

Physical and Response Properties of Side-chain Liquid Crystalline Polymers Containing Siloxane Bond in the Spacer Component

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The synthesis and mesomorphic properties of the side-chain liquid crystalline polymers (SCLCP) containing a very flexible siloxane bond in the spacer component were investigated. The introduction of siloxane component resulted in the great decrease of glass transition temperature of the polymers. The copolymers were prepared by radical polymerization of 4'-cyanobiphenyl-4-oxyhexyl acrylate (CBHA) with a few methacrylate-type comonomers having a siloxane spacer between the mesogen and the methacryloyl group. The obtained copolymers exhibited a nematic phase, when the composition of the comonomer was below 40 mol%. T_g and T_i of the copolymers were decreased with increase of the comonomer component. Also, the optical switching of the copolymers in the electric field were observed at the lower temperature range than the case of homopolymer, poly-CBHA.

1. Introduction

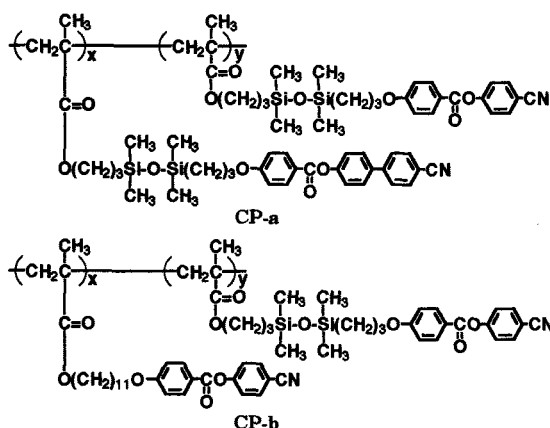
Recently, a large variety of side-chain liquid crystalline polymers (LCPs) has been investigated, which has become of increasing interest because of their theoretical and technological aspects¹. In order to obtain the mesophase of side-chain LCPs, the introduction of flexible spacer groups between the polymer main chain and the mesogenic side chain is necessary to decouple the motions of the backbone component from those of the anisotropically oriented mesogenic group². In these years, we have been investigating the synthesis and thermal properties of side-chain LCPs containing a siloxane bond in the spacer component³⁻⁷. In this paper, the synthesis and mesomorphic properties of the side-chain liquid crystalline polymethacrylates and their copolymers containing a very flexible siloxane bond in the spacer component are discussed. Also, the optical response ability of a series of the

copolymers containing siloxane spacer are disclosed.

2. Synthesis of monomers and polymers

The synthetic diagram of the monomers containing a siloxane spacer is shown in *Scheme 1*. For the synthesis of suitable monomers **4** and **5**, novel silanol compounds **3** carrying mesogenic groups were prepared from the corresponding mesogenic alkenyloxy compounds **1** via hydrosilylation with dimethylethoxysilane, followed by hydrolysis of the ethoxysilyl group. The monomer **4** having a disiloxane unit was prepared by condensation of **3** with 3-(chlorodimethylsilyl)propyl methacrylate in good yields.

The polymethacrylates were obtained by an ordinary radical polymerization of the monomers in the presence of 2,2'-azoisobutyronitrile (AIBN) as an initiator⁴. The copolymers were also prepared by the same manner with comonomers^{5,7}.



At first, we prepared the copolymers containing a biphenyl benzoate mesogen and a phenyl benzoate mesogen with the same backbone and spacer structures (CP-a)⁵. The parent homopolymer of x component showed a smectic A phase between 26 and 235°C, and that of y component showed no mesophase. Successfully, the copolymer CP-a exhibited a nematic phase with wide temperature range. This y component would disturb the orientation of mesogens in x component to exhibit a nematic phase. In this case, T_g and T_i tend to decrease with increase of the comonomer units. Furthermore, when the y

component was over 60 mol%, no mesophase was observed.

Next, the copolymers with a methacrylate-type monomer containing polymethylene spacer (CP-b) was investigated⁷. The parent homopolymer of x component also exhibited smectic phases including a highly ordered one. In this case, however, the smectic phase was observed in the copolymer of the y component with around 20 mol%. The nematic phase appeared only in the composition of x/y = 50/50. Probably, this long polymethylene spacer in x component would promote the orientation of the side chain.

Acrylate/methacrylate copolymers (CP-c, CP-d and CP-e) were also prepared by radical polymerization of 4'-cyanobiphenyl-4-oxyhexyl acrylate (CBHA) with a few methacrylate-type comonomers having a siloxane spacer, as shown below. Poly-CBHA has been known as one of the nematic LCs¹. The obtained copolymers exhibited a nematic phase, when the composition of the comonomer was below 30 - 40 mol%, as seen in Table 2. T_g and T_i of the copolymers were decreased with increase of the comonomer component.

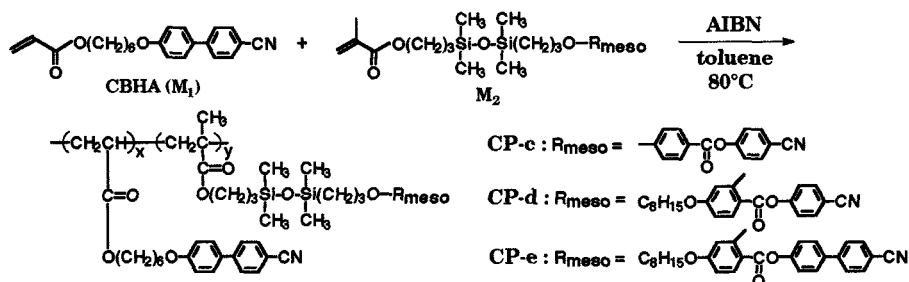


Table 2 Characterizations of copolymers CP-c, CP-d and CP-e.

Code	M ₁ /M ₂	x/y	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	Transition Temp. (°C)
poly-CBHA	100/0	100/0	4.63	7.16	g 32 N 117 I
CP-c1	90/10	92/ 8	3.21	4.32	g 13 N 82 I
CP-c2	75/25	71/29	4.52	7.52	g 12 N 63 I
CP-c3	60/40	60/40	10.6	13.4	g 10 N 40 I
CP-c4	40/60	42/58	13.3	18.3	g 9 I
CP-d1	95/ 5	94/ 6	5.74	9.54	g 28 N 95 I
CP-d2	92/ 8	90/10	8.39	16.4	g 24 N 85 I
CP-d3	90/10	81/19	8.06	12.0	g 11 N 43 I
CP-d4	70/30	68/32	9.24	14.8	g 10 I
CP-e1	90/10	89/11	8.56	19.4	g 29 N 89 I
CP-e2	70/30	67/33	13.2	19.7	g 17 N 48 I

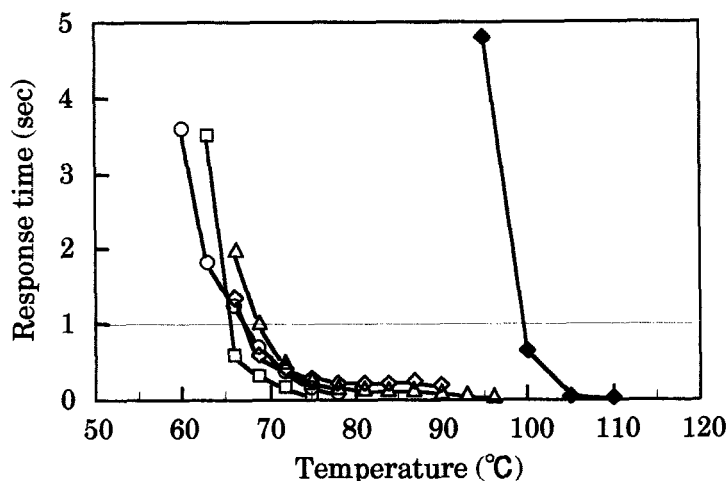


Fig. 1 Effect of temperature on the response time of polymers (Applied voltage = 200 Vp-p).
 ◆: poly-CBHA, □: CP-c1, △: CP-d1, ○: CP-d2, ◇: CP-e1.

4. Optical switching property

The preliminary study for the optical switching in the electric field was carried out. Copolymer samples were placed between the ITO glass plates (thickness: 9 μm), and it was placed in the hot stage. Then, the rectangular alternating current of 200 Hz was applied to the sample, and the transmitted light intensity through the optical polarizing microscope was observed by the photomultiplier. When the nematic copolymer responds to the current, the mesogens orient homeotropically. At that time, the transmittance was recorded on the Oscilloscope, and the response time from 100 % transmittance to 0 % was determined. Thus, the effect of temperature on the switching behavior was investigated.

Fig. 1 shows the effect of temperature on the response time. Such a well-known nematic LCP, poly-CBHA, responded to the current just below the isotropization temperature (117°C). When the temperature was below 100 °C, the switching becomes very slow, where the response takes a few seconds. On the other hand, the response temperature of the copolymers were lower than that of poly-CBHA, as T_i 's of copolymers were decreased. Interestingly, the temperature range of the first switching was wider than the case of

poly-CBHA, especially for these laterally attached mesogens (CP-d1 and CP-e1). The level of switching time was below 100 msec.

In conclusion, the siloxane spacer enables such LCPs to lower not only the temperature range of mesophase, but also the response temperature in the electric field. It would be due to the high flexibility of the siloxane bond.

REFERENCES

1. C. B. McArdle, Ed. "Side Chain Liquid Crystal Polymers", Chapman and Hall, New York, 1989.
2. H. Finkelmann, H. Ringsdorf and J. H. Wendorff, *Makromol. Chem.*, **179** (1978) 273.
3. Y. Nagase and Y. Takamura, *Makromol. Chem.*, **193** (1992) 1225.
4. Y. Nagase, Y. Takamura, H. Abe, T. Saito and E. Akiyama, *Makromol. Chem.*, **194** (1993) 2517.
5. Y. Nagase, T. Saito, H. Abe and Y. Takamura, *Macromol. Chem. Phys.*, **195** (1994) 263.
6. E. Akiyama, M. Yamazaki, Y. Takamura and Y. Nagase, *Macromol. Rapid Commun.*, **15** (1994) 161.
7. E. Akiyama, Y. Takamura and Y. Nagase, *Polym. J.*, **26** (1994) 1277.