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Synthesis of side-chain liquid crystalline polyacrylates, polymethacrylates and polysiloxanes containing 4-cyano-biphenyl 4-alkanyloxybenzyl ether side groups

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Summary

The synthesis and characterization of side-chain liquid crystalline polyacrylates, polymethacrylates and polysiloxanes containing 4-cyanobiphenyl 4-alkanyloxybenzyl ether side groups are presented. All polymers display respectively a smectic A mesophase. The influence of the polymer backbone flexibility on the phase transition temperatures of the synthesized side-chain liquid crystalline polymers is discussed. The results demonstrate that flexible backbones enhance the decoupling of the motions of the side chain and main chain. Therefore, among three kinds of polymer backbones which contain the same mesogenic side groups, the most flexible one, i.e., polysiloxane, reveals a highest isotropization temperature and a widest temperature range of mesophase.

Introduction

Side-chain liquid crystalline polymers (LCPs) have been widely studied in the past decade because these polymers are of both theoretical and parctical interest. This field has been repeatedly reviewed (1-5). The vast majority of LCPs synthesized, contain rigid rod-like mesogens. Recently, we demonstrated the possibility to synthesize a side-chain LCP containing flexible rigid rod-like mesogens (6-8). The particular examples refer to mesogenic units in which the interconncting group between two aromatic units represents a flexible "ethyl" or "methyleneoxy" linkage. The mesogens are flexible and therefore undergo free rotation, leading to a number of different conformational isomers which are in dynamic equilibrium. Consequently, a polymer containing these flexible rod-like mesogens behaves as a copolymer containing anti or gauche isomeric mesogens.

In this paper, we present the synthesis and characterization of side-chain LC polyacrylates, polymethacrylates and polysiloxanes containing 4-cyanobiphenyl 4-alkanyloxybenzyl ether side groups. The effects of polymer backbone and spacer length on the phase transition temperatures of the obtained polymers are discussed.

Experimental

Materials

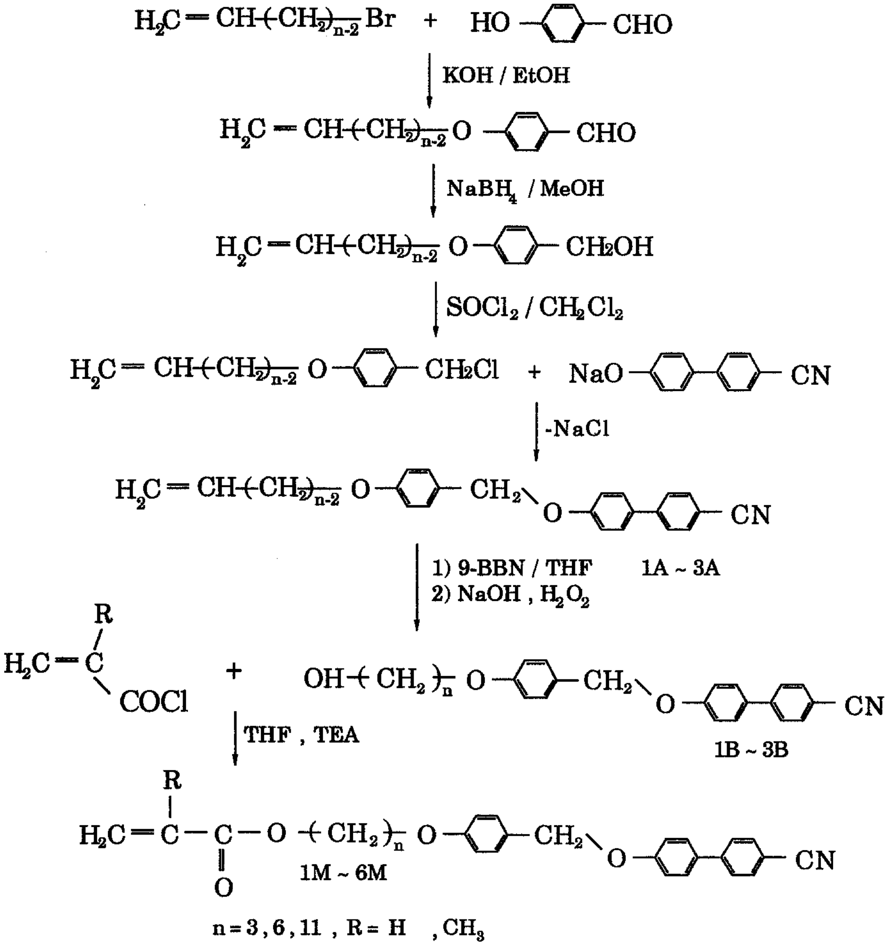
Poly(methylhydrogensiloxane) $(\overline{Mn} = 4500 - 5000)$ was obtained from Petrarch System, Inc. and was used as received. All other reagents were purchased from Aldrich and used as received. Toluene and 1,3-dioxane used in the polymerization reactions were first reflexed over sodium and then distilled under nitrogen. Dicyclopentadienylplatinium (II) chloride catalyst was synthesized according a literature procedure (9,10).

Techniques

The characterization of all polymers was pereformed by a combination of differential scanning calorimetry (DSC) optical polarizing microscopy and gel permeation chromatography (GPC) according to standard procedures used in our laboratory (6,7).

Synthesis of monomers 1M - 6M

The synthesis of the polyacrylate monomers 1M - 3M and polymethacrylate monomers 4M - 6M is outlined in Scheme 1. The detailed synthetic procedures for the intermediary compounds and monomers are similar to those reported previously (4,5). Table 1 summarizes the ^1H - NMR chemical shifts of monomers 1M - 6M.



Scheme 1 : Synthesis of monomers **1M ~ 6M**

Table 1. Characterization of monomers **1M ~ 6M**

Monomer	n	yield (%)	400 M Hz ^1H - NMR (δ, ppm)
1M	3	75	2.15 (m, 2H, $-C\underline{H}_2-$) , 4.06 (t, 2H, $-C\underline{H}_2O-$) 4.35 (t, 2H, $-COO-C\underline{H}_2-$), 5.02 (s, 2H, $-Ph-C\underline{H}_2O-$), 5.80- 6.43 (m, 3H, $\underline{H}_2C = C\underline{H}-$), 6.89 - 7.69 (m, 12 aromatic protons)
2M	6	78	1.18 - 1.81 [m, 8H, $-(C\underline{H}_2)_4-$] , 3.89 (t, 2H, $-C\underline{H}_2O-$), 4.08 (t, 2H, $-COO-C\underline{H}_2-$), 4.97 (s, 2H, $-Ph-C\underline{H}_2O-$) ,5.81- 6.37 (m, 3H, $\underline{H}_2C = C\underline{H}-$), 6.81 - 7.72 (m, 12 aromatic protons)
3M	11	90	1.18 - 1.81 [m, 18H, $-(C\underline{H}_2)_9-$] , 3.94 (t, 2H, $-C\underline{H}_2O-$), 4.13 (t, 2H, $-COO-C\underline{H}_2-$), 5.02 (s, 2H, $-Ph-C\underline{H}_2O-$) ,5.77- 6.41 (m, 3H, $\underline{H}_2C = C\underline{H}-$), 6.88 - 7.69 (m, 12 aromatic protons)
4M	3	69	1.87 (s, 3H, $-C\underline{H}_3-$) , 2.06 - 2.12 (m, 2H, $-C\underline{H}_2-$) , 4.01 (t, 2H, $-C\underline{H}_2O-$), 4.28 (t, 2H, $-COO-C\underline{H}_2O-$), 4.97 (s, 2H, $-Ph-C\underline{H}_2O-$) ,5.49 and 6.04 (m, 2H, $\underline{H}_2C =$), 6.84 - 7.63 (m, 12 aromatic protons)
5M	6	64	1.18 - 1.80 [m, 8H, $-(C\underline{H}_2)_4-$] , 1.87 (s, 3H, $C\underline{H}_3-$), 3.90 (t, 2H, $-C\underline{H}_2O-$) , 4.09 (t, 2H, $-COO-C\underline{H}_2-$),4.97 (s, 2H, $-Ph-C\underline{H}_2O-$) ,5.84 and - 6.03 (m, 2H, $\underline{H}_2C =$), 6.85 - 7.63 (m, 12 aromatic protons)
6M	11	56	1.30 - 1.81 [m, 18H, $-(C\underline{H}_2)_9-$], 1.95 (s, 3H, $C\underline{H}_3-$), 3.97 (t, 2H, $-C\underline{H}_2O$) , 4.14 (t, 2H, $-COO-C\underline{H}_2O-$), 5.04 (s, 2H, $-Ph-C\underline{H}_2O-$) ,5.55 and 6.10 (m, 2H, $\underline{H}_2C =$), 6.91 - 7.71 (m, 12 aromatic protons)

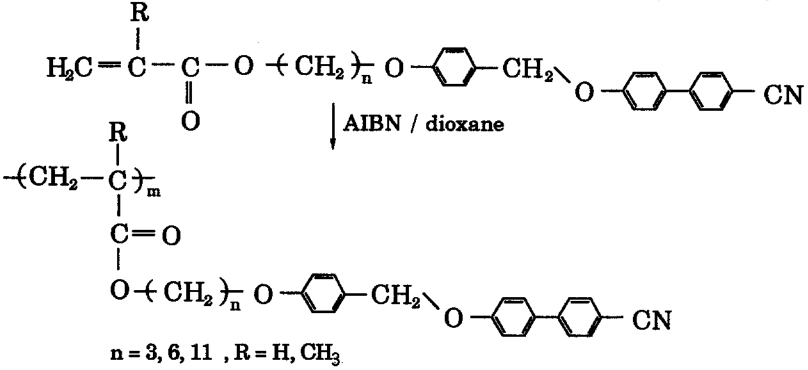
n according to scheme 1.

Synthesis of side-chain LC polyacrylates 1P~3P and polymethacrylates 4P-6P

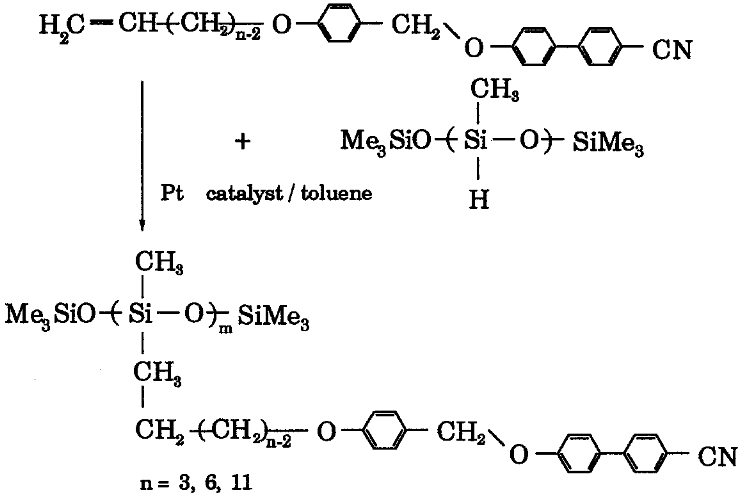
The synthesis of polymers 1P-6P is outlined in Scheme 2. Radical polymerization of the monomers were carried out on Schlenk-tubes, equipped with septums, under argon. The polymerization tubes, containing the monomer solution in 1,4-dioxane (10 g/dl) and the initiator (AIBN : 1 wt.-% vs. monomer) were first degassed by seversl freeze-pump-thaw cycles under vacuum, and then filled with argon. All polymerizations were carried out at 60 °C for 15 h. After the polymerization time the polymers were precipitated into methanol, filtered and purified by reprecipitation from THF solutions into methanol.

Synthesis of side-chain LC polysiloxanes 7P-9P

All the polymers 7P-9P were synthesized by the hydrosilylation of the poly(methylhydrogensiloxane) with the olefinic monomers (1A~3A) in the presence of a Pt catalyst (Scheme 3). Experimental details concerning the synthesis and purification are identical to those reported previously (8,11).



Scheme 2 : Synthesis of polyacrylates **1P ~ 3P** and polymethacrylates **4P ~ 6P**.



Scheme 3 : Synthesis of polysiloxanes **7P ~ 9P** .

Results and Discussion

Table 2 summarizes the thermal transition and thermodynamic parameters of the synthesized intermediary compounds and monomers 1M-6M. Compounds 1A~3A are the olefinic compounds which were used for the hydrosilylation reaction. Among three compounds, 1A and 2A present an enantiotropic nematic mesophase while 3A show an enantiotropic smectic A mesophase. Figures 1A and 1B display the typical nematic schlieren texture and smectic A fan texture exhibited respectively by 1A and 3A. The results reveal that a longer alkenyloxy end group will lead to the formation of a wider and a more ordered mesophase. The compounds 1B~3B which were synthesized by the hydroboration of the corresponding alkenes 1A~3A, show very similar mesomorphic behavior to that of the compounds 1A~3A. The thermal transitions of monomers 1M-6M are also summarized in Table 2. Only those data on their DSC heating scans were recorded because the monomers were polymerized above certain temperature and hence the DSC cooling scans were not reproducible. All monomers present mesomorphic behavior. Those containing 3 or 6 methylene units in the spacers show a nematic mesophase while the other two monomers containing 11 methylene units in the spacers present a smectic A mesophase.

Table 2. Thermal transitions and thermodynamic parameters of compounds **1A ~ 3A** and **1B ~ 3B** and monomers **1M ~ 6M**.

Compound[a] or monomer	n[a]	Thermal transition, °C (corresponding enthalpy changes, Kcal / mol)[b] heating	cooling
1A	3	k 153 (5.35) N 170 (0.56) i	i 169 (0.49) N 107 (4.64) k
2A	6	k 91 (3.32) N 148 (0.27) i	i 148 (0.35) N 53 (2.82) k
3A	11	k 61 (6.14) S_A 147 (1.48) i	i 146 (1.27) S_A 43 (5.02) k
1B	3	k 150 (5.98) N 193 (0.67) i	i 192 (0.77) N 121 (5.43) k
2B	6	k 105 (3.90) N 184 (0.13) i	i 177 (0.08) N 92 (4.50) k
3B	11	k 123 (10.2) S_A 141 (1.01) i	i 137 (0.96) S_A 88 (8.82) k
1M	3	k 118 (10.7) N 141 (0.50) i	---
2M	6	k 109 (10.9) N 114 (0.20) i	---
3M	11	k 107 (10.1) S_A 119 (0.36) i	---
4M	3	k 114 (10.6) N 127 (0.3) i	---
5M	6	k 111 (10.2) N 126 (0.4) i	---
6M	11	k 110 (16.0) S_A 124 (1.4) i	---

[a] According to Scheme 1.

[b] k = crystalline , N = nematic , S = smectic.

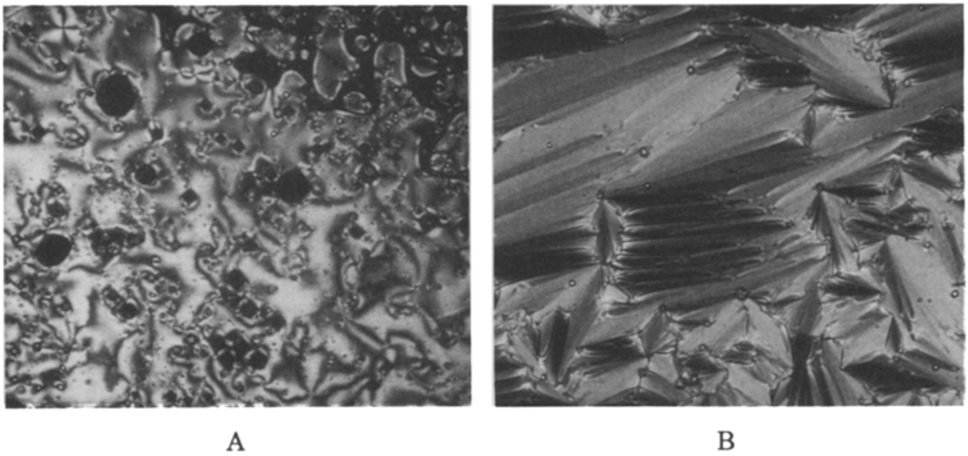
Table 3 summarizes the thermal transitions and thermodynamic parameters of the synthesized polymers 1P~9P. All polymers present smectic mesomorphism. Figure 2 displays two representative DSC traces of polymer

Table 3. Characterization of polymers **1P** ~ **6P**.

polymers[a]	$\overline{Mn}$	$\frac{\overline{Mw}}{\overline{Mn}}$	$\overline{DP}$	Thermal transition , °C (corresponding enthalpy charges , Kcal / mru)[b]
1P	6020	1.34	14	g 26 S_A 148 (0.52) i i 139 (0.47) S_A
2P	6500	1.29	14	g 22 S_A 145 (0.48) i i 140 (0.43) S_A
3P	14870	1.38	28	g 20 S_A 174 (1.06) i i 156 (1.05) S_A
4P	16660	1.47	39	g 50 S_A 114 (0.49) i i 110 (0.40) S_A
5P	17490	1.42	37	g 41 S_A 142 (0.48) i 134 (0.44) S_A
6P	31300	1.38	58	g 25 S_A 178 (1.05) i i 161 (0.89) S_A
7P	--	--	80	g 15 S_A 154 (0.50) i i 153 (0.53) S_A g
8P	--	--	80	g -8 S_A 159 (0.63) i 151 (0.60) S_A
9P	--	--	80	g 15 S_A 217 (1.08) i 197 (1.08) S_A

[a] According to Schemes 2 and 3.

[b] mru = mole repeating , g = glassy , S = smectic , i = isotropic.

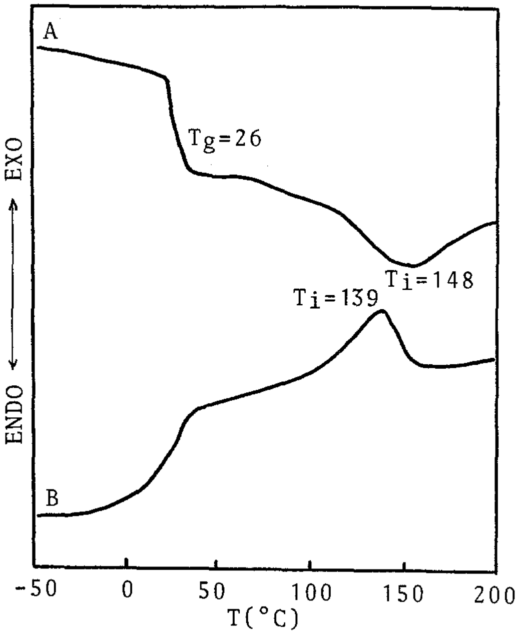


A B

Figure 1 : Optical polarizing micrographs (320 x) : A) The nematic texture displayed by 1A at 165 °C ; B) The smectic A texture displayed by 3A at 143 °C.

1P. It reveals a glass transition temperature at 26 °C, followed by a smectic A to isotropic phase transition at 148 °C. Upon cooling, the isotropic to semectic A phase transition presents at 139 °C. Figure 3 show the typical focal-conic smectic A texture exhibited by 1P. Comparing the mesomorphic behavior of polymers with that of corresponding monomers, we can find that the mesophase formed by a side-chain LCP is more organized than the one exhibited by the correspinding monomers. This phenomenon is so called "polymer effect" and always true in most cases.

Figure 2 : DSC thermograms of polymers 1P : A) heating scan; B) cooling scan.



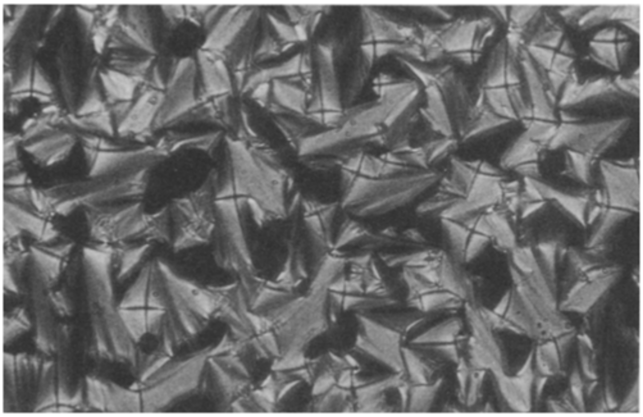


Figure 3 : Optical polarizing micrograph (320x) displayed by polymer 1P at 135 °C.

Finally we could make some comments on the influence of polymer backbone on the phase transition within each series of polymers based on the same spacer length. Since the molecular weights of different kinds of polymers have very different value, we should first consider the effect of molecular weight on the phase transitions of the LCPs. So far, there is a general agreement that on increasing the molecular weight of a LC polymer, both glassy and liquid crystalline transition temperatures increase up to a certain molecular weight beyond which they are molecular weight independent. In most cases of side-chain LCPs, thermal transition temperatures are molecular weight independent when the degree of polymerization is greater than about 10-12 (1, 12,-15). As can be seen from Table 3, the degree of polymerization of all synthesized polymer is higher than 14 and therefore we can quantitatively investigate the effect of polymer backbone on the phase transitions of the LCPs. The data listed in Table 3 reveal that the glass transition temperatures decrease with increasing the polymer backbone flexibility while the isotropization temperatures increase. Therefore the mesomorphic overall temperature range of smectic A increases with increasing polymer backbone flexibility. This means that flexible polymer backbones enhance the decoupling of the motions of the side chain and main chain in the side-chain LCPs.

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