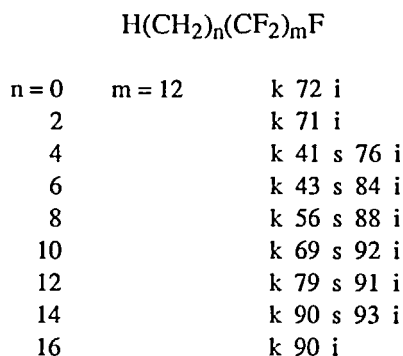
dence of the phase transitions and the effect of the length of the *n*-alkoxy substituents have been determined [14]. That is, both the glass and *n*-*i* transition temperatures become independent of molecular weight at approximately 25 repeat units. The glass transition and isotropization temperatures decrease with increasing *n*-alkoxy length. Isotropization decreases in an odd-even alternation, with the even-membered substituents having broader and more stable mesophases than the odd-membered substituents. Since the basic structure/property relationships of these polynorbornenes have already been established, we will use analogous polymers to test the routes shown in Scheme 6 for inducing smectic layering, particularly *s*_C mesophase formation, in SCLCPs with laterally attached mesogens. This first requires synthesis of the corresponding low molar mass model compounds.

The 1,4-bis[3',3''-difluoro-4',4''-di-*n*-alkoxyphenyl]benzenes with *n* = 1-6 were prepared by the one pot, phase transfer, Pd(0)/Cu(I) catalyzed, three-step coupling of 1,4-diodobenzene with 2-methyl-3-butyn-2-ol and the appropriate 1-bromo-3-fluoro-(4-*n*-alkoxy)benzene described previously [4]. This completes the series for *n* = 1-12. The preliminary characterization of the thermotropic behavior of the new compounds in this series is presented in Table 4, along with the phase behavior of the *n* = 7-12 compounds. Table 4 demonstrates that the *s*_C-*n*-*i* phase is exhibited with *n* = 6-12.

We initially attempted to synthesize the perfluorinated 1,4-bis[4'-*n*-(alkoxybenzoyl)oxy]benzene model compounds by the route shown in Scheme 8 in which the ethyl (4-*n*-alkenyloxy)benzoates were prepared by Williamson etherification of ethyl 4-hydroxybenzoate with the corresponding bromoolefin. Perfluorinated segments were introduced by free-radical addition of perfluorohexyl or per-



SCHEME 6.

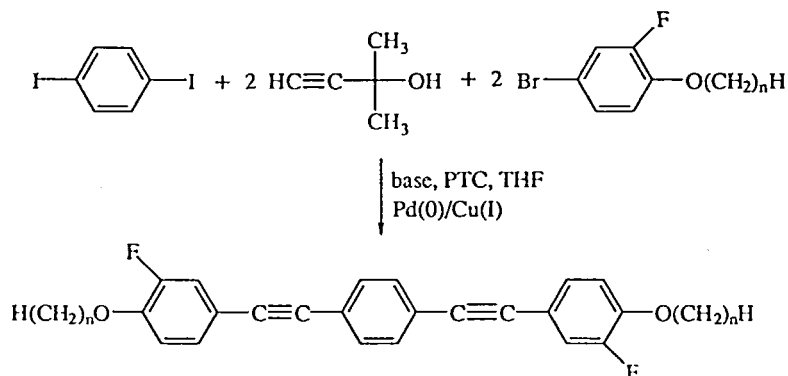


SCHEME 7.

fluorooctyl iodide across the double bond, followed by reduction of the iodide using tributyltin hydride. Unfortunately, saponification of the esters yielded semifluorinated benzoic acids which were only marginally reactive to chlorination using PCl_5 , and which were insoluble in most solvent systems due to the disparate solubilities of the hydrocarbon segment, the fluorocarbon segment, and the carboxylic acid group. A more profitable synthetic route to the model compounds is outlined in Scheme 9. In this case the ethyl (4-*n*-alkenyloxy)benzoates were saponified and coupled with hydroquinone or methylhydroquinone prior to introduction of the perfluorinated segment. Although addition of the perfluoroalkyl iodides to 1,4-bis[4'-*n*-(alkenyloxybenzoyl)oxy]benzenes ($\text{R} = \text{H}$) yielded insoluble products, the 2,5-bis[4'-*n*-(alkenyloxybenzoyl)oxy]toluenes ($\text{R} = \text{CH}_3$) remained in solution and could be reduced.

The thermotropic behaviors of the resulting 2,5-bis{[(4'-*n*-(perfluoroalkyl)alkoxybenzoyl)oxy]toluenes are summarized in Table 5. Comparison of the data in Tables 2 and 5 demonstrates that termination of the *n*-alkoxy substituents with perfluorinated segments induces smectic layering. That is, whereas the 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes form nematic mesophases, the 2,5-bis{[(4'-*n*-(perfluoroalkyl)alkoxybenzoyl)oxy]toluenes exhibit what appears to be a s_A - s_C phase sequence. Although the temperature range of the s_A mesophases are relatively narrow (4–9°C), that of the s_C mesophases are quite broad (78–99°C). Termination of the *n*-alkoxy substituents with perfluorohexyl and perfluorooctyl groups has little effect on either the melting or isotropization temperatures compared to the nonperfluoroalkyl-terminated 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes. Smectic C and/or s_A

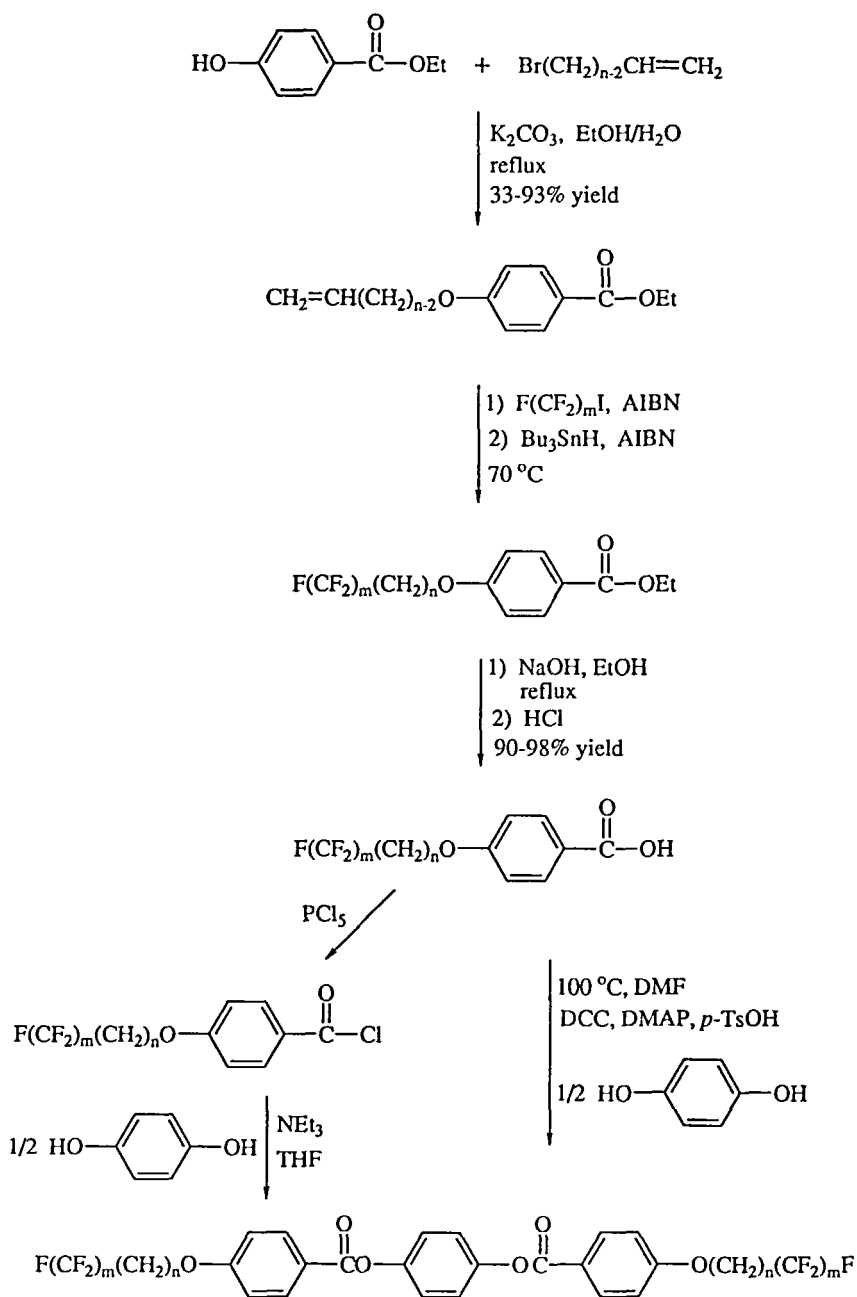
TABLE 4. Thermotropic Behavior of 1,4-Bis[(3',3''-difluoro-4',4''-di-*n*-alkoxyphenyl)ethynyl]benzenes



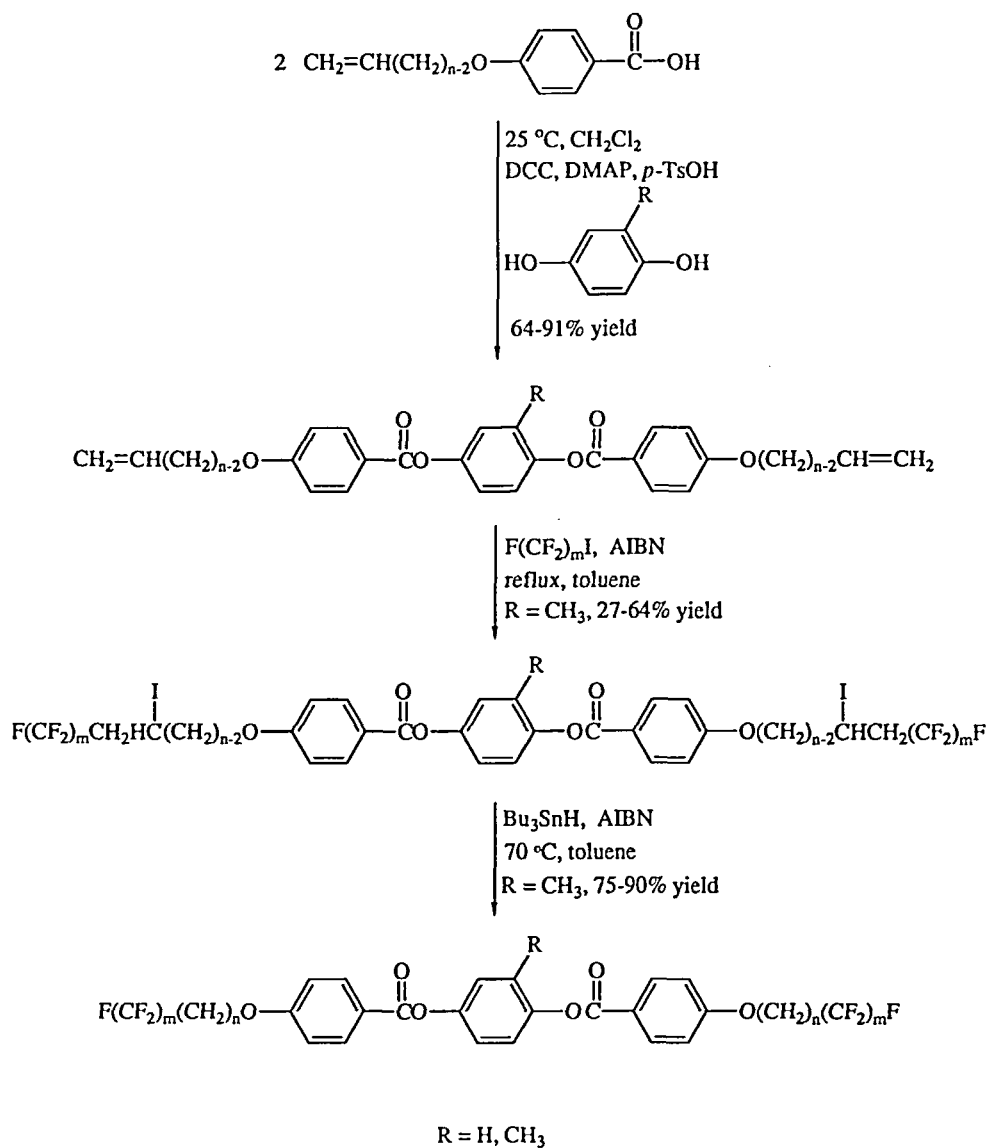
<i>n</i>	Phase transitions, °C					Ref.
1	k 192				n 263 i	Current
2	k 188				n 256 i	Current
3	k 134		s_E 179		n 226 i	Current
4	k 84		s_E 167		n 225 i	Current
5	k 122		s_E 152		n 205 i	Current
6	k 112		s_E 132	s_C 148	n 198 i	Current
7	k 57	k 100	s_E 130	s_C 156	n 196 i	4
8		k 99	s_E 128	s_C 159	n 183 i	4
9		k 107	s_E 123	s_C 152	n 162 i	4
10	k 86	k 95	s_E 117	s_C 156	n 169 i	4
11	k 82	k 104	s_E 116	s_C 161	n 173 i	4
12	k 70	k 104	s_E 112	s_C 154	n 158 i	4

mesophases were also formed by other LMMLCs containing a perfluoroalkyl substituent [21].

Finally, the clearing and decomposition temperatures of 3,6-bis[(4'-*n*-alkoxybenzoyl)oxy]pyridazines are summarized in Table 6. These model compounds were prepared by esterification of maleic hydrazide. The model compounds with $n = 1-3$ produce extremely viscous melts which crystallize slowly upon cooling. The melt viscosity decreases as the *n*-alkoxy chain length increases; those compounds with $n = 4-10$ form what appears to be a s_E mesophase upon cooling from the isotropic melt. At this time, only the clearing temperatures are reported because it is not yet clear whether or not the compounds are thermally stable in the chemical structures drawn.

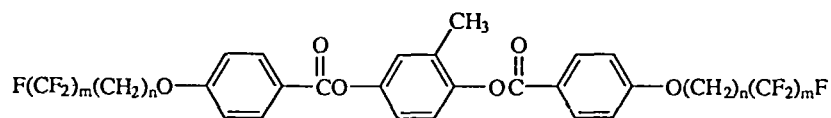


SCHEME 8.



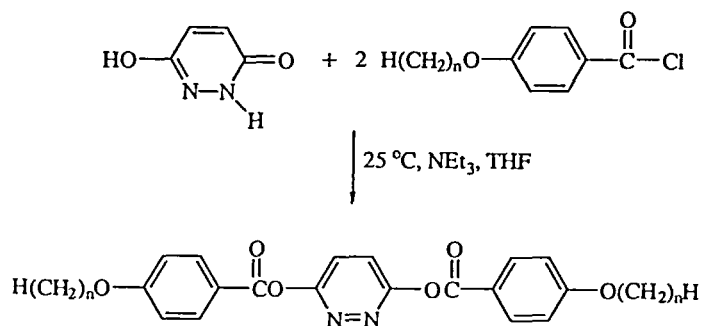
SCHEME 9.

TABLE 5. Thermotropic Behavior of
2,5-Bis{[4'-*n*-(perfluoroalkyl)alkoxybenzoyl]oxy}toluenes



<i>n</i>	<i>m</i>	Phase transitions, °C			
4	6	k 106	<i>s_C</i> 205	<i>s_A</i> 214 i	
5	6	k 101	<i>s_C</i> 197	<i>s_A</i> 207 i	
6	6	k 99	<i>s_C</i> 197	<i>s_A</i> 203 i	
4	8	k 130	<i>s_C</i> 218	<i>s_A</i> 226 i	
5	8	k 121	<i>s_C</i> 214	<i>s_A</i> 221 i	
6	8	k 128	<i>s_C</i> 211	<i>s_A</i> 217 i	
8	8	k 124	<i>s_C</i> 201	<i>s_A</i> 205 i	

TABLE 6. Thermotropic Behavior of
3,6-Bis[(4'-*n*-alkoxybenzoyl)oxy]pyridazines



<i>n</i>	Yield, %	Clearing temperature, °C	Decomposition temperature, °C	% Weight loss
1	48	167	269	74
3	54	168	325	86
4	44	175	350	76
5	46	168	341	82
6	64	164	344	83
7	60	146	350	83
8	64	154	348	93
9	36	156	350	91
10	45	146	350	77

ACKNOWLEDGMENT

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REFERENCES

- [1] (a) V. Percec and C. Pugh, in *Side Chain Liquid Crystalline Polymers* (C. B. McArdle, Ed.), Chapman and Hall, New York, 1989, Chap. 3; (b) V. Percec and D. Tomazos, in *Comprehensive Polymer Science*, First Supplement (S. L. Aggarwal and S. Russo, Eds.), Pergamon Press, Oxford, 1992, Chap. 14.
- [2] P. LeBarney and J. C. Dubois, in *Side Chain Liquid Crystal Polymers* (C. B. McArdle, Ed.), Chapman and Hall, New York, 1989, Chap. 5.
- [3] D. Demus and H. Zschke, *Flussige Kristalle in Tabellen II*, VEB Deutscher Verlag, Leipzig, 1984.
- [4] C. Pugh, S. K. Andersson, and V. Percec, *Liq. Cryst.*, **10**, 229 (1991).
- [5] V. Percec, Q. Zheng, and M. Lee, *J. Mater. Chem.*, **1**, 611 (1991).
- [6] (a) J. M. Guglielminetti, G. Decobert, and J. C. Dubois, *Polym. Bull.*, **16**, 411 (1986); (b) B. Messner and H. Finkelmann, *Makromol. Chem.*, **192**, 2383 (1991).
- [7] See for example: (a) R. Zentel, G. F. Schmidt, J. Meyer, and M. Benalia, *Liq. Cryst.*, **2**, 83 (1987); (b) H. Kapitza and R. Zentel, *Makromol. Chem.*, **192**, 1859 (1991); (c) H. Mensinger, A. Biswas, and H. Poths, *Macromolecules*, **25**, 3156 (1992).
- [8] F. Hessel and H. Finkelmann, *Makromol. Chem.*, **189**, 2275 (1988).
- [9] (a) Z.-F. Zhou, H.-M. Li, and X.-D. Feng, *Macromolecules*, **20**, 233 (1987); (b) Q.-F. Zhou, H.-M. Li, and X.-D. Feng, *Mol. Cryst. Liq. Cryst.*, **155**, 73 (1988).
- [10] (a) F. Hessel and H. Finkelmann, *Polym. Bull.*, **14**, 375 (1985); (b) F. Hessel, R.-P. Herr, and H. Finkelmann, *Makromol. Chem.*, **188**, 1597 (1987).
- [11] R. W. Lewthwaite, G. W. Gray, and K. J. Toyne, *J. Mater. Chem.*, **2**, 119 (1992).
- [12] F. Hardouin, S. Mery, M. F. Achard, M. Mauzac, P. Davidson, and P. Keller, *Liq. Cryst.*, **8**, 565 (1990).
- [13] P. Keller, F. Hardouin, M. Mauzac, and M. F. Achard, *Mol. Cryst. Liq. Cryst.*, **155**, 171 (1988).
- [14] C. Pugh and R. R. Schrock, *Macromolecules*, **25**, 6593 (1992).
- [15] (a) H. F. Leube and H. Finkelmann, *Makromol. Chem.*, **191**, 2707 (1990); (b) H. F. Leube and H. Finkelmann, *Ibid*, **192**, 1317 (1991).
- [16] See for example: (a) W. Mahler, D. Guillon, and A. Skoulios, *Mol. Cryst. Liq. Cryst., Lett.*, **2**, 111 (1985); (b) T. P. Russell, J. F. Rabolt, R. J. Twieg, R. L. Siemens, and B. L. Farmer, *Macromolecules*, **19**, 1135 (1986); (c) J. Hoepken, C. Pugh, W. Richtering, and M. Moeller, *Makromol. Chem.*, **189**, 911 (1988); (d) J. Hoepken and M. Moeller, *Macromolecules*, **25**, 2482 (1992).
- [17] J. M. G. Cowie, in *Comprehensive Polymer Science*, Vol. 4 (G. Allen and J. C. Bevington, Eds.), Pergamon Press, Oxford, 1989, Chap. 22.
- [18] (a) H. Ringsdorf, R. Wustefeld, E. Zerta, M. Ebert, and J. H. Wendorff,

- Angew. Chem., Int. Ed. Engl.*, 28, 914 (1989); (b) H. Ringsdorf and R. Wustefeld, *Philos. Trans. R. Soc. London, Ser. A.*, 330, 95 (1990); (c) M. M. Green, H. Ringsdorf, J. Wagner, and R. Wustefeld, *Angew. Chem., Int. Ed. Engl.*, 29, 1478 (1990); (d) H. Bengs, R. Renkel, H. Ringsdorf, C. Baehr, M. Ebert, and J. H. Wendorff, *Makromol. Chem., Rapid Commun.*, 12, 439 (1991).
- [19] (a) D. Demus, G. Petzl, H. K. Sherma, and W. Weissflog, *Mol. Cryst. Liq. Cryst.*, 76, 241 (1981) and references therein; (b) E. Chino, Y. Matsunaga, and M. Suzuki, *Bull. Chem. Soc. Jpn.*, 57, 2371 (1984).
- [20] (a) J. M. Rodriguez-Parada and V. Percec, *Macromolecules*, 19, 55 (1986); (b) C. Pugh and V. Percec, *ibid*, 19, 65 (1986); (c) C. Pugh, J. M. Rodriguez-Parada, and V. Percec, *J. Polym. Sci., Polym. Chem. Ed.*, 24, 747 (1986); (d) V. Percec, H. G. Schild, J. M. Rodriguez-Parada, and C. Pugh, *Ibid*, 26, 935 (1988).
- [21] T. Doi, Y. Sakurai, A. Tamatani, S. Takenaka, S. Kusabayashi, Y. Nishihata, and H. Terauchi, *J. Mater. Chem.*, 1, 169 (1991) and references therein.