LIQUID CRYSTALLINE POLYMERS CONTAINING
HETEROCYCOALKANE MESOGENS 4 DIPHA. (U) CASE WESTERN
RESERVE UNIV CLEVELAND OH DEPT OF MACROMOLECULAR...
UNCLASSIFIED C S HSU ET AL. 1986 TR-9 N00014-86-K-0284 F/G 7/6
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

By

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**Title:**
Liquid Crystalline Polymers Containing Heterocycloalkane Mesogens. 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

**Personal Authors:**
C. S. Hsu and V. Percec

**Abstract:**
See Attached.
The synthesis and characterization of side-chain liquid crystalline polysiloxanes and copolysiloxanes containing trans 5-(n-undecanyl)-2-(4-methoxyphenyl)-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 cooperative motion of the side chains.
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-
oxanes 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-
zaaldehyde and the other reagents (Aldrich) were used as received. Toluene
was used in the hydroisolation reaction was first refluxed over sodium and then
distilled under argon.

B. Techniques
Experimental techniques used in the characterization of intermediary
CH₂=CH + CH₂=C₃Cl + Na₇CH₂CO₂H₃ → CH₂=CH + CH₂=C₃CH₂CO₂H₃

LiAlH₄/Et₂O

OHC—OH₃ + CH₂=CH + CH₂=C₃CH₂OH

T₃OH → C₆H₆

CH₂=CH + CH₂=C₃

trans + CH₂=CH + CH₂=C₃

cis

Me₃SiCH₂CH₂CH₂CH₂SiMe₃ + x CH₂=CH-Rₙ

Pt catalyst

CH₃

Me₃SiCH₂CH₂CH₂CH₂SiMe₃

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 (2.4g, 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 \( \text{Na}_2\text{SO}_4\), 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 \(^1\text{H-NMR}\) (CDCl\(_3\), TMS, \( \delta \), ppm): 1.13 to 2.08 (m, 24 H, -(C\(_2\))- and CH\(_2\)0), 3.30 (t, 1 H, -HC(CO)\(_2\)), 4.20 (m, 4H, -CH\(_2\)0), 4.94 (m, 2 H, CH\(_2\)=), 5.80 (m, 1 H, =CH-).

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

A solution of diethyl 2-(undecylenyl)malonate (39g, 0.125 mole) in 50ml of dried ethyl ether was added dropwise to a suspension of LiAl\(_4\)H\(_4\) (4.75g, 0.125 mole) in 250ml of dried ethyl ether. After the addition was complete, the reaction mixture was stirred at 40\(^\circ\)C for 20 hrs, cooled to room temperature, and excess LiAl\(_4\)H\(_4\) 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 \( \text{Na}_2\text{SO}_4\). 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\(^\circ\)C. 200 MHz \(^1\text{H-NMR}\) (CDCl\(_3\), TMS, \( \delta \), ppm): 1.06 to 2.16 (m, 18 H, -(CH\(_9\))-CH\(_2\)=), 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-).

**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-decylleynyl)-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>
<thead>
<tr>
<th>No</th>
<th>Rn</th>
<th>x*</th>
<th>y*</th>
<th>Tg1</th>
<th>Tc</th>
<th>Tm1</th>
<th>Tm2</th>
<th>Tg2</th>
<th>T1</th>
<th>T1</th>
<th>Ti</th>
<th>Ti</th>
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<td>1</td>
<td>R1</td>
<td>80</td>
<td>0</td>
<td>-126</td>
<td>--</td>
<td>--</td>
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<td>63</td>
<td>-5</td>
<td>57</td>
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<tr>
<td>2</td>
<td>R1</td>
<td>20</td>
<td>10</td>
<td>---</td>
<td>--</td>
<td>--</td>
<td>--</td>
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<td>16</td>
<td>52</td>
<td>9</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>R2</td>
<td>80</td>
<td>0</td>
<td>-126</td>
<td>--</td>
<td>--</td>
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<td>-7</td>
<td>84</td>
<td>93</td>
<td>77</td>
<td>84</td>
</tr>
<tr>
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<td>R2</td>
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<td>--</td>
<td>0</td>
<td>80</td>
<td>-123</td>
<td>-79</td>
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<td>-27</td>
<td>--</td>
<td>--</td>
<td>--</td>
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<td>--</td>
</tr>
</tbody>
</table>

* x and y according to Scheme 1.
thylenic unit in the aliphatic spacer than R₂. The mesogenic units of the
two side groups are constitutional isomers.

Figure 1 presents typical differential scanning calorimetric traces of
an LC copolysiloxane containing R₂ side groups (curves A and C heating scans; 
curve B, cooling scan) and of a polydimethylsiloxane (curve D). The polydi-
methylsiloxane sample exhibits the expected glass transition temperature
(T_g1), followed by a crystallization exotherm (T_c), and two melting exotherms
(T_ml, T_m2) (7). The LC copolysiloxane exhibits the glass transition tempera-
ture of the polysiloxane backbone (T_g1), followed by the crystallization of
the polysiloxane backbone (T_c), the glass transition temperature of the side
groups (T_g2), and the two meltings of the polysiloxane backbone (T_ml, T_m2).
Since the glass transition temperature of the side groups, T_g2, 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 polydimethylsil-
oxane 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 occurring 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 trans-
jitions due to the polysiloxane backbone. For the case of homopolymers, R₂
yields a more stable mesophase, while R₁ 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 tempera-
tures 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 least 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.

Acknowledgements

Financial support of this work by the Office of Naval Research is great-
fully acknowledged.

References

Polym. Chem., in press
24, 1363(1986)
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