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Synthesis and mesomorphic behavior of poly(methylsiloxane)s containing *trans*-cyclohexane-based mesogenic side groups

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SUMMARY

The synthesis and characterization of poly(methylsiloxane)s containing either trans-4-methylcyclohexyl 4-alkenyloxybenzoate or trans-4-methylcyclohexyl 4'-alkenyloxybiphenyl-4-carboxylate mesogenic side groups are presented. All polymers except two which contain either trans-4-methylcyclohexyl 4-allyloxybenzoate or trans-methylcyclohexyl 4-(5-hexene-1-yloxy)benzoate side groups, display liquid crystalline phases. The dependence of phase trasition temperature on the spacer length and the mesogenic core length as well as the thermal stalility of the prepared liquid crystalline polymers (LCPs) are described.

INTRODUCTION

In the past few years, we reported on systematic investigations concerning the replacement of aromatic structures from mesogenic side groups of a side-chain LCP by heterocycloalkane units, e.g. the 1,3-dioxane rings (1-8). We have demonstrated that mesogenic units based on trans-1,3-dioxane ring can be used to synthesize noncrystallizable side-chain LCPs even when the polymers contain up to eleven methylene in the spacers. The conformational isomers of trans-1,3-dioxane based mesogens are in a dynamic equilibrium and this depresses their crystallization when they are attached as polymeric side chains. However, the trans-1,3-dioxane based mesogens are not very stable and undergo a thermal induced trans-cis isomerization at higher temperature. The mesophases of the polymers are destroyed because the cis isomers present no liquid crystalline properties (16). This disadvantage could be improved if the cyclohexane rings are used instead of the 1,3-dioxane rings.

Since Demus et al. (9) reported the nematic cyclohexane carboxylate in 1973, several kinds of low molar mass liquid crystals containing a cyclohexane ring have been synthesized (10-15). These liquid crystals, which are low in viscosity and have nematic mesophasic ranges near room temperature, are suitable for TN-display devices. The goal of this study is to present the synthesis and characterization of side-chain liquid crystalline polysiloxanes containing trans-4-methylcyclohexyl 4-alkenyloxybenzoate and trans-4-methylcyclohexyl 4'-alkenyloxybiphenyl-4-carboxylate side groups.

EXPERIMENTAL

Materials

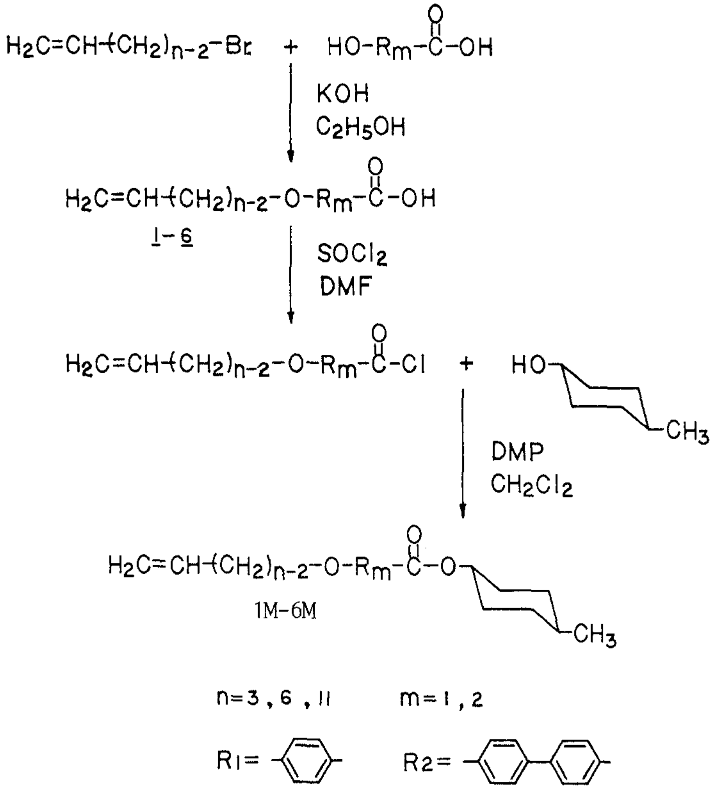
Poly(methylhydrogensiloxane) ($\overline{Mn}$=2270) was obtained from Petrarch System, Inc. and was used as received. trans-4-Methylcyclohexanol (TCI) and all other reagents were purchased from commercial sources and were used as received. Toluene used in the hydosilylation reaction was first refluxed over sodium and then distilled under nitrogen. Dicyclopentadienylplatinium(II) chloride catalyst was synthesized according to a literature procedure (16,17).

Techniques

Experimental techniques used in the characterization of intermediate compounds and of polymers are identical to those previously reported (1-6)

Synthesis of Monomers

The synthesis of the olefinic derivatives 1M-6M is outlined in Scheme 1.



Monomer	1M	2M	3M	4M	5M	6M
n	3	6	11	3	6	11
R_m	R_1	R_1	R_1	R_2	R_2	R_2

Scheme 1 : Synthesis of Monomers 1M-6M.

Synthesis of 4-alkenyloxybenzoic and (1-3) and 4'-alkenyloxybiphenyl-4-carboxylic acid (4-6).

Compounds **1-6** were synthesized by etherification of the corresponding alkenyl halides with either 4-hydroxybenzoic acid or 4'-hydroxybiphenyl-4-carboxylic acid. An example is described below. 4-Hydoxybenzoic acid (8 g, 0.058 mol) was added to a solution of potassium hydroxide (7.8 g, 0.139 mol) in 150 ml 90% ethanol. Potassium iodide (0.2 g) was added and the solution was heated to reflux temperature for 1 h. 6-Bromo-1-hexene (10.86 g, 0.067 mole) was slowly added and the solution was refluxed overnight. The solution was cooled and acidified with 6 N hydrochloric acid solution. The solid carboxylic acid was removed by filtration and recrystallized from a mixture of ethanol and water to yield 9 g (71%) of a white crystal : m.p=95.7 C. ^{1}H-NMR($CDCl_3$, δ,ppm):1.55-2.20 (m, 6H, $\text{-}(C\underline{H}_2)_3\text{-}CH_2\text{-}O\text{-}$), 4.05 (t, 2H,$\text{-}C\underline{H}_2\text{-}O\text{-}$), 5.02 (m, 2H, $=C\underline{H}_2$), 5.85 (m, 1 H, $\text{-}C\underline{H}=$), 6.92 and 8.05 (dd, 4 aromatic protons).

Synthesis of monomers 1M-6M

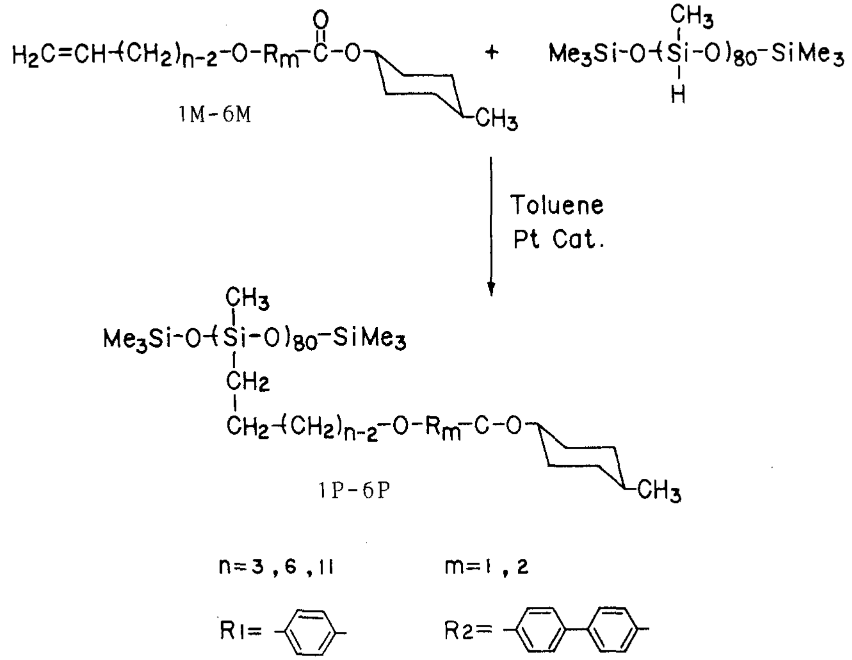
The olefinic derivatives 1M-6M were synthesized by the esterification of trans-4-methylcyclohexanol with either 4-alkenyloxybenzoic acid or 4'-alkenyloxybiphenyl-4-carboxylic acid. An example is described below. 4'-Allyloxybiphenyl-4-carboxylic acid (1.1 g, 4.33 mmol) was reacted at room temperature with excess thionyl chloride containing a drop of dimethyl formamide in 7 ml of methylene chloride for 2 h. The solvent was removed under reduced pressure to give the crude acid chloride. The product was dissolved in 10 ml of methylene chloride and slowly added to a cold solution of trans-4-methylcyclohexanol (0.543 g, 4.76 mmol) and 4-dimethylaminopyridine (0.7 g) in 100 ml of methylene chloride. The solution was allowed to stand for 2 h and then the solvent was removed by heating over a boiling water bath. The obtained crude product was purified by column chromatography (silica gel, ethyl acetate/n-hexane = 1:20 as eluent) to yield 0.8 g (53%) of a white crystal. Table 1 summarized the ^{1}H-NMR chemical shifts for all synthesized monomers 1M-6M.

Table 1 : Characterization of Monomers 1M-6M

Compound	300 MHz ^{1}H-NMR ($CDCl_3$, δ, PPM)
1M	0.92 to 2.07(m,12H,$\underline{H}_3C\text{-}C\underline{H}<^{C\underline{H}_2\text{-}C\underline{H}_2}_{C\underline{H}_2\text{-}C\underline{H}_2}$), 4.59(d,2H,$\text{-}C\underline{H}_2\text{-}O\text{-}$), 4.88 (tt,1$\underline{H}$,$\text{-}\overset{\overset{O}{\Vert}}{C}\text{-}O\text{-}C\underline{H}<$), 5.38(m,2H,$=C\underline{H}_2$), 6.06(m,1H,$\text{-}C\underline{H}=$), 6.91 and 7.97(dd, 4 aromatic protons).
2M	0.92 to 2.17(m,18H,$\text{-}(C\underline{H}_2)_3\text{-}$ and $\underline{H}_3C\text{-}C\underline{H}<^{C\underline{H}_2\text{-}C\underline{H}_2}_{C\underline{H}_2\text{-}C\underline{H}_2}$), 4.02(t,2H, $\text{-}C\underline{H}_2\text{-}O\text{-}$), 4.88(tt,1H,$\text{-}\overset{\overset{O}{\Vert}}{C}\text{-}O\text{-}C\underline{H}<$), 5.02(m,2H,$=C\underline{H}_2$), 5.85(m,1H, $\text{-}C\underline{H}=$), 6.89 and 7.79(dd,4 aromatic protons).
3M	0.90 to 2.06(m,28H,$\text{-}(C\underline{H}_2)_8\text{-}$ and $\underline{H}_3C\text{-}C\underline{H}<^{C\underline{H}_2\text{-}C\underline{H}_2}_{C\underline{H}_2\text{-}C\underline{H}_2}$), 3.79(t,2H, $\text{-}C\underline{H}_2\text{-}O\text{-}$), 4.88(tt,1H,$\text{-}\overset{\overset{O}{\Vert}}{C}\text{-}O\text{-}C\underline{H}<$), 4.96(m,2H,$=C\underline{H}_2$), 5.79(m,1H, $\text{-}CH=$), 6.86 and 7.94(m, 4 aromatic protons).
4M	0.92 to 2.07(m,12H,$\underline{H}_3C\text{-}C\underline{H}<^{C\underline{H}_2C\underline{H}_2}_{C\underline{H}_2C\underline{H}_2}$), 4.57(d,2H,$\text{-}C\underline{H}_2\text{-}O\text{-}$), 4.90 (tt,1H,$\text{-}\overset{\overset{O}{\Vert}}{C}\text{-}O\text{-}C\underline{H}<$), 5.38(m,2H,$=C\underline{H}_2$), 6.06(m,1H,$\text{-}C\underline{H}=$), 6.98 to 8.06(m,8 aromatic protons).
5M	0.92 to 2.16(m,18H,$\text{-}(C\underline{H}_2)_3\text{-}$ and $\underline{H}_3C\text{-}C\underline{H}<^{C\underline{H}_2\text{-}C\underline{H}_2}_{C\underline{H}_2\text{-}C\underline{H}_2}$), 4.00(t,2H, $\text{-}C\underline{H}_2\text{-}O\text{-}$), 4.90(tt,1H,$\text{-}\overset{\overset{O}{\Vert}}{C}\text{-}O\text{-}C\underline{H}<$), 5.00(m,2H,$=CH_2$), 5.81(m,1H, $\text{-}C\underline{H}=$), 6.94 to 8.06(m, 8 aromatic protons).
6M	0.91 to 2.09(m,28H,$\text{-}(C\underline{H}_2)_8\text{-}$ and $\underline{H}_3C\text{-}C\underline{H}<^{C\underline{H}_2\text{-}C\underline{H}_2}_{C\underline{H}_2\text{-}C\underline{H}_2}$), 3.98(t,2H, $\text{-}C\underline{H}_2\text{-}O\text{-}$), 4.87 to 5.05(m,3H,$\text{-}\overset{\overset{O}{\Vert}}{C}\text{-}O\text{-}C\underline{H}<$ and $=C\underline{H}_2$), 5.80(m,1H, $\text{-}C\underline{H}=$), 6.94 to 8.06(m, 8 aromatic protons).

Synthesis of Polymers 1P-6P

All of the polymers 1P-6P were synthesized by the hydrosilylation of the poly(methylhydrogensiloxane) with the olefinic monomers 1M-6M in the presence of a Pt catalyst (Scheme 2). Experimental details concerning the synthesis and purification of these polymers are identical to those previously reported (2-4).



polymer	1P	2P	3P	4P	5P	6P
n	3	6	11	3	6	11
Rm	R1	R1	R1	R2	R2	R2

Scheme 2 : Synthesis of Polysiloxanes 1P-6P.

RESULTS AND DISCUSSION

The phase transitions and enthalpies for the monomers 1M-6M are summarized in Table 2. Among monomers 1M to 3M, which are the trans-4-methylcyclohexyl 4-alkenyloxybenzoates, monomers 1M and 2 M show no liquid crystilline phase while monomer 3M show a monotropic nematic phase. All of the monomers 4M-6M, which are the trans-4-methylcyclohexyl 4'-alkenyloxybiphenyl-4-carboxylates, diplay mesophases. Monomer 4M presents an enantiotropic nematic phase while monomers 5M and 6M present enantiotropic nematic and S_A phase. The results demonstrate that as the length of alkenyloxy groups increases, the tendency toward smectic mesomorphism increases and the isotropization temperature decreases. Furthermore, increasing the mesogenic core length from a phenyl group to a biphenyl group is conductive to the formation of a more stable mesophase.

Table 3 summarizes the phase transitions and thermodynamic parameters of the synthesized plymers. All of the polymers except 1P and 2P exhibit liquid crystalline phases. Both polymers 1P and 2P show only a glass transition (Tg) on either heating or cooling scan. Polymer 3P presents a Tg and an enantiotropic smectic phase while polymer 4P presents a Tg and an enantiotropic nematic phase. Figure 1 illustrates some representative DSC traces of polymer 5P. On the first heating scan (curve A), it shows a Tg at 19 °C, two melting transitions at 73°C and 93°C, a smectic to nematic transition at 182°C and a nematic to isotropic transition at 194°C. On the cooling scan (curve B), the melting transition is supercooled and overlappes with the Tg. This gives rise to a recrystallization transitions (Tr) at 64°C on the next heating scan (curve C) followed by a melting transition at 84 °C. Figure 2. shows the typical nematic and smectic textures exhibited by polymer 5P . Polymer 6P presents a melting transition and a smectic to isotropic transition on both heating and cooling scans.

Table 2 : Phase transitions and thermodynamic parameters of the monomers 1M-6M

Monomer	Phase Transitions (°C), and Enthalpy Changes, ΔH (Kcal/mol)[a]					
	Heating			Cooling		
	$T_m(\Delta H_m)$	$T_1(\Delta H_1)$	$T_i(\Delta H_i)$	$T_i(\Delta H_i)$	$T_1(\Delta H_1)$	$T_c(\Delta H_c)$
1M	K 31(4.60)	--(---)	--(---) I	I --(---)	--(---)	-8(0.17)K
2M	K 38(5.50)	--(---)	--(---) I	I --(---)	--(---)	-4(3.96)K
3M	K 37(9.17)	--(---)	--(---) I	I 24(0.36)N	--(---)	2(4.52)K
4M	K117(4.60)	--(---)	N146(0.18)I	I142(0.15)N	--(---)	97(3.57)K
5M	K109(4.98)	--(---)	N138(0.19)I	I137(0.20)N	105(0.20)S_A	80(3.57)K
6M	K 81(4.47)S_A	119(0.70)N	127(0.37)I	I125(0.36)N	118(0.84)S_A	13(3.40)K

a) K = crystalline, S = smectic, N = nematic, I = isotropic.

Table 3 : Phase transitions and thermodynamic parameters of the polymers 1P-6P

Polymer	Phase Transitions (°C), and Enthalpy Changes, ΔH(Kcal/mru)[a]						
	Heating				Cooling		
	T_g	$T_m(\Delta H_m)$	$T_1(\Delta H_1)$	$T_i(\Delta H_i)$	$T_i(\Delta H_i)$	$T_1(\Delta H_1)$	$T_c(\Delta H_c)$
1P	G22	--(---)	--(---)	--(---)I	II--(---)	--(---)	--(---)
2P	G 7	--(---)	--(---)	--(---)I	I --(---)	--(---)	--(---)
3P	G-1	--(---)	--(---)S	63(0.83)I	I 58(0.84)S	--(---)	--(---)
4P	G47	--(---)	--(---)N	178(0.20)I	I176(0.21)N	--(---)	--(---)
5P	G32	K84(0.39)S_A	179(--)N	193(0.67^b)I	I191(0.73^b)S_A	176(--)N	49(0.07)K
6P	G16	K62(0.20)S_A	--(--)	218(1.29)II	I212(1.08) S_A	--(--)	58(0.16)K

a) mru = mole of repeating units. G = glassy, K = crystalline, S = smectic, N = nematic, I = isotropic.

b) overlapped transitions, $\Delta H_i = \Delta H_i + \Delta H_1$.

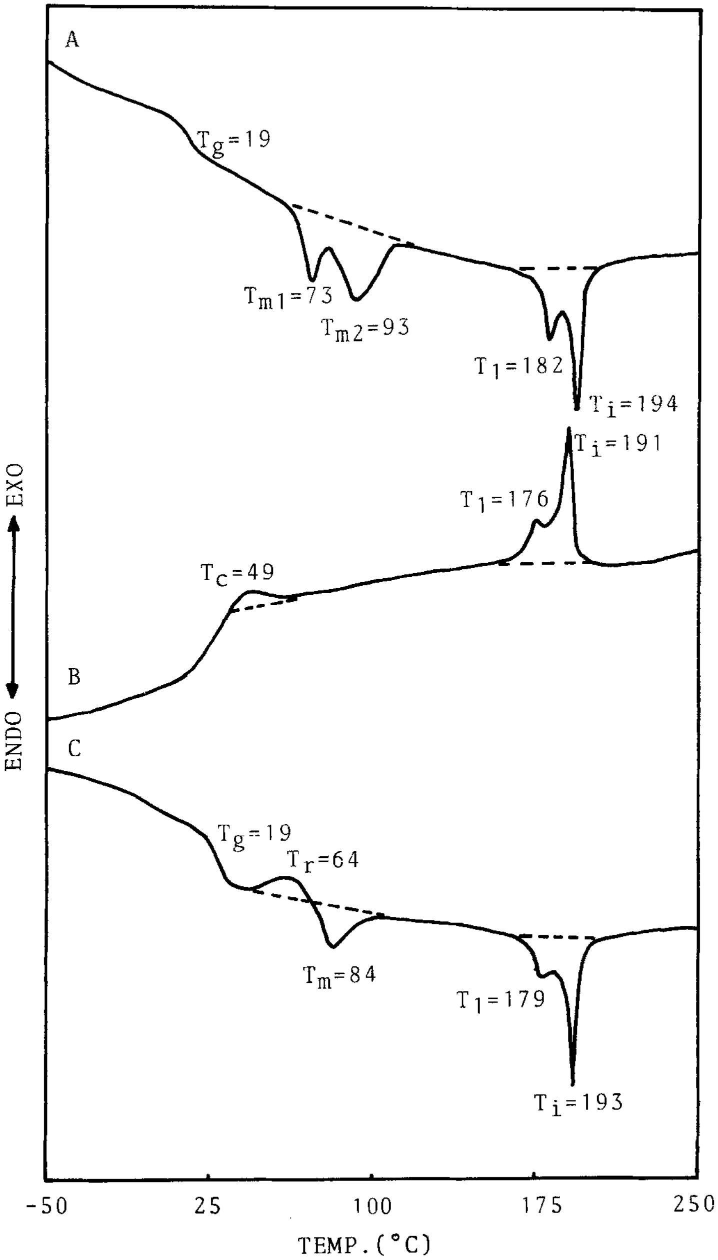


Figure 1: Normalized DSC thermograms (10°C/min) of polymer 5P : A) First heating scan; B) First cooling scan; C) Second heating scan.

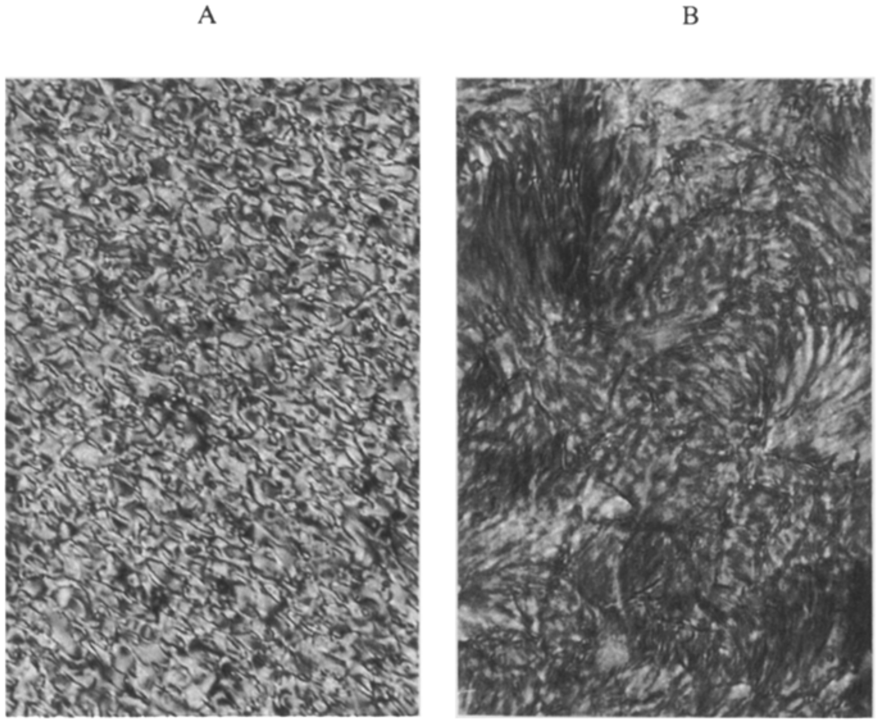


Figure 2 : Optical polarizing micrographs displayed by polymer 5P upon cooling from isotropic phase : A) The nematic schlieren texture obtained at 191.7℃; B) The smectic texture obtained at 170℃.

In conclusion, the mesophase formed by a side chain liquid crystalline polymer is more organized than the one exhibited by the corresponding monomer. As the mesogenic core length changes from a phenyl group to a biphenyl group, the tendency toward mesophase formation increases and the thermal stability of the formed mesophases also increases. The glass transition temperature decreases with increasing spacer length while the isotropization temperature and the tendency toward side chain crystallization increase. In order to study the thermal stability of prepared polymers, they were heated to the temperature above 200°C and then measured by ^{1}H-NMR spectroscopy and DSC. Both the 300 MHz ^{1}H-NMR spectra and DSC traces of the heat treated samples are completely identical to those of the untreated samples. The results reveal that the cyclohexane ring is very stable and no trans-cis isomerization for the trans-cyclohexane based mesogens occures.

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