

## Liquid crystalline side-chain polysiloxanes containing mesogenic groups attached by esterification

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### SUMMARY

Liquid crystalline side-chain polysiloxanes were prepared without metal complex catalyst. Mesogenic groups such as cholesteryl, 4-cyano-4'-biphenyl and 4-methoxy-4'-biphenyl group were introduced into polysiloxane by esterification and from DSC measurements they were compatible with other liquid crystalline polysiloxanes reported previously.

### INTRODUCTION

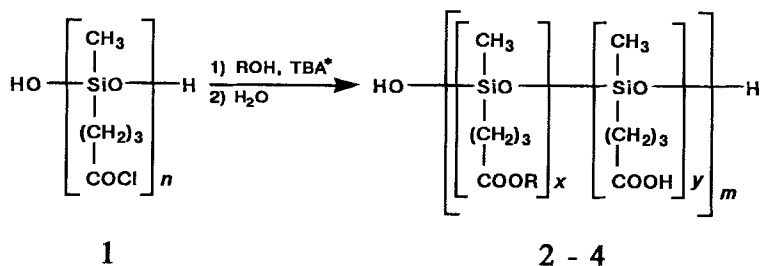
Studies on liquid crystalline side-chain polymers have focused on the influences of nature, size, or structure of mesogenic groups on liquid crystalline properties(1, 2). Liquid crystalline polymers usually exhibit a mesophase in the range from glass transition temperature ( $T_g$ ) to clearing temperature ( $T_c$ ). So, polysiloxane, which has a low  $T_g$ (3, 4), is often used as a backbone of a liquid crystalline side-chain polymer in order to make a mesophase appear in a lower temperature range. Though there are many such types of liquid crystalline polysiloxanes, they have been prepared by means of hydrosilation reaction(5) catalyzed by metal complexes between Si-H groups of polysiloxane backbone and vinyl substituted mesogen. In hydrosilation reaction, Gray *et al.*(6) have reported, unfavorable side reactions occur and metal complex catalyst can not be removed completely after the reaction. Metals remained in the polymer influence undesirably on its conductivity, dielectric constant, and so on. Therefore it is of deep significance to prepare liquid crystalline side-chain polysiloxanes without metal complex catalyst.

In the present article, a pathway for preparing it by esterification, instead of hydrosilation, without metal complex catalyst and its thermal behaviors are described.

### EXPERIMENTAL

Poly[(3-chlorocarbonylpropyl)methylsiloxane] 1 was prepared by the method reported elsewhere(7). Cholesterol was obtained from Kanto Chemical Co., Inc. and recrystallized from ethanol before use. 4-Cyano-4'-hydroxy-biphenyl was purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. 4-Methoxy-4'-hydroxybiphenyl was prepared from 4,4'-dihydroxybiphenyl (Tokyo Kasei Kogyo Co., Ltd.) and dimethylsulfate following the method of Percec *et al.*(8). Preparation of the liquid crystalline side-chain polysiloxanes was carried out by the methods as follows. Under a dry nitrogen atmosphere, a dry tetrahydrofuran (THF) solution (40 ml) of a hydroxyl substituted mesogenic group with 1.39 g (7.52 mmol) of tri-*n*-butylamine was added dropwise to a dry THF solution (10 ml) of 1.65 g (6.84 mmol) of 1 ( $\overline{M}_n=2500$ ,  $\overline{M}_w/\overline{M}_n=2.02$  determined by GPC), and the reaction mixture was stirred for 18 h. Molar ratios of mesogenic groups in

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Polymer	R
2	
3	
4	

\*TBA: tri-*n*-butylamine

Scheme 1. Pathway for the syntheses of liquid crystalline side-chain polysiloxanes.

the feed are given in Table 1. After an addition of 30 ml of chloroform to the reaction vessel, this mixture was poured into 200 ml of water and stirred at ambient temperature in order to completely convert residual COCl groups into COOH groups. The organic layer was washed with water several times and dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude products were purified by reprecipitation with a diethylether/methanol system for polymer 2, with a chloroform/methanol system for polymer 3, and with a THF/diethylether system for polymer 4. Then the obtained products were dried at 80°C *in vacuo*. The compositions of the resulting polysiloxanes were determined from <sup>1</sup>H-NMR spectra (Hitachi R-1100). Polarized microscopy observations were performed using a OLYMPUS BH-2. DSC measurements were carried out on a Shimadzu DSC-50 at a heating rate of 10 °C/min and a He flow rate of 20 ml/min. All DSC results were obtained from second heating of samples.

## RESULTS AND DISCUSSION

Table 1 shows the characterization of the resulting polysiloxanes, and Figure 1 shows some DSC curves of them. They were obtained with yields of 70%-90%. Introduction ratio of the mesogenic groups seems to be controlled by varying in molar ratio of the mesogenic groups in the feed. The increase in the introduction ratio of mesogenic groups in these

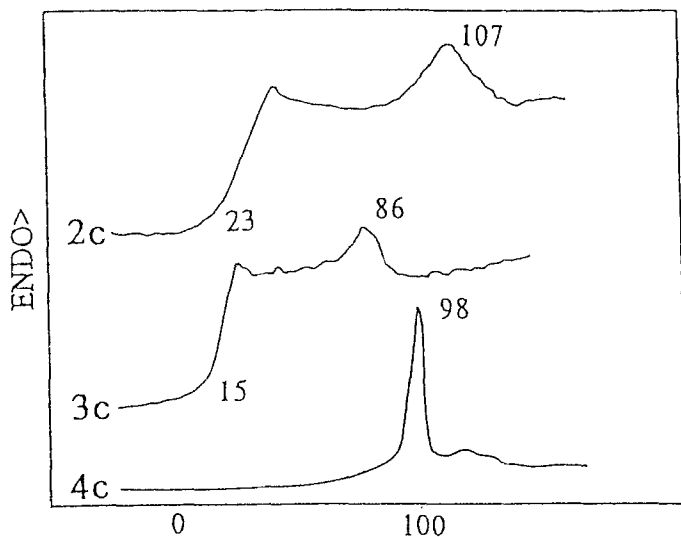


Figure 1. DSC thermograms of polymer 2c, 3c and 4c (second heating scan, 10°C/min)

Table 1. Characterization of polysiloxanes					
polymer	molar ratio of mesogen/1 in the feed	$x^a$ (%)	$y^a$ (%)	$T_g^b$ (°C)	$T_c^b$ (°C)
2a	1.0	86	14	16	58
2b	1.5	91	9	22	95
2c	2.0	98	2	23	107
3a	1.0	91	9	7	61
3b	1.5	95	5	9	64
3c	2.0	99	1	15	86
4a	1.0	81	19	---	91
4b	1.5	83	17	---	95
4c	2.0	88	12	---	98

a) Determined from  $^1\text{H-NMR}$  spectra.

b) Determined from DSC thermograms (second heating scan)

polymers caused  $T_g$  and  $T_c$  to be raised. In case of polymer 2 and 3, when the introduction ratio of mesogenic groups is over ca. 85 mol%,  $T_c$  peaks could be observed on DSC thermograms. Glass transition of a series of polymer 4 was not observed on the DSC thermograms, and accurate identification of them is not yet available to us. According to polarized microscopy observations, polymers 2a-c and polymers 3a-c displayed batonnet formation and mosaic texture, respectively. Therefore, their mesophases are considered to be certain kinds of smectic mesophases. In comparison polymer 2c, 3c and 4c with polymers which were synthesized by Finkelmann *et al.*(9) and Ringsdorf *et al.*(10) by applying hydrosilation reaction and had similar structure for the polymer 2c, 3c and 4c, there are not great differences in the temperature ranges of mesophase and transition temperatures.

In conclusion, the present method for preparation of liquid crystalline side-chain polysiloxanes is effective, because it can be performed without metal complex catalyst which is difficult to be removed after the reaction.

### ACKNOWLEDGEMENT

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