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Thermal and i.r.-dichroic properties of side-chain type liquid-crystalline elastomers

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Several liquid-crystalline elastomers (LCEs) have been prepared by crosslinking side-chain type liquid-crystalline polymers (precursors) in which mesogens are dangling from flexible main chains through spacers. Thermal properties and phase behaviour of the precursors and LCEs have been investigated by means of differential scanning calorimetry (d.s.c.) and polarizing microscopy. The glass transition and meso-to-isotropic phase transition temperatures are slightly affected by an introduction of crosslinks to precursors. Orientation of the mesogens in the LCEs under uniaxial elongation has been evaluated in terms of order parameter for orientation (f) obtained by i.r.-dichroism measurements. All the LCEs under deformation show negative values of f, meaning the orientation direction of mesogens perpendicular to the axis of elongation. The value of f changes greatly in the small deformation region, and reaches equilibrium at ca. 70% elongation, suggesting that a high degree of orientation for the mesogens in LCEs is achieved by a relatively small elongation. Dependence of f on elongation ratio is not influenced by spacer length nor by crosslinking density, implying that the interaction between mesogens is the most dominant factor for the orientational order of mesogens in the LCE system in this study. © 1997 Elsevier Science Ltd

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INTRODUCTION

Liquid-crystalline elastomers (LCEs) have been highlighted as a new type of liquid-crystalline (LC) material in recent years[1–11]. LCEs have a three-dimensional network structure in which mesogens are included in the main chains (backbones) and/or in the side chains dangling from backbones. In particular, side-chain-type LCEs in which the backbones consist of flexible polymers have a unique feature originating from rubber elasticity: orientation of the mesogens can be controlled by mechanical forces as well as by electric and magnetic fields. As a result of this remarkable character, side-chain-type LCEs are expected to be a promising material for opto-electrical applications[12–15]. Also, the effect of mechanical stress on the meso-to-isotropic phase transformation of LCEs attracts attention as a noticeable phenomenon in the physics of LCs[9–11].

Orientation properties for various side-chain-type LCE systems under mechanical forces have been investigated by means of photoelastic measurements[1,3,4], X-ray scattering[2,5], or i.r.-dichroism measurements[4,7]. The orientation behaviour of mesogens is strongly influenced by the degree of the coupling between mesogens and polymer backbones. Finkelmann *et al.*[1,3] reported an odd–even effect for the length of flexible spacer, which links a mesogen with a polymer backbone, on the orientation of mesogens: the director of the nematic phase is oriented perpendicular to the axis of deformation in the case of $m = 3$, but it is parallel for $m = 4$. Here, m is the number of methylene units in a flexible spacer. However, in the case of LCEs with $m = 6$, orientations parallel and perpendicular to the axis of elongation were reported by Mitchell *et al.*[5] and Brauchler *et al.*[7], respectively. The LCEs in their studies have the same type of mesogen, but they are different in the details of network structure: chemical structure of the polymer backbone, crosslinking density, and the number of dangling chains with mesogen per polymer backbone. The discrepancy in the orientation behaviour between their studies suggests that the coupling between mesogens and polymer backbones is influenced by many structural factors of LCEs. However, the correlation of these structural factors of LCEs with the orientation of mesogens has not yet been fully elucidated.

In order to utilize the rubber elasticity of flexible backbones and to use LCEs as elastomers at about room temperature, the glass transition temperature (T_g) of the LCE must be considerably lower than room temperature. However, this point seems to have been treated very lightly in earlier studies[1–7]. Relatively high values of T_g for side-chain-type LCEs have been reported in the earlier studies: T_g was more than 30°C for LCEs with polyacrylate[2,5,7] or polymethacrylate[7] backbones; more than 0°C for those with polysiloxane backbones[1,3,4]. The high T_g for LCEs with polyacrylate or polymethacrylate backbones is clearly attributable to the high T_g for the polymer backbone itself. Though polysiloxane itself has

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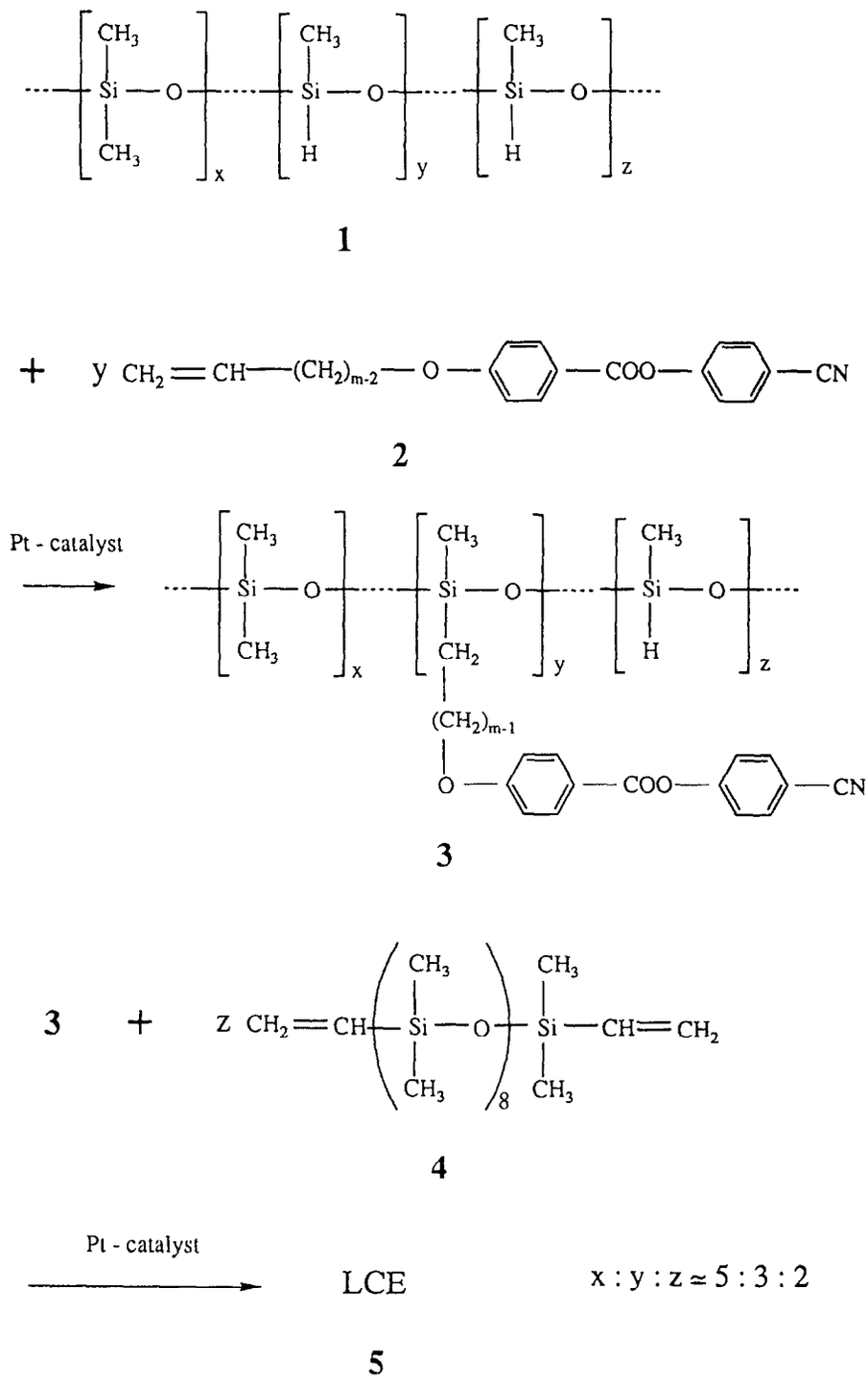
a T_g much lower than room temperature, the LCEs in these studies [1,3,4] have a large number of mesogens; the mesogens dangle from all the monomer units in the main chains, which lowers the degree of freedom for polysiloxane backbones. In this study, we have employed polysiloxane as a backbone, and prepared LCEs in which the content of mesogens per main chain is relatively small (ca. 20 mol%) in order to maintain the flexibility of the backbones.

We have also investigated the effects of spacer length and crosslinking density on the orientation of mesogens. The orientation of mesogens under uniaxial force has been evaluated in terms of the order parameter (f) which is obtained by i.r.-dichroism measurements. The influence of the introduction of crosslinks on the thermal properties of the original side-chain-type LC polymers (precursors) has been examined by differential scanning calorimetry (d.s.c.) and polarizing microscopy. Temperature dispersions of storage modulus (E') for LCEs have also been investigated.

EXPERIMENTAL

Synthesis of liquid-crystalline elastomers

The synthetic route of the LCEs used in this study is shown in *Scheme 1*. Random copolymer **1** (Toshiba Silicone Co.) comprising methylhydrosiloxane and



Scheme 1

dimethylsiloxane units was employed as a prepolymer. The molar ratio of methylhydrosiloxane units to dimethylsiloxane units is 1 : 1, and the molecular weight of copolymer **1** is 6000 (catalogue value). Six kinds of monomer **2**, different in the number of methylene units in the spacer, were synthesized in our laboratory[16]. Monomer **2** consists of mesogen, cyano group, and spacer comprising vinyl and alkyl groups. Phenyl benzoate was used as a mesogen.

Precursor **3** was prepared by hydrosilylation reaction between Si–H groups in prepolymer **1** and vinyl groups in monomer **2**. *Cis* $PtCl_2(P(C_6H_5)_3)_2$ (Johnson Mackey Chemicals Co.) was used as a catalyst. The molar ratio of the (Si–H) group to the vinyl group was 0.60. The prepolymer **1**, the monomer **2** and the catalyst were dissolved in toluene, and the reaction was carried out under reflux for 48 h. After the toluene was removed from the solution, the extract was dissolved in trichloromethane. The precursor **3** was purified by reprecipitating the extract with methanol. Six kinds of precursor **3** were designated P*m* ($m = 3, 4, 5, 6, 8, 10$) where *m* represents the number of methylene units in the spacer. Content of the mesogens introduced in each precursor **3** was evaluated from the area ratio of the peak assigned to the mesogens to that corresponding to the $Si–CH_3$ groups by means of ^{1}H-n.m.r. measurements. The content of monomer units having a mesogen in each precursor **3** was ca. 20 mol%, as listed in *Table 1*.

Table 1 Sample code, content of introduced mesogens (M.C.), glass transition temperature, transition temperature for LC phase, and mesophase temperature range (M.R.) for precursors

Sample	M.C. (mol%)	Phase transition temperature (°C)							M.R. (°C)
P3	22.2	g[a]	−17.4	n[b]	40.0	i[c]			57.4
P4	24.9	g	−19.5	n	52.6	i			72.1
P5	23.7	g	−15.6	n	79.7	i			95.3
P6	24.2	g	−23.7	n	73.0	i			96.7
P8	22.1	g	−20.3	s[d]	91.9	i			112.2
P10	22.5	g	−21.8	−5.0	14.3	s	99.8	i	121.6

[a] Glassy state
[b] Nematic phase
[c] Isotropic phase
[d] Smectic phase

LCE **5** was prepared by hydrosilylation between precursor **3** and crosslinker **4** in toluene. Vinyl-terminated polydimethylsiloxane (Chisso Co.) was employed as a crosslinker. The molar ratio of vinyl groups in the crosslinker **4** to residual Si–H groups in the precursor **3** was 1.1. The reaction was performed under reflux. The reaction time was varied from 0.1 h to 6 h, as listed in *Table 2*. After the reaction had continued for a certain period, the solution was transferred to a Teflon mould. Film specimens were obtained by casting the solution at 80°C for 48 h. The LCE samples were designated E*m* according to the system used for the precursor P*m*. Four kinds of E4 (E4a, -b, -c, -d) and two kinds of E5 (E5a, -b) and E8 (E8a, -b), different in crosslinking density, were prepared by varying the reaction time. The difference in crosslinking density was demonstrated by swelling experiments, as described later. Crosslinked polydimethylsiloxane with no mesogens, designated E0, was prepared by the same procedure. The molar ratio of vinyl groups in the crosslinker **4** to [Si–H] groups in the prepolymer **1** was 1 : 3 for E0.

Measurements

^{1}H-n.m.r. spectra were acquired with a Hitachi NMR R1000 ^{1}H-n.m.r. spectrometer and a GE QE300 ^{1}H-n.m.r. spectrometer, using $CDCl_3$ as a solvent.

D.s.c. measurements were performed at a heating rate of 10°C min^{-1} with Seiko DSC-20 and Rigaku DSC-8230 equipment.

The texture of the precursors and LCEs was observed with a Nikon Optiphot2-Pol polarizing microscope. The temperature was controlled by Mettler FP82 Hot Stage equipment.

Swelling experiments for the LCE samples were carried out in tetrahydrofuran (THF). After the samples had been immersed in THF for 24 h at room temperature, the weight of the specimens was measured. The degree of swelling was estimated by the ratio of weight in the swollen state to that in the dry state. The degree of swelling for each sample is summarized in *Table 2*.

Table 2 Sample code, degree of swelling, glass transition temperature, transition temperature for LC phase, and mesophase temperature range (M.R.) for LCE samples

Sample	Reaction time (h)	Degree of swelling	Phase transition temperature (°C)					M.R. (°C)
E0	0.1	3.80	g[a]	−116.0	i[b]			0
E3	5.0	17.7	g	−15.3	n[c]	36.2	i	51.5
E4a	0.5	9.50	g	−18.3	n	49.3	i	67.6
E4b	3.0	10.6	g	−17.2	n	48.5	i	65.7
E4c	1.0	14.3	g	−20.0	n	47.3	i	67.3
E4d	3.5	19.3	g	−18.1	n	49.1	i	67.2
E5a	5.3	9.30	g	−15.4	n	73.1	i	88.5
E5b	2.5	12.2	g	−14.6	n	75.3	i	89.9
E6	3.3	10.4	g	−21.2	n	71.0	i	92.2
E8a	4.0	13.2	g	−18.8	n	88.6	i	107.4
E8b	3.0	19.1	g	−18.1	n	90.1	i	107.4
E10	3.0	13.3	g	−17.9	n	96.7	i	114.6

[a] Glassy state
[b] Isotropic phase
[c] Nematic phase

I.r.-dichroism measurements[17] for the LCEs in nematic phase under uniaxial extension were performed with a Shimadzu FT-IR4100 Fourier transform infrared spectrometer, using a stretching device and a polarizer. Dichroic absorbance of the C≡N stretching vibration at 2230 cm^{-1} was used to determine the orientation of mesogens in the LCEs[4,7]. After the specimen had been kept under a certain extension for 2.5 min, its i.r. spectrum was measured at room temperature (at which the phase is nematic) under two conditions: the transmission axis of polarizer is (a) perpendicular, and (b) parallel to the stretching direction. From the absorbance in each case ($A_\perp$ and $A_\parallel$), f is evaluated by the following equation[4,7]

$$f = \frac{D-1}{D+2} \tag{1}$$

where $D = A_\parallel / A_\perp$. The value of f is zero for random orientation for mesogens.

Temperature dispersions of E' for the LCEs were measured by FT-Rheospectra DVE-V4 (Reoroji Co.) in the temperature range −60 to 120°C at a heating rate 2°C min^{-1} and at a frequency of 10 Hz.

RESULTS AND DISCUSSION

Phase behaviour of precursors

Table 1 shows phase transition temperatures with respect to glass transition and nematic-to-isotropic to smectic-to-isotropic phase transformation for the precursors. The phase transition temperatures were determined from the location of the peaks in the d.s.c. curves.

It is found that T_gs for all the precursors are rather lower than those (more than 0°C) for side-chain-type LC polysiloxanes reported in earlier studies[1,3,4,18]. The lower T_g in this study results from the rather smaller number of mesogens per main chain (ca. 20 mol%) in comparison with that in the earlier studies (100 mol%). The interfering effect of mesogens on the flexibility of main chains should be much smaller in this study.

It can be seen in *Table 1* that T_gs for a series of precursors are almost constant, and that m dependence on T_g is weak. This result is different from the well-known fact[18] that T_g for side-chain-type LC polymers decreases monotonically with increasing m as long as m is not too large ($m < 10$). Strong dependence of T_g on m has been obtained for samples in which all the monomer units in a main chain have dangling chains with mesogens. The difference between the earlier and our studies is explained by the lower degree of the interfering effect of mesogens on the flexibility of backbones, resulting from a smaller number of mesogens per main chain in this study.

The dependence of m on the meso-to-isotropic phase transition temperature ($T_{n,i}$) for the precursors is found to be somewhat complicated. The temperature $T_{n,i}$ increases with the increase of m as a whole, but $T_{n,i}$ for $m = 6$ is lower than that for $m = 5$. This implies an odd–even effect of the spacer length on $T_{n,i}$, though the effect is not observed for $m = 4$. The consistent odd–even effect of m on $T_{n,i}$ for side-chain-type LC polymers has been known for various systems[19,20], while a complicated dependence of $T_{n,i}$ on m as seen in this study has been also reported for other systems[21,22]. The odd–even effect is considered to originate from the strong correlation of the conformation of methylene units with the alignment of mesogens. However, the odd–even effect is eliminated when the interaction between mesogens overcomes the thermodynamic stability for the conformation of methylene units. In this case, the dependence of $T_{n,i}$ on m should show a monotonic increase: the interfering effect of the backbone flexibility on the interaction between mesogens is more effectively reduced by a longer spacer (decoupling effect via spacer). The complex dependence of $T_{n,i}$ on m obtained here should be a result of competition between these effects.

A Schlieren texture, representative of nematic phase, was observed in the mesophase temperature range by polarizing microscope for all the precursors except P8 and P10. These precursors showed a Mosaic texture, characteristic of smectic phase, in the mesophase temperature region. The emergence of the higher order mesophase for P8 and P10 is explained by the decoupling effect via the long spacer. The d.s.c. curve of P10 suggested the existence of another two LC phases, but these phases were not identified by polarizing microscope.

The mesophase temperature range for each precursor is also shown in *Table 1*. It is found that the region where mesophase appears is broader with increasing spacer length. This result is due to the rise of $T_{n,i}$ by the increase of m and the independence of T_g on m.

Phase behaviour of LCEs

T_g and $T_{n,i}$ and the mesophase temperature range for the LCEs are shown in *Table 2*. It is found that T_g for the LCEs prepared in this study is much lower than room temperature, and rather lower than those (more than 0°C) for LCEs with polysiloxane backbones prepared in earlier studies[1,3,4]. The lower T_g of the LCEs in this study originates from the low T_g for the precursors used, which have a small number of mesogens per main chain. The LCEs in this study satisfy the condition of an elastomer that T_g is appreciably lower than room temperature, whereas the LCEs used in other studies[1–7] did not satisfy this condition.

As can be seen in *Tables 1* and *2*, T_g for the LCEs is slightly higher than that for the corresponding precursor, while $T_{n,i}$ for the LCEs is somewhat lower than that for the precursor concerned. Polarizing microscopy indicated that the smectic phase for P8 and P10 changed into the nematic phase for E8 and E10, and Schlieren textures in E3, E4 and E6 were not clearly observed in comparison with those in P3, P4 and P6. However, the independence of T_g on m, and the weak odd–even effect of m on $T_{n,i}$, are the same as those for the precursors. The increase of T_g caused by crosslinking implies that crosslinks reduce the flexibility of polysiloxane chains. The decrease of $T_{n,i}$ by crosslinking suggests that crosslinks interfere with the interaction between mesogens. The unclear Schlieren textures and the disappearance of smectic phase for the LCEs support this idea. On the other hand, Schatzle *et al.*[4] reported that T_g and $T_{n,i}$ for the precursors are not changed by crosslinking. This may be due to the rather smaller degree of crosslinking (ca. 5 mol% per main chain) in their samples in comparison with that (ca. 26 mol% in the case of complete progress of the crosslinking reaction) in ours. The mesophase temperature range for the LCEs is somewhat narrow relative to that for the corresponding precursors, resulting from the increase of T_g and the decrease of $T_{n,i}$ caused by the introduction of crosslinks.

The mesophase temperature range is broader as m grows larger, as for the precursors.

The effect of crosslinking density on T_g and $T_{n,i}$ has been investigated for a series of E4. As is seen in *Table 2*, a series of E4 showed the different degrees of swelling. Generally, polymer networks show a larger degree of swelling as crosslinking density decreases. The temperatures T_g and $T_{n,i}$ for E4 do not seem to be strongly dependent on crosslinking density, suggesting that the difference in crosslinking density over the range investigated here does not have much influence on the interaction between mesogens.

I.r.-dichroic properties of LCEs under uniaxial elongation

Figure 1 shows the dependence of f on the elongation ratio (λ) for the LCEs with different lengths of spacer in the nematic phase. All the LCEs in the figure indicated negative values of f in the entire range of λ. A negative value of f means that mesogens in the LCEs are oriented perpendicular to the axis of elongation. No noticeable dependence of the shape of the curves on m is seen, nor is the odd–even effect of m on the orientation of mesogens is observed here. This result indicates that interaction between mesogens mainly controls their orientation behaviour, and that the thermodynamic stability for the conformation of methylene units is not so strong as to exceed the interaction between mesogens in the systems used in this study. The weak odd–even effect of m on $T_{n,i}$ for LCEs, as described before, also supports this consideration.

The f–λ curves have some common features: the values of f reach almost the same equilibrium value (ca. -0.20) in the large deformation region $\lambda > 1.7$; they decrease rapidly in the small deformation region $\lambda < 1.5$. These features suggest that the high degree of orientation of mesogens in the LCEs is achieved by a small deformation. Brauchler *et al.*[7] also reported a significant change of f in a small deformation region for the side-chain-type LCE in which the backbone is polymethacrylate.

Schatzle *et al.*[4] reported that a polydomain–monodomain transition occurs in the process of elongation of LCE in the nematic phase. Polydomain–monodomain transition means that the polydomain structure, in which the orientation of the director strongly fluctuates spatially ($f = 0$) in the undeformed state, is discontinuously changed by an external force into a monodomain structure having a unique orientation of the director field. This transition is recognized as a large jump of f at a certain stress. It can be seen in *Figure 1* that the value of f changes monotonically, and that discontinuous change of f is not observed. This difference between their studies and ours should result from the content of mesogens and crosslinks per main chain. In their study, the content of dangling chains with mesogens per main chain is 94 mol%, and the residual sites of the main chain (4 mol%) are used as crosslinking sites; whereas, in this study, the content of side chains with mesogens is ca. 22 mol%, and that of crosslinking sites is maximized to be ca. 28 mol%. The LCEs in their study have a much larger amount of mesogen and a rather smaller number of crosslinks than those in this study. A large number of dangling chains with mesogens and a low degree of crosslinking seem to be necessary for the occurrence of polydomain–monodomain transition. This transition may require a high degree of interactions between the mesogens.

Figure 2 indicates dependence of f on λ for LCEs with different crosslinking density. As can be seen, crosslinking density does not have any large influence on the orientation behaviour of mesogens. This suggests that

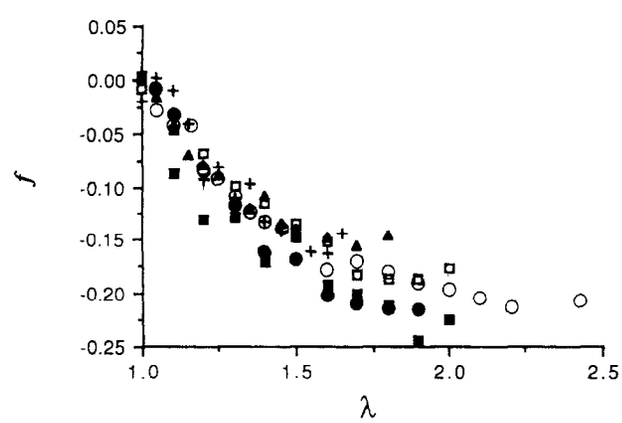


Figure 1 Dependence of order parameter for orientation (f) on elongation ratio (λ) for LCEs with different spacer length in nematic phase. Symbols: (○) E3; (□) E4b; (●) E5a; (+) E6; (■) E8b; (▲) E10

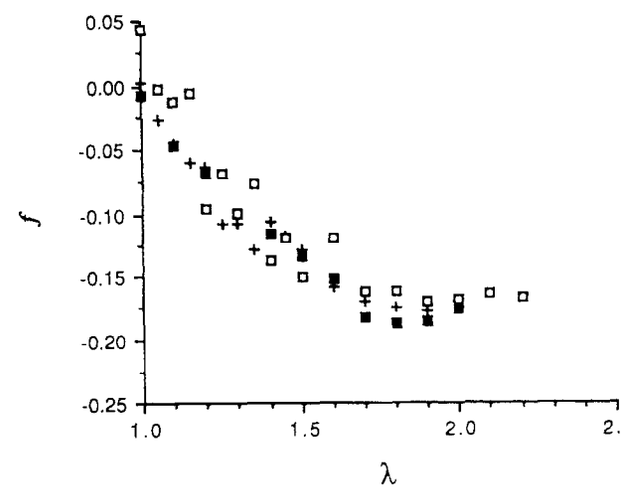


Figure 2 Dependence of order parameter for orientation (f) on elongation ratio (λ) for LCEs with different crosslinking density in nematic phase. Symbols: (■) E4b; (+) E4c; (□) E4d

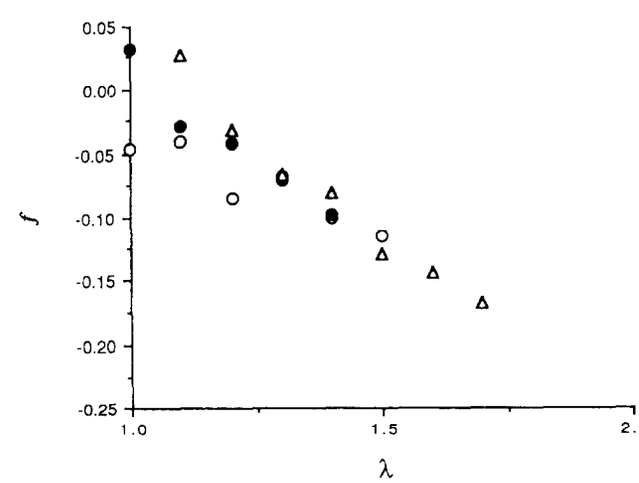


Figure 3 Dependence of the order parameter for orientation (f) on elongation ratio (λ) for E5b in the cycle of extension. Symbols: (○) 1st extension; (●) release process; (△) 2nd extension

the effect of crosslinking density is not so strong as to overcome the interaction between mesogens.

Figure 3 shows the orientation behaviour of mesogens in a cycle of extension for E5b. The sample was elongated to $\lambda = 1.5$, then reduced to $\lambda = 1$; then a second extension was carried out. The values of f in the first elongation, the release, and the second elongation process agree well with each other. The reversible orientation behaviour of mesogens results from the rubber elasticity of the network composed of flexible backbones.

Temperature dispersions of storage modulus of LCEs

Figure 4 shows temperature dispersions of E' for E0, E4a, E5b and E8b. The elastomer E0, with no mesogens, shows the plateau region of E' in the temperature region above T_g, suggesting a uniform network structure. On the other hand, E' for the LCEs decreases gradually with increase of temperature in the range between T_g and $T_{n,i}$, then decreases abruptly around $T_{n,i}$. This temperature dependence of E' is similar to the results for the LCEs in which mesogens are included in both the main and the side chains, reported by Pakula and Zentel[6]. The unclear plateau of E' in the temperature range between T_g and $T_{n,i}$ and the softening around $T_{n,i}$ suggest that the aggregates of mesogens may act as additional crosslinks or reinforcing fillers in the rubbery matrix. The size of the aggregates should not be uniform, and non-negligible numbers of small (weak) aggregates which dissociate at temperatures below $T_{n,i}$ should exist. The smaller the size of the aggregate is, the lower the temperature of dissociation becomes. As the temperature increases, the number of aggregates acting as crosslinks or fillers decreases, which gives rise to the gradual decrease of E'. The dissociation of most of the aggregates occurs around $T_{n,i}$, which leads to the abrupt decrease of E' around $T_{n,i}$.

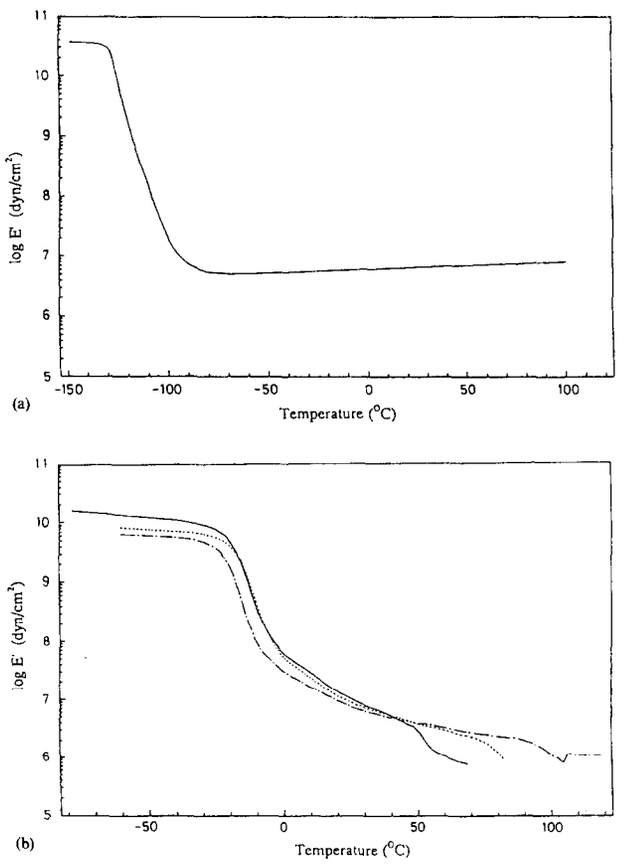


Figure 4 (a) Temperature dependence of storage modulus (E') for E0. (b) Temperature dependence of E' for E4a, E5b and E8b. Solid line, E4a; dashed line, E5b; dash–dot line, E8b

CONCLUSIONS

Effects of spacer length and crosslinking density on the thermal and orientation properties of LCEs have been investigated by means of d.s.c., polarizing microscopy and i.r.-dichroism spectroscopy. LCEs were prepared by crosslinking the precursors, which have flexible polysiloxane as a main chain, and mesogens with a spacer as a dangling chain. The content of the introduced mesogens was controlled in order to maintain the flexibility of polysiloxane backbones. The results of d.s.c. indicated that T_g for the LCEs is much lower than room temperature, meaning that the LCEs in this study satisfy the condition of an elastomer around room temperature. D.s.c. and polarizing microscopy showed that the introduction of crosslinks causes a small increase in T_g and a slight decrease in $T_{n,i}$, suggesting that the existence of crosslinks reduces the flexibility of polysiloxane chains and interferes with the interaction between mesogens. The crosslinking density did not have much influence on the thermal properties of LCEs.

The order parameter for orientation f for the LCEs under uniaxial strain was estimated by i.r.-dichroism measurements. It was found that mesogens are oriented perpendicular to the axis of deformation, and a high degree of orientation is achieved by a small deformation. Dependence of f on elongation ratio was found to be not influenced by spacer length or crosslinking density. These results suggest that the interaction between mesogens is the more dominant factor for the orientation of mesogens relative to spacer length and crosslinking density in the LCE system used in this study.

Temperature dependence of storage modulus for the LCEs showed a gradual decrease in the temperature region between T_g and $T_{n,i}$, suggesting that mesogen aggregates act as additional crosslinks or reinforcing fillers, and that the small aggregates dissociate as the temperature increases.

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