Liquid crystalline polymers containing heterocycloalkane mesogens
4. Biphasic side-chain liquid crystalline polysiloxanes containing trans 5-(n-undecanyl)-2-(4-methoxyphenyl)-1,3-dioxane and trans 2-(n-decanyl)-5-(4-methoxyphenyl)-1,3-dioxane mesogens

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Summary
    The synthesis and characterization of side-chain liquid crystalline poly-
siloxanes and copolysiloxanes containing trans 5-(n-undecanyl)-2-(4-methoxy-
phenyl)-1,3-dioxane and respectively trans 2-(n-decanyl)-5-(4-methoxyphenyl)
-1,3-dioxane side groups is presented. In most cases the resulting polymers
exhibit two glass transition temperatures, i.e., one due to the independent
motion of the main chain, and the other due to the independent but coopera-
tive motion of the side chains.

Introduction
    The previous papers from this series reported on the synthesis and cha-
racterization of thermotropic side-chain liquid crystalline polymers (LCP)
containing trans 2,5-disubstituted-1,3-dioxane mesogens attached to the po-
lymer backbone through spacers containing eleven and respectively ten me-
thylenic units (1, 2). Most of the previously synthesized LCP containing
long spacers and calamitic mesogens underwent side-chain crystallization
(3, 4). Since the trans 2,5-disubstituted-1,3-dioxane mesogens present a
number of conformational isomers which are in a thermodynamic equilibrium,
side-chain LCP containing long spacers and 1,3-dioxane based mesogens do
not undergo side-chain crystallization. This particularity of the 2,5-disub-
stituted-1,3-dioxane mesogens let us design the first examples of thermotro-
pic side-chain LCP exhibiting two glass transition temperatures, i.e., one
due to the independent motion of the polymer backbone, and the other due to
the independent but cooperative motion of the side-chains (5). These side-
chain LCP are biphasic systems, and therefore can be regarded as polymers
resembling the behavior of phase separated graft copolymers.
    The goal of this paper is to present the synthesis and characterization
of two new examples of biphasic side-chain LC polysiloxanes and copolysilo-
xanes containing side-chains whose mesogenic units are constitutional iso-
mers, i.e., trans-5-(n-undecanyl)-2-(4-methoxyphenyl)-1,3-dioxane and trans
2-(n-decanyl)-5-(4-methoxyphenyl)-1,3-dioxane.

Experimental
A. Materials
    Poly(methylhydrosiloxane)s ($\bar{M}n$ = 4500 – 5000 and $\bar{M}n$ = 2270) and poly[(
30-35%) – methylhydro-(65-70%)-dimethylsiloxane] ($\bar{M}n$ = 2000 – 2100) were ob-
tained from Petrarch Systems Inc., and were used as received. 4-Methoxyben-
zaldehyde and the other reagents (Aldrich) were used as received. Toluene
used in the hydrosilation reaction was first refluxed over sodium and then
distilled under argon.
B. Techniques
    Experimental techniques used in the characterization of intermediary

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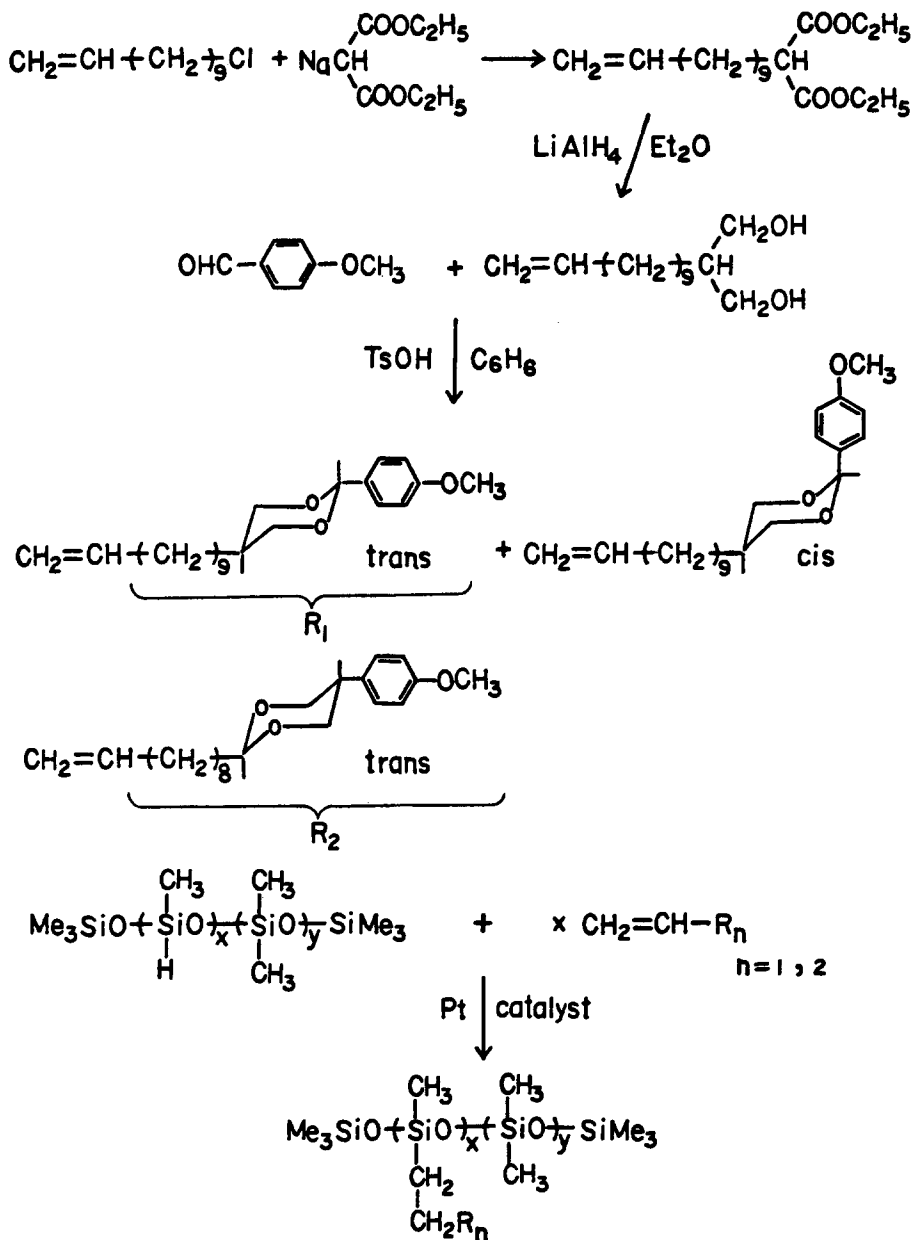
Scheme 1: Synthesis of LC Polysiloxanes and Copolysiloxanes
Containing 2,5-Disubstituted-1,3-Dioxane Based
Side-Groups

compounds and of polymers are identical to those previously reported (6).

C. Synthesis of Monomers and Polymers

2-(10-Decylenyl)-5-(4-methoxyphenyl)-1,3-dioxane was synthesized as previously reported (2). The syntheses of 5-(11-undecylenyl)-2-(4-methoxyphenyl)-1,3-dioxane and of the LC polysiloxanes and copolysiloxanes are outlined in Scheme 1.

Diethyl-2-(11-undecylenyl)malonate

Cleanly cut Na (3.45g, 0.15 mole) was added in portions to absolute ethanol (150 ml). After the sodium was completely dissolved, diethyl malonate (24g, 0.15 mole) was added to the reaction mixture and the solution was stirred for 1hr. 11-Chloro-1-undecene (28.3g, 0.15 mole) was then added to the reaction mixture. After 16 hrs of stirring at room temperature, the ethanol was evaporated on a rotavapor. The residue was dissolved in ethyl ether, washed several times with water, dried over anhydrous Na_2SO_4, and ethyl ether was removed on a rotavapor. The product was distilled at 155-158°C/10-12 mm Hg, to yield 39g (83%). 200 MHz ^{1}H-NMR (CDCl$_3$, TMS, δ, ppm): 1.13 to 2.08 (m, 24 H, -(CH$_2$)$_9$- and CH$_3$CH$_2$O-), 3.30 (t, 1 H, -HC(CO)$_2$), 4.20 (m, 4H, -CH$_2$O), 4.94(m, 2 H, CH$_2$=), 5.80 (m, 1 H, =CH-).

2-(11-Undecylenyl)-1,3-propanediol

A solution of diethyl 2-(undecylenyl)malonate (39g, 0.125 mole) in 50ml of dried ethyl ether was added dropwice to a suspension of LiAlH$_4$ (4.75g, 0.125 mole) in 250ml of dried ethyl ether. After the addition was complete, the reaction mixture was stirred at 40°C for 20 hrs, cooled to room temperature, and excess LiAlH$_4$ was reacted with ethyl acetate. The resulting solution was treated with dilute hydrochloric acid and extracted with ethyl ether. The organic phase was washed with 2% aqueous solution of NaHCO$_3$, water, and dried over anhydrous Na$_2$SO$_4$. The crude product obtained after the solvent was evaporated was recrystallized from ethyl ether at 0°C to yield 27g (94%). m.p.=58-59°C. 200 MHz ^{1}H-NMR (CDCl$_3$, TMS, δ, ppm): 1.06 to 2.16 (m, 18 H, -(CH$_2$)$_9$-), 3.30 to 3.81 (m, 5 H, -HC(CH$_2$O-)$_2$), 4.94 (m, 2 H, CH$_2$=), 5.80 (m, 1 H, =CH-).

Trans-5-(11-Undecylenyl)-2-(4-methoxyphenyl)-1,3-dioxane

2-(11-Undecylenyl)-1,3-propanediol (6g, 0.0262 mole), 4-methoxybenzaldehyde (3.6g, 0.0262 mole) and p-toluene sulfonic acid (250 mg) were dissolved in 250 ml of dried benzene. The reaction mixture was refluxed until 0.47 ml of water was collected on a Dean-Stark trap. After cooling to room temperature, the solution was washed with 2% aqueous solution of NaHCO$_3$, water, dried over anhydrous Na$_2$SO$_4$, and the solvent was evaporated on a rotavapor. The obtained solid was recrystallized several times from n-hexane at 0°C to yield 5.3g (58%). m.p.= 50°C. 200 MHz ^{1}H-NMR (CDCl$_3$, TMS, δ, ppm): 1.11 to 2.16 (m, 19 H, -(CH$_2$)$_9$-CH(CH$_2$-)$_2$), 3.51 and 4.18 (m, 4 H, two -CH$_2$O), 3.79 (s, 3 H, -OCH$_3$), 4.94 (m, 2 H, CH$_2$=), 5.36 (s, 1 H, PhCH), 5.80(m, 1 H, =CH-), 6.86 and 7.38 (2d, four aromatic protons).

Synthesis of Polymers and Copolymers

Polysiloxanes and copolysiloxanes were synthesized by hydrosilation of the corresponding olefins with poly(hydrogenmethylsiloxane)s or poly[(30-35%)-hydrogenmethyl-(65-70%)-dimethylsiloxane] using dicyclopentadienyl platinum (II) chloride as catalyst in toluene. A detailed description of a procedure for complete hydrosilation free of side reactions was previously reported (2).

Results and Discussion

Scheme 1 outlines the synthesis of trans 5-(11-undecylenyl)-2-(4-methoxyphenyl)-1,3-dioxane, shows the structure of trans 2-(10-decylenyl)-5-(4-methoxyphenyl)-1,3-dioxane, and presents the synthesis of the LC polysiloxanes and copolysiloxanes. The mesogenic unit and the aliphatic part of the side groups are denoted by R$_1$ and R$_2$ respectively. R$_1$ contains one more me-
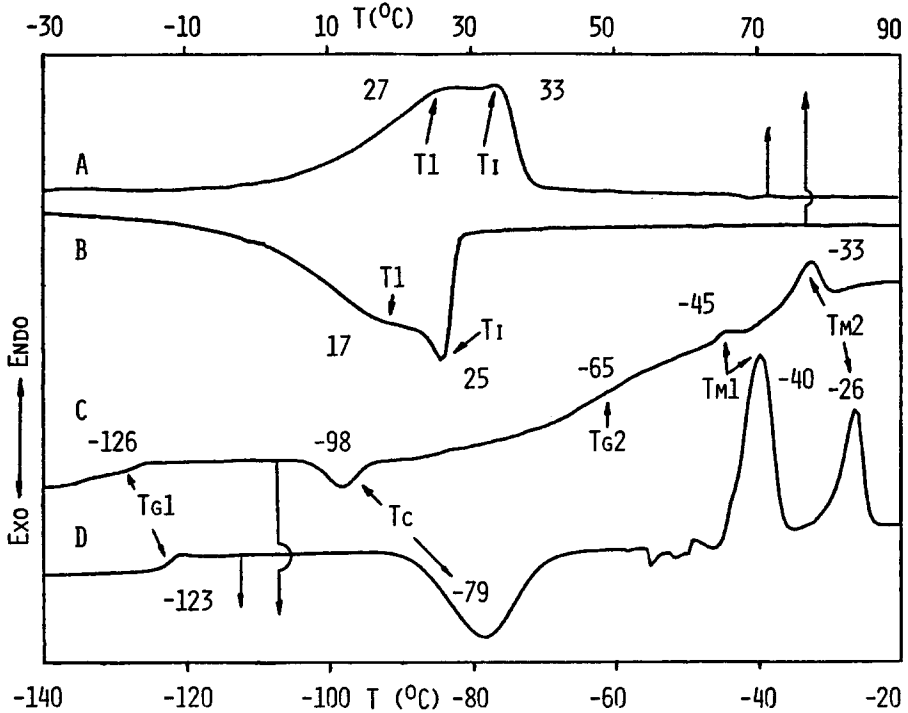
Figure 1: DSC thermograms (20°C/min) of: A) copolymer No.4 from Table I, heating scan; B) cooling scan; C) heating scan; D) polydimethylsiloxane sample No.5 from Table I, heating scan

TABLE 1: THERMAL TRANSITIONS OF POLYSILOXANES

				THERMAL TRANSITIONS IN °C								
POLYMER				HEATING							COOLING	
No	RN	X*	Y*	Tg1	Tc	Tm1	Tm2	Tg2	T1	TI	T1	TI
1	R1	80	0	-126	--	--	-35	-17	3	63	-5	57
2	R1	20	10	---	--	--	--	-46	16	52	9	46
3	R2	80	0	-126	--	--	-34	-7	84	93	77	84
4	R2	20	10	-127	-98	-45	-33	-65	27	33	17	25
5	--	0	80	-123	-79	-40	-27	--	--	--	--	--

* X AND Y ACCORDING TO SCHEME 1.

thylenic unit in the aliphatic spacer than R_2. The mesogenic units of the two side groups are constitutional isomers.

Figure 1 presents typical differential scanning calorimetric traces of an LC copolysiloxane containing R_2 side groups (curves A and C heating scans; curve B, cooling scan) and of a polydimethylsiloxane (curve D). The polydimethylsiloxane sample exhibits the expected glass transition temperature (Tg1), followed by a crystallization exotherm (Tc), and two melting exotherms (Tm1, Tm2) (7). The LC copolysiloxane exhibits the glass transition temperature of the polysiloxane backbone (Tg1), followed by the crystallization of the polysiloxane backbone (Tc'), the glass transition temperature of the side groups (Tg2), and the two meltings of the polysiloxane backbone (Tm1, Tm2). Since the glass transition temperature of the side groups, Tg2, is situated below the melting temperature of the polymer backbone, it demonstrates that the mobility of the LC domains is completely independent of the mobility of the backbone domains although they are interconnected.

The differential scanning calorimetric thermograms C and D from Figure 1 are quite similar, suggesting that at least the last methylenic unit of the spacer is part of the polymer backbone. The shifts observed for the thermal transitions of the LCP backbone versus those of the free polydimethylsiloxane backbone should be related to the weight ratio of the domains, domain size, and interfacial miscibility.

The high temperature range of the differential scanning calorimetric thermograms revealed both for homopolymers as well as for copolymers, two highly ordered mesophases (curves A and B in Figure 1), which have not been yet completely assigned. Preliminary X-ray diffraction data suggest higher order than smectic-B for the LC mesophase occuring at room temperature.

Table I summarizes the thermal transitions for all LCP. Only in the case of the copolymer No. 2 from this table we could not detect the thermal transitions due to the polysiloxane backbone. For the case of homopolymers, R_2 gives a more stable mesophase, while R_1 gives a more stable mesophase for copolymers. Since the lengths of the spacer are not the same, and because the LCP morphology is expected to affect also the mesomorphic behavior of the LC domains, it is not yet possible to comment further on these results. Nevertheless, it seems to be certain that the behavior of biphasic versus monophasic side-chain liquid crystalline polymers should be different.

Previously, comb-like polymers exhibiting two glass transition temperatures were seldom encountered in the literature (8, 9). Our previous results (5) together with the present data, suggest that with a proper selection of the polymer backbone and of the side groups, at list for high weight percent of side groups and long spacers, it should be quite easy to tailor a large variety of biphasic side chain LCP. It has to be mentioned that miscibility rules could play an important role in the design of such systems.

References

1. C. S. Hsu, J. M. Rodriguez-Parada and V. Percec, Makromol. Chem., in press
2. C. S. Hsu, J. M. Rodriguez-Parada and V. Percec, J. Polym. Sci. Part A: Polym. Chem., in press
3. H. Finkelmann and G. Rehage, Adv. Polym. Sci., 60/61, 99(1984)
4. V. P. Shibaev and N. A. Plate, Adv. Polym. Sci., 60/61, 173(1984)
5. C. S. Hsu and V. Percec, Makromol. Chem. Rapid Commun., submitted
6. J. M. Rodriguez-Parada and V. Percec, J. Polym. Sci. Part A: Polym. Chem., 24, 1363(1986)

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7. S. J. Clarson, K. Dodgson and J. A. Semlien, Polymer, $\underline{26}$, 930(1985)
8. J. M. G. Cowie, Z. Hag and I. J. McEwen, J. Polym. Sci., Polym. Lett. Ed., $\underline{17}$, 771(1979)
9. J. M. G. Cowie, Z. Hag, I. J. McEwen and J. Velickovic, Polymer, $\underline{22}$, 327(1981)