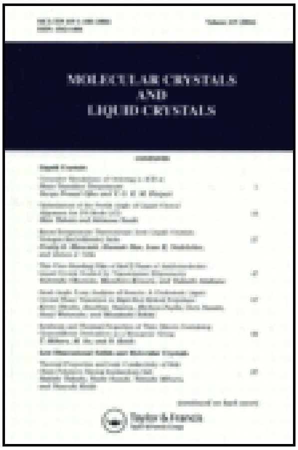

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Chiral Smectic Liquid Crystalline Polymers

Bruce Hahn [a] & Virgil Percec [a]

[a] Department of Macromolecular Science, Case Western Reserve University, Cleveland, 44106, OH

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CHIRAL SMECTIC LIQUID CRYSTALLINE POLYMERS

BRUCE HAHN AND VIRGIL PERCEC
Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106

Abstract

The synthesis of side-chain liquid crystalline polysiloxanes, copolysiloxanes and of tetracyclosiloxanes containing chiral mesogenic side groups, i.e, trans-2[p-(1-undecanyl-11-oxy)phenyl]-5-[(p-2(S)-methyl-1-butoxy)phenyl]-1,3-dioxane, trans-2-[p-(2(S)-methyl-1-butoxy)phenyl]-5-(11-undecalenyl)-1,3-dioxane and 2-[4-(2(S)-methyl-butoxy)-phenyl]-5-(ω-alkyl)-1,3,2-dioxaborinane with alkyl being undecanyl, octyl, and hexyl is discussed. Differential scanning calorimetry and thermal optical polarization microscopy revealed chiral smectic mesomorphism for polymers containing eleven methylene units in the flexible spacer. The polymers containing undecanyl spacers present a chiral smectic C mesophase. The polysiloxanes with hexyl spacers exhibit a chiral nematic mesophase.

Introduction

In 1975 Meyer et.al.(1,2) predicted that tilted chiral smectic liquid crystals should exhibit ferroelectricity. Low molar mass ferroelectric chiral smectic liquid crystals have been synthesized and are presently under extensive research in a number of laboratories (3,4). The reported synthesis of side chain liquid crystalline polymers containing chiral smectic liquid crystalline mesogenic units are very few (5,6). This paper will discuss our accomplishments in synthesizing chiral smectic side chain liquid crystalline polymers.

Side chain liquid crystalline polymers are obtained by attaching mesogenic compounds to polymer backbones through flexible spacers (7). Chiral smectic side chain polymers are obtained using a mesogenic compound which contains a chiral center. Side chain liquid crystalline polymers containing more than 6 or 7 methylenic units in the flexible spacer usually undergo side chain crystallization (8), however recent work from our laboratory has shown that the use of mesogenic units which undergo conformational isomerism will drastically depress the side chain crystallization. This is due to the presence of a mixture of conformers which are in a dynamic equilibrium. These different conformers are more difficult to crystallize than an individual isomer (9,10). Based on these facts, we prepared chiral smectic side chain liquid crystalline polymers containing chiral mesogenic units based on trans-2,5-disubstituted-1,3-dioxane and 2,5-disubstituted-1,3,2-dioxaborinane. The trans-2,5 disubstituted-1,3-dioxane mesogens exhibit a chair conformation, and the substituents in the 2 and 5 positions are either in an axial or an equatorial placement which are in a dynamic equilibrium. Although in the case of low molar mass compounds there is little difference between the axial and equatorial isomers, once these mesogenic units are attached as side groups to polymeric systems, this mixture of isomers depresses the side chain crystallization (Figure 1). The synthesis of these polymers is outlined in Scheme 1.

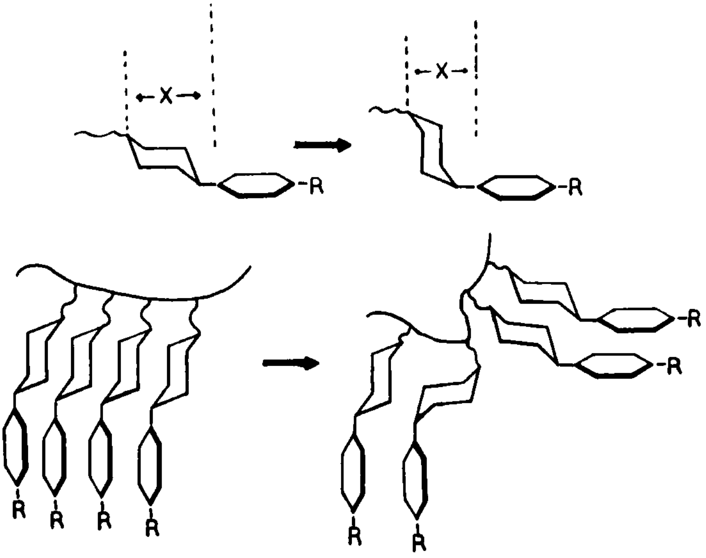
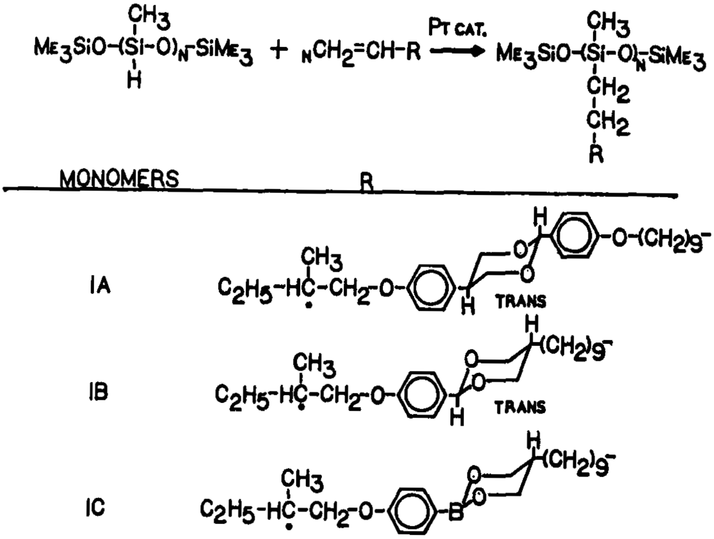


Figure 1: Drawing depicting effect of equatorial to axial isomerization



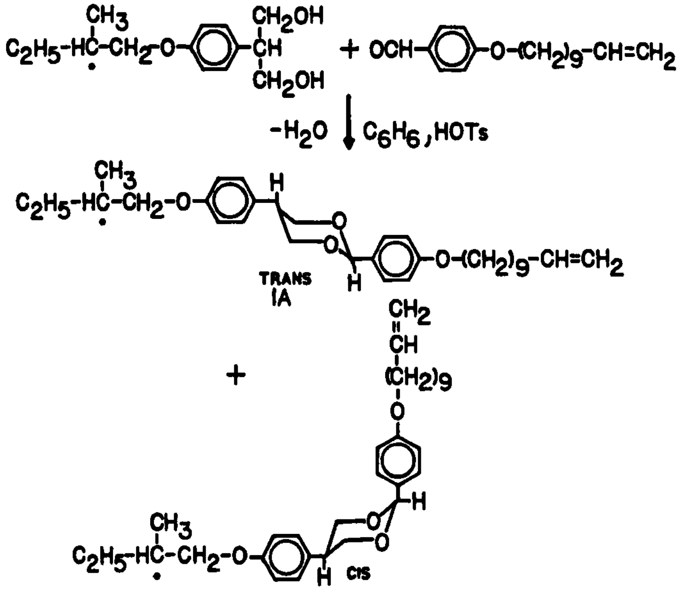
Scheme 1: Synthesis of polysiloxane liquid crystals

EXPERIMENTAL

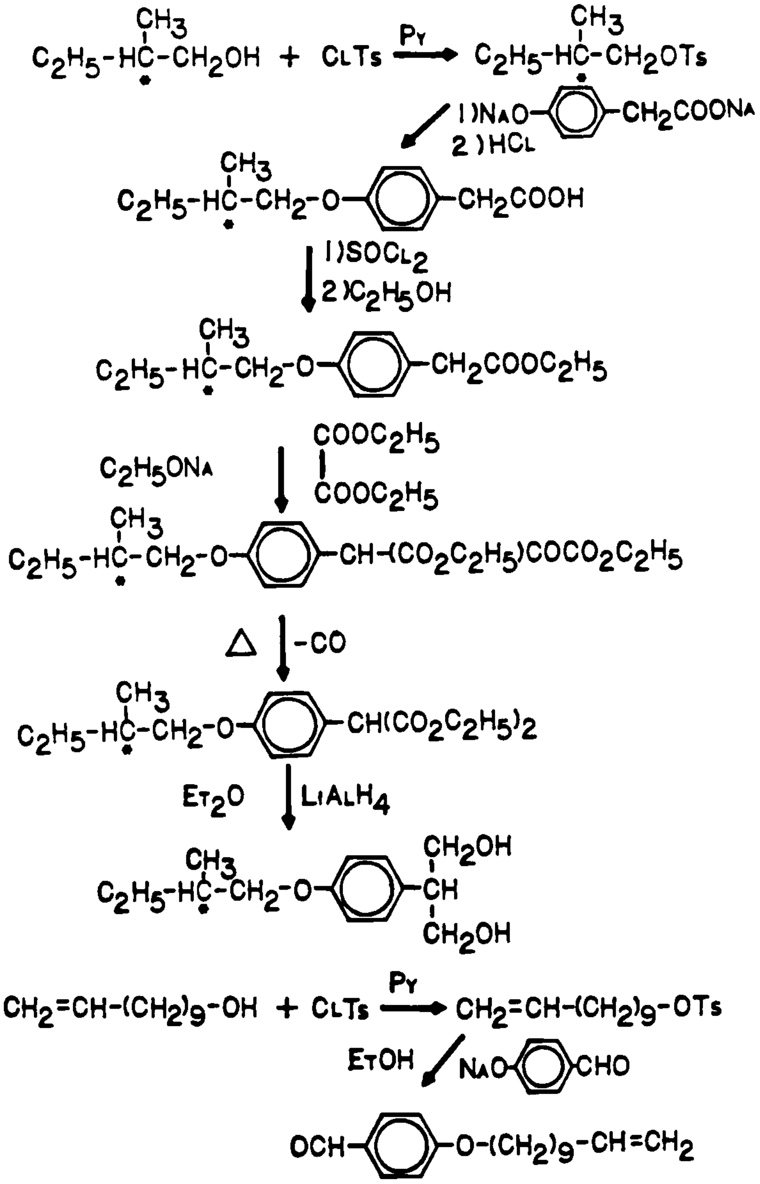
Detailed experimental conditions concerning the synthesis and characterization of these polymers are in press elsewhere (11).

RESULTS AND DISCUSSION

The synthesis of trans-2[p-(1-undecanyl-11-oxy)phenyl]-5-[(p-2(S)-methyl -1-butoxy)-1,3-dioxane (1) is outlined in Scheme 2. The chiral group was inserted onto this mesogenic unit by starting with commercially available S(-)-2-methyl-1-butanol. The synthetic steps were chosen to avoid its racemization. The formation of the dioxane ring (Schemes 2a,2b) resulted in both cis and trans isomers, however the trans isomer could easily be separated by fractional crystallization.

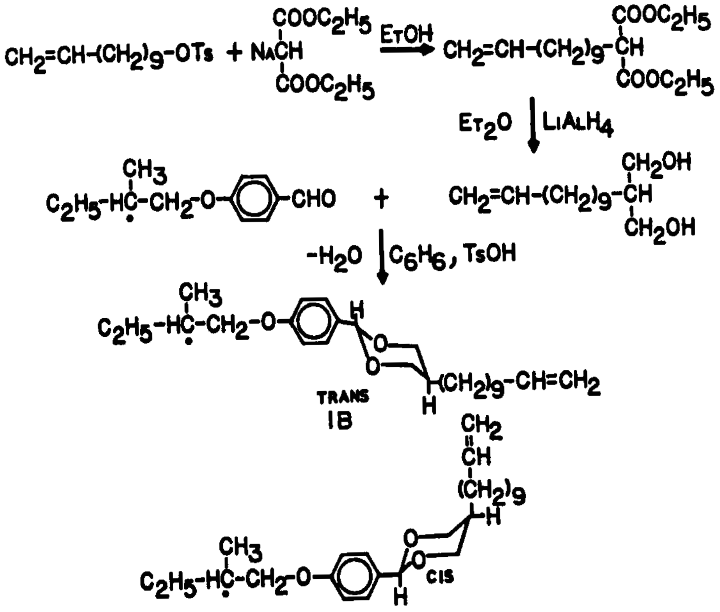


Scheme 2a: Synthesis of mesogen type 1A



Scheme 2b: Synthesis of mesogen type 1A

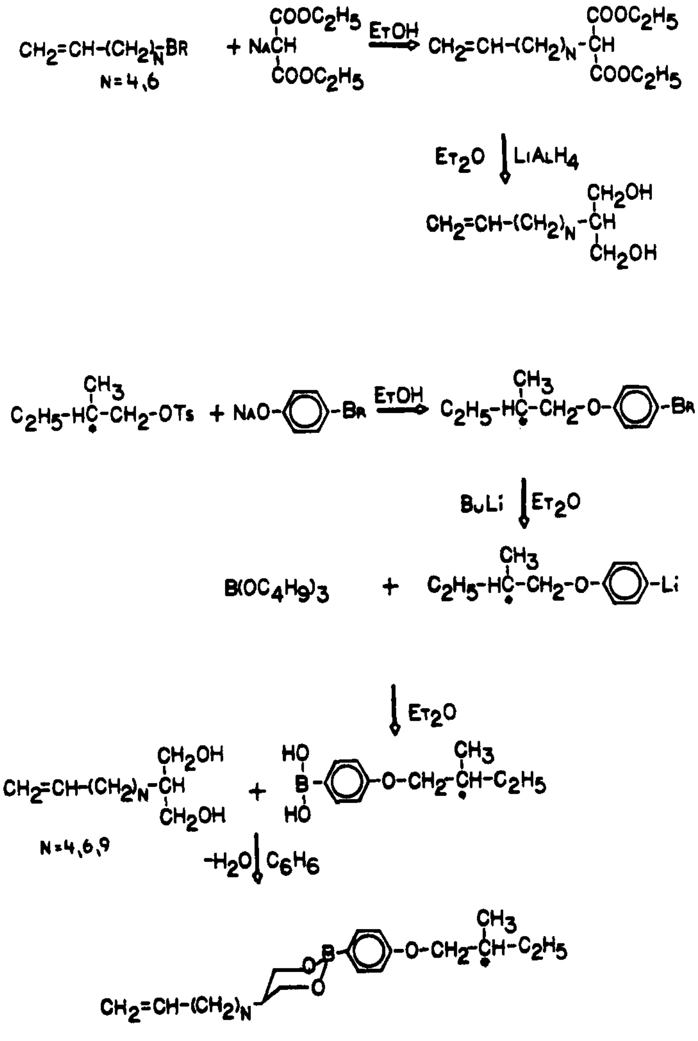
Scheme 3 outlines the synthesis of trans-2-[p-(2(S)-methyl-1-butoxy)phenyl]-5-(11-undecylenyl)-1,3-dioxane (1B).



Scheme 3: Synthesis of mesogen type 1B

The formation of the dioxane ring for this compound resulted in a mixture of cis and trans isomers with the cis content being as high as 23%. This mixture was liquid at room temperature and required multiple crystallizations at -70°C from diethyl ether in order to obtain the pure trans isomer.

One of the goals of this research was to study the effect of the flexible spacer length on the mesomorphic behavior of these polymers, however due to the difficulty of isolating the pure trans isomer of the dioxane compounds, we decided to prepare a comparable mesogen based on the 1,3,2-dioxaborinane ring. The dioxaborinane ring does not exhibit cis-trans isomerism due to the trivalent boron atom at position 2 on the dioxaborinane ring. The synthesis of the 2,5-disubstituted-1,3,2-dioxaborinanes (1C) is outlined in Scheme 4.



Scheme 4: Synthesis of mesogen type 1C

The synthesis of the liquid crystalline polysiloxanes is depicted in Scheme 1. The mesogenic units were purified by column chromatography before performing the hydrosilation reaction. It is essential that the hydrosilation reaction is complete, especially in those polymers which exhibit a low glass transition temperature. Crosslinking can occur during the drying of the polymer if any unreacted Si-H remains.

The monomeric compounds, 1A, 1B, and 1C (Scheme 1) were characterized by both differential scanning calorimetry (DSC) and thermal polarized optical microscopy. Monomers 1B and 1C undergo crystalline melting. The monomer 1A exhibits a liquid crystalline S_B mesophase from 91.4°C to 120.2°C on heating and between 118.4°C and 71.4°C on the cooling scan. A monotropic S_E mesophase appears between 71.4°C and 66°C.

Figure 2 depicts the DSC traces for the polysiloxane containing 1A side groups. The first heating scan reveals a melting transition at 73°C. This transition can be assigned to melting due to its lower enthalpy change in the second heating curve (Table 1) and due to its high degree of supercooling in the cooling scan (i.e. from 73°C to 38°C). Optical polarization microscopy and the enthalpy of isotropization support a smectic mesophase.

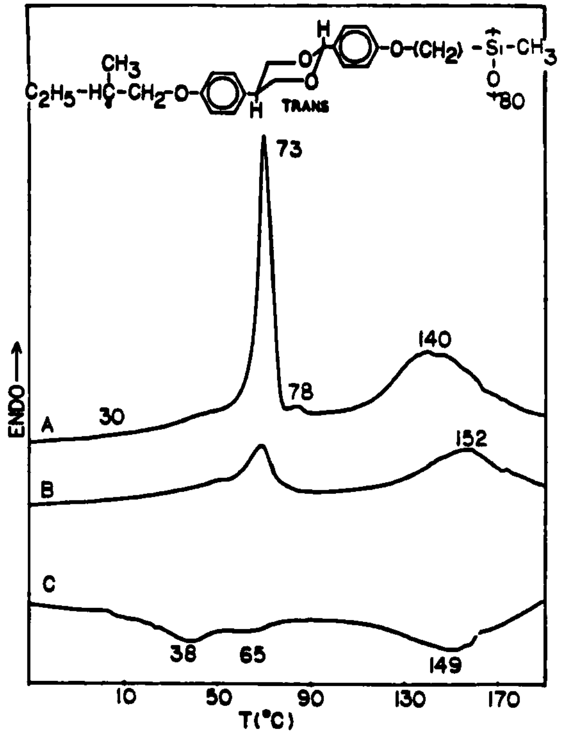


Figure 2: Nornalized DSC Thermograms for polysiloxanes containing mesogen 1A; A) first heating scan after annealing above Tg; B) second heating scan; C) second cooling scan

Table 1
Thermal Transitions and Thermodynamic Parameters of Polysiloxanes

Mesogen			Heating			Cooling		
Type	Scan	Tg	T1 ΔH	T2 ΔH	Ti ΔH	Ti ΔH	T2 ΔH	T1 ΔH
1A	1	30	73a	78	140a	-	-	-
			1.8	0.005	1.6	-	-	-
	2	30	69b	-	152	149	65	38
			0.56	-	1.2	1.0	0.05	0.1
1B	1	4	50a	-	91a	-	-	-
			0.4	-	0.2	-	-	-
	2	4	50	-	97	97	-	48
			0.03	-	0.2	0.2	-	.05
1C	2	-7	19	-	85	79	-	17
			0.1	-	1.5	1.5	-	0.1

a) after annealing above Tg, b) overlapped transitions
T=°C, ΔH=kcal/mru (mru=mole repeat unit)

The DSC traces for the polysiloxane with 1B type side groups are depicted in Figure 3. This polymer undergoes a smectic-smectic transition at 50°C. This transition is characterized as a smectic-smectic transition, even though its enthalpy changes on subsequent scans. This is due to its non-supercooling on the cooling scan. The smectic phase between 50 and 97°C resembles a pseudo-homeotropic petal texture characteristic of a S_a mesophase. On increasing the temperature from 50°C to 97°C, the color of the mesophase changes from blue to red , in the opposite way a cholesteric mesophase does (12,13). The enthalpy of isotropization is in the range expected for a nematic or cholesteric mesophase to an isotropic liquid (14), however this is not unexpected with mesogenic units exhibiting conformational isomerism. The cooling scan exhibits the formation of a smecitc A mesophase at 97°C (the formation of bâtonnets is seen in the optical microscope) directly followed by a smectic-smectic transition.

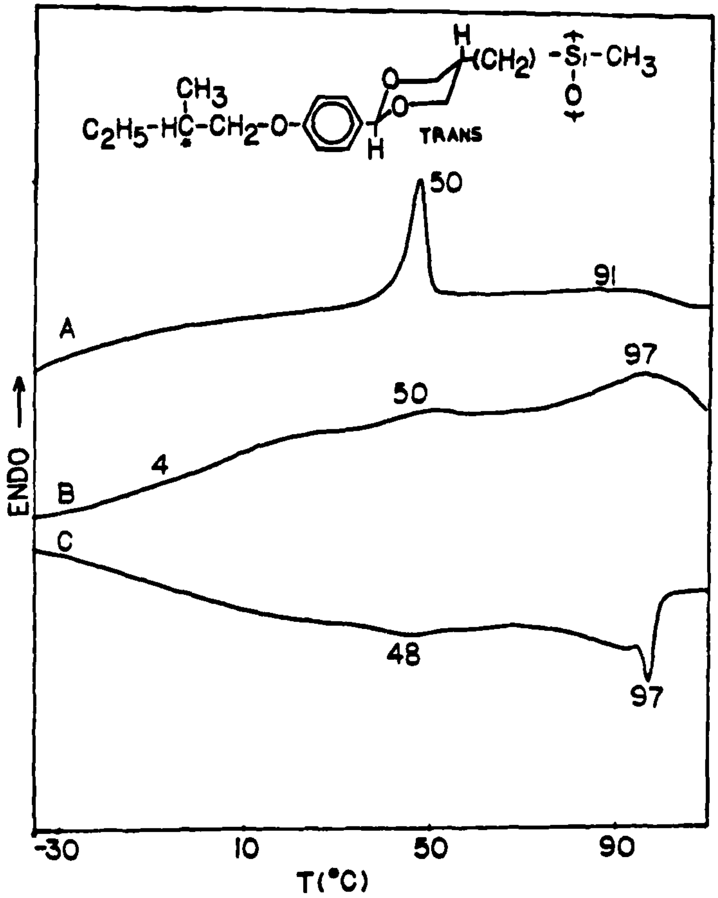


Figure 3: Normalized DSC Thermograms for polysiloxanes containing mesogen 1B: A) first heating scan after annealing above Tg; B) second heating scan; C) second cooling scan

Heating and cooling DSC traces for the polysiloxane containing 1C type side groups are shown in Figure 4.

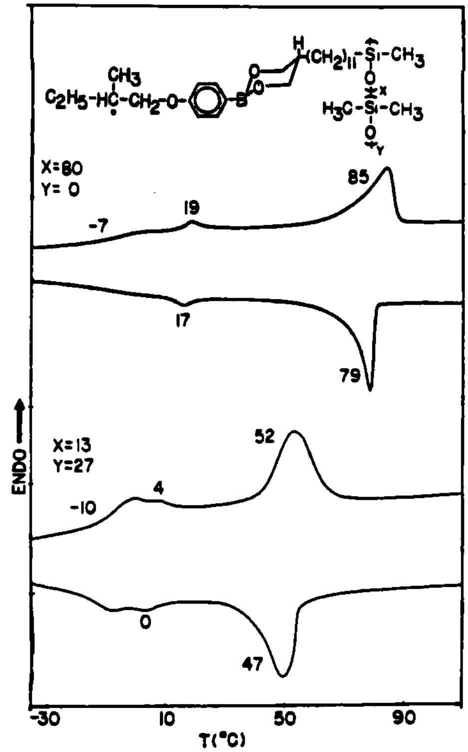


Figure 4: Normalized DSC thermograms for polysiloxane containing mesogen type 1C

The polymer exhibits a smectic mesophase just above the glass transition temperature (-7°C) which could not yet be assigned. At 19°C the polymer undergoes a smectic-S_c transition. The S_c phase goes isotropic at 85°C. The cooling scan presents a very narrow S_A mesophase which transforms to S_C at 79°C. The DSC barely discriminates between these two transitions. Optical polarization microscopy can clearly reveal the formation of båtonnets just before 79°C. These bâtonnets undergo a direct transition into a pseudo-homeotropic petal texture similar to the polysiloxane containing 1A type side groups.

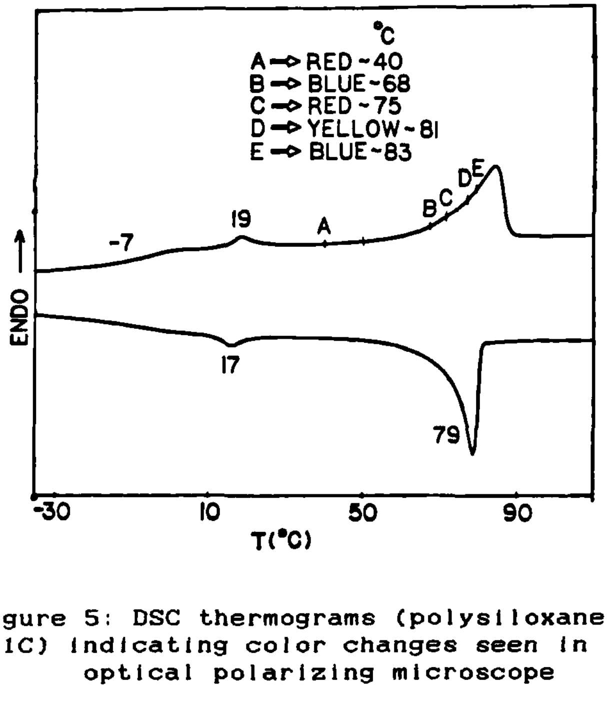


Figure 5: DSC thermograms (polysiloxane with 1C) indicating color changes seen in the optical polarizing microscope

Figure 5 represents the reproducible color changes this polymer undergoes during heating in the optical polarized microscope. Based upon these textures, enthalpy changes (Table 1) and color changes (Figure 5) we have assigned this polymer as having a chiral smectic C mesophase.

Figure 4 also shows the DSC traces of a polysiloxane copolymer consisting of dimethylsiloxane (67%) and methyl siloxane containing mesogen 1C. It is interesting to point out that by changing the composition and by changing the molecular weight of the polymer one can affect the temperature ranges of the mesophases. The copolysiloxane in Figure 4 has the S_c mesophase at room temperature. The effect of molecular weight and copolymer composition is currently being studied in our laboratories.

One of the potentially most important results obtained from studying these systems is the biphasic behavior exhibited by the copolymers. Figure 6 represents the low temperature DSC traces of the polysiloxane copolymers (Traces A and B).

Two glass transitions are seen in both of these copolymers. The lower glass transition is assigned to the independant motion of the dimethylsiloxane main chain (i.e. Trace C) and the higher glass transition is assigned to the cooperative but independant motion of the side groups. This biphasic behavior suggests that not only is the spacer length important in decoupling the motion of the polymer

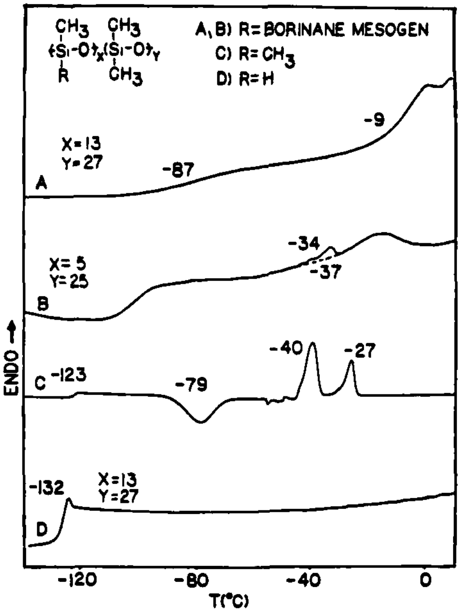


Figure 6: Low temperature DSC thermogram of polysiloxane copolymers containing mesogen type 1C

backbone from the mesogenic unit, but also the miscibility between the polymer backbone and the side groups. Evidence for a high degree of decoupling is the presence of backbone crystallization and its melting overlapping the Tg of the side groups. This certainly demonstrates that the two motions are independant.

The mesogenic unit of type 1C was also prepared with different flexible spacer lengths, $(-CH_2-)_n$, n being 6, 8 and 11. The DSC traces of these polymers are depicted in Figure 7. The polysiloxanes with 6 and 8 methylenic units spacers display a glass transition temperature and an isotropization. Neither polymer exhibits the smectic-smectic transition just above Tg as seen with the 11 methylenic units spacer. The enthalpy of isotropization (Table 2) for the 8 methylenic units spacer is in the range expected for a smectic mesophase, however the isotropization enthalpy for the 6 methylenic units spacer is in the range expected for a nematic or cholesteric mesophase. No definitive assignment of this mesophase is availible at the present time.

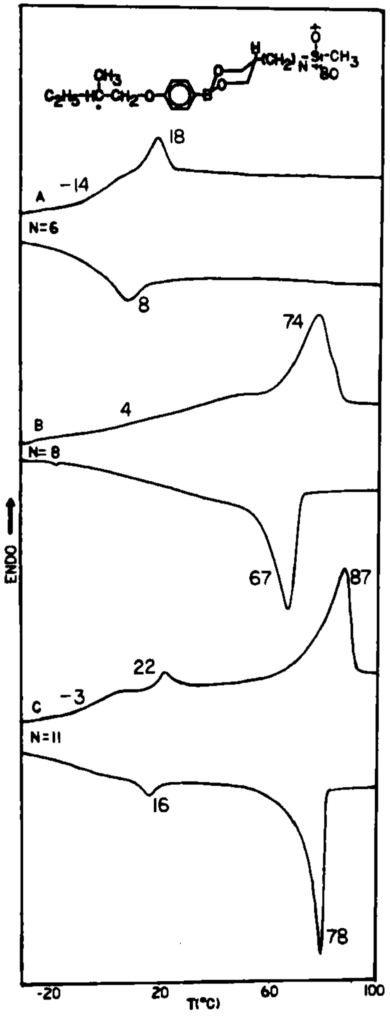
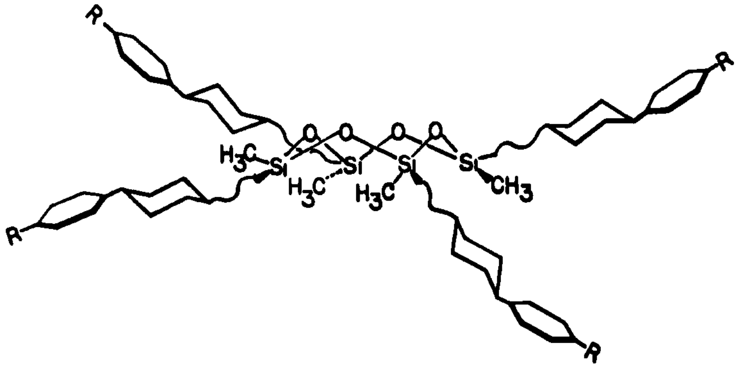
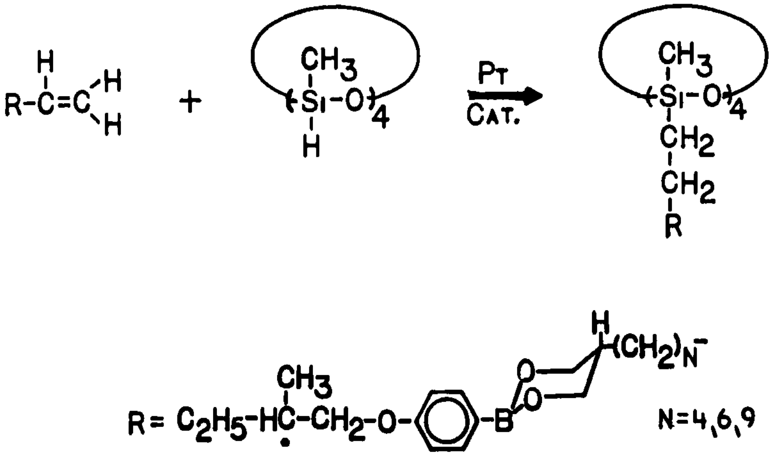


Figure 7: DSC thermograms of polysiloxanes containing mesogen type 1C with different methylene units spacers (6,8 and 11)

A novel type of liquid crystal has also been prepared using the mesogen type 1C and by attaching it to the eight membered ring 1,3,5,7-tetramethylcyclotetrasiloxane (Schemes 5 and 6). The DSC traces of these crown like liquid crystals are shown in Figure 8. It is interesting to note the similarities in the thermal behavior between these cyclic compounds and the polymers (Figures 7 and 8, Tables 2 and 3). It is not yet clear whether these crown compounds exhibit calamitic or discotic mesophases. However optical polarization microscopy seems to indicate discotic type mesophases which were recently predicted for this class of liquid crystalline compounds (15). Whether the disk-like mesophase represents the first example of a chiral smectic C disk-like mesophase or not, it is difficult to speculate at this time. A complete detailed report of these polymers is in progress.



Scheme 5: Crown like liquid crystal



Scheme 6: Synthesis of crown like liquid crystals

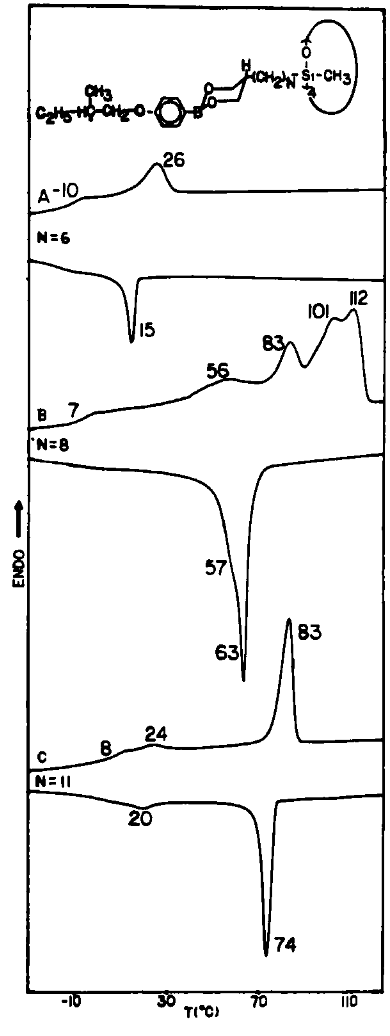


Figure 8: DSC Thermograms of cyclic siloxanes containing mesogen type 1C with different methylene units spacers (6,8, and 11)

Table 2
Thermodynamic Transitions and Parameters of Polysiloxanes

		Heating			Cooling	
Spacer Length	Scan	Tg	T1 ΔH	Ti ΔH	Ti ΔH	T1 ΔH
6	2	-14	-	18	8	-
			-	0.27	0.25	-
8	2	4	-	74	67	-
			-	1.4	1.4	-
11	2	-3	22	87	79	16
			0.13	1.65	1.65	0.12

T=°C, ΔH=kcal/mru (mru=mole repeat unit)

Table 3
Thermal Transitions and Thermodynamic Parameters of Siloxane Rings

		Heating			Cooling	
Spacer Length	Scan	Tg	T1 ΔH	Ti ΔH	Ti ΔH	T1 ΔH
6	2	-10	-	25	14	-
			-	2.7	2.7	-
8	2	-6	56	111	63	-
			a	11.6	10.4	a
11	2	8	24	83	74	20
			0.33	8.5	8.3	0.40

T=°C, ΔH=kcal/mole, a) overlapping transitions

Acknowledgements

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References

1. R.B.Meyer, L.Libert, L.Strzelecki, and P.Keller, J.Phys., 36 L-69 (1975)
2. R.B.Meyer, Mol.Cryst.Liq.Cryst. 40, 33 (1977)
3. J.W.Goodby, Science 231, 350 (1986)
4. D.M.Walsa, S.C.Slater, W.N.Thurmes, N.A.Clark, M.A.Handschy, and F.Sapon, J.Am.Chem.Soc. 108, 5210 (1986)
5. G.Decobert, F.Loyer, and J.C.Dubois, Polym.Bull. 14, 179 (1985)
6. G.Decobert, J.C.Dubois, S.Esselin, and C.Woel, Liq.Crystals 1, 307 (1986)
7. H.Finkelman, H.Ringsdorf, and J.Wendroff, Makromol.Chem. 179, 273 (1978)
8. H.Finkelman and G.Rehage, Adv.Polym.Sci. 60/61, 99 (1984)
9. C.S.Hsu, J.M.Rodriguez-Parada, and V.Percec, Makromol.Chem. 188, 1017 (1987)
10. C.S.Hsu, J.M.Rodriguez-Parada, and V.Percec, J.Polym.Sci. Part A: Polym.Chem.,25, 2425 (1987)
11. B.Hahn and V.Percec, Macromolecules, in press
12. G.W.Gray and J.W. Goodby, "Smectic Liquid Crystals. Textures and Structures", Leonard Hill, Glasgow and London, P.63
13. D.Demus and L.Richter, "Textures of Liquid Crystals", Verlag Chemie, Weinheim and New York, 1978
14. W.R.Krigbaum, J.Appl.Polym.Sci.: Appl.Polym.Symp., 41, 105, (1985)
15. D.R.R. Everitt, C.Care and R.Wood, Mol.Cryst.Liq.Cryst., in press