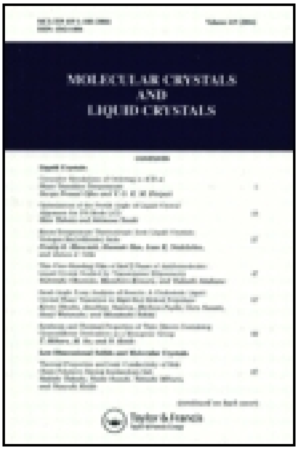

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Thermally Reversible Distortion Observed for Monodomain Nematic Elastomer of Cross-Linked Main-Chain Polyester

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Thermoelastic response of a cross-linked main-chain polyester was examined in the nematic temperature region from 80°C to 150°C. The monodomain nematic elastomer decreased its length in the orientation direction by 45% on heating from 80°C to 150°C and recovered it on cooling to 80°C without change in the degree of orientational ordering. This reversible distortion of the nematic elastomer is well explained by the configurational change of the polymer chain including hairpin folding, the probability of which is proportional to the Boltzmann factor of hairpin energy.

Keywords: cross linking; main-chain polymer; nematic elastomer; reversible distortion; stretching

1. INTRODUCTION

The simplest liquid crystalline polymer has been given by alternately introducing of rigid aromatic mesogenic groups and flexible methylene spacers into a polymer backbone. It is called the main-chain liquid crystalline polymer, and has generated much interest in recent years because of increased efforts to understand the polymeric effects on the liquid crystal structure and properties [1,2]. However the configuration of the semiflexible backbone has been obscure even in the simplest nematic liquid crystalline (LC) phase. This is due to the complex

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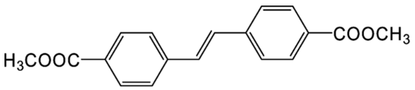
interplay between the polymeric and mesogenic properties. While the semiflexible chain tends to maximize its entropy to fall into a variety of conformational types, the long-range orientational order of the liquid crystal compels the chain to stretch entirely along the director. de Gennes [3] pointed out that to compensate the chain entropy, the chain folds into a hairpin shape which requires the minimum energy cost due to the chain bending elastic energy and the orientational order, and then Williams and Warner [4] developed the statics and dynamics of hairpin folding in the nematic polymers. In fact, the hairpin configuration has been deduced for main-chain nematic LC polyesters by the small-angle neutron scattering (SANS) method [5,6]. The chain folding lamellar structure including the hairpin configuration has also been observed in the smectic CA phase of the main-chain polymer [7,8]. In this article, we report the reversible distortion of a cross-linked nematic main-chain polyester by a heating and cooling cycle, which is explained on the basis of the hairpin chain configuration in the nematic state.

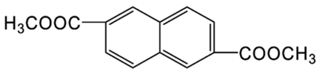
2. EXPERIMENTAL

Synthesis of Nematic Elastomer

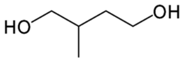
The nematic elastomer, SbN4(2-Me)/6E, was synthesized by melt transesterification of dimethyl trans-stilbene-4,4′-dicarboxylate (Sb), dimethyl 2,6-naphthalene dicarboxylate (N), 2-methyl-1,4-butanediol (C4-2Me), and hexanediol (C6), with trimethylbenzene-1,3,5- tricarboxylate (BT) as the cross-linker. The composition of the reactants was 0.1 mol of Sb, 0.1 mol of N, 0.16 mol of C4-2Me, 0.16 mol of C6 and 4 mmol of BT. The excess diols were evacuated during the melt condensation. The chemical structures of the reactants are shown below,



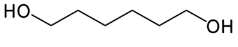
Sb



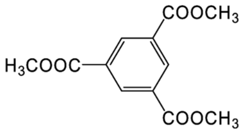
N



C4-2Me



C6



BT

and the schematic illustration of the nematic elastomer is shown in Figure 1.

On heating process of differential scanning calorimetry at a rate of 10°C min^{-1} (Perkin-Elmer Pyris 1 DSC), the elastomer showed the glass transition at 45°C and the isotropization of the nematic LC at 191°C ($\Delta H = 4.3\,\text{kJ mol}^{-1}$), while the polymer without BT component showed the glass transition at 43°C and the isotropization at 197°C with the enthalpy change of $\Delta H = 5.4\,\text{kJ mol}^{-1}$. The effect of introducing 2 mol% of the cross-linker on the transition behavior and nematic structure is thus small.

The molecular weight between cross-link points, M_s, is related to the tensile modulus (E) according to

$$E = 3RT\rho/M_s \qquad (1),$$

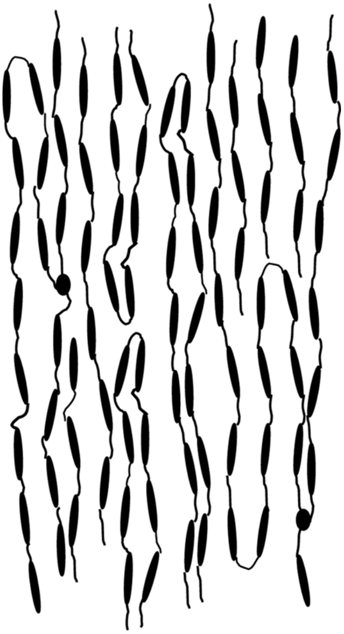


FIGURE 1 Schematic illustration of nematic elastomer of the resulting main-chain SbN4(2-Me)/6 polyester.

where ρ is the bulk density, R the gas constant, and T the temperature [9]. Using $E = 566\,\text{kPa}$ and $\rho = 1.11\,\text{g cm}^{-3}$ determined for the isotropic liquid at 220°C (thermomechanical analysis, a Seiko Instruments TMA 150 C), M_s was calculated as $2.41 \times 10^4\,\text{g mol}^{-1}$, which indicates that two successive cross-link points are connected by a polymer chain with 76 repeat units on average. This number is comparable to the 50 repeat units expected from the molar ratio (2.0 mol%) of the cross-linker BT, therefore cross-linking proceeded reasonably.

Measurements

Wide-angle X-ray Diffraction (WAXD) patterns were taken by irradiating Ni-filtered CuKα radiation (Rigaku RU-200BH generator) to the sample elongated to a predetermined length by a home-made stretcher. The sample temperature was regulated by the heater equipped in the home-made stretcher holder. The two-dimensional diffraction pattern was recorded on the flat imaging plate and analyzed by a Rigaku Automatically X-ray Imaging System, RAXIS-IID.

3. RESULTS AND DISCUSSION

Figure 2 shows the stress-strain curve of the nematic elastomer measured by TMA at 100°C at a strain rate of 100% min^{-1}. Here the strip specimen with a cross section of $1.5 \times 2.0\,\text{mm}^2$ was used for the experiments. The strain (%) was defined as $\{(L_f - L_i)/L_i\} \times 100$ where L_f and L_i are the strained and unstrained lengths, respectively. On stretching the sample to a strain of 500%, the nominal stress increased rapidly within increasing strain up to 10%, which indicates an initial elastic constant of 76.2 kPa, and finally reached a constant value of 7.7 kPa. On decreasing the strain from 500%, the strain rapidly reached zero. Then, the sample strip became bent, but after relaxation it recovered the straight shape. This is attributable to the viscoelastic mechanical property of the polymeric materials and suggests that on decreasing the strain, the sample shrinkage is slower as the grips of the TMA approach each other. When the sample was removed from the grips of the TMA and left at 100°C for enough time (for example, two hours) to equilibrate the sample deformation, strain of 330% was found to remain. Interestingly, this remained strain of 330% is invariable at 100°C if the elastomer is elongated beyond this value. The wide-angle X-ray diffraction (WAXD) patterns taken for the initial sample, the sample stretched up to a strain of 500% and the sample relaxed after the elongation are presented in the insets of (a), (b) and (c) of Figure 2, respectively. In the WAXD patterns, a broad outer halo attributed to

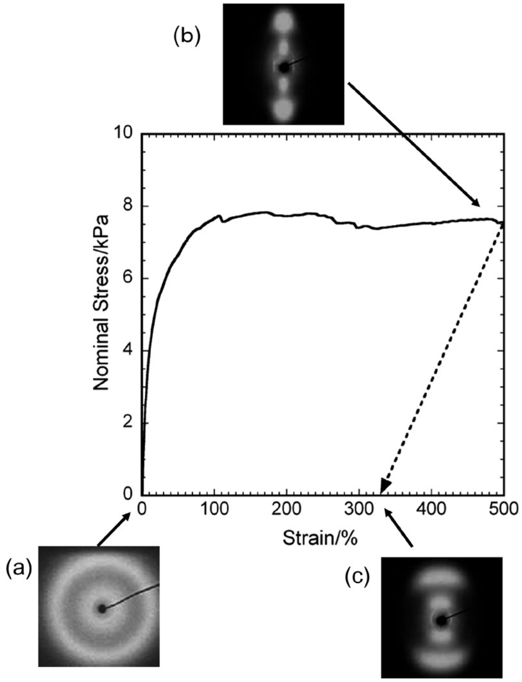


FIGURE 2 Stress-strain curve of the nematic SbN4(2-Me)/6 elastomer at 100°C measured at a strain rate of 100% min^{-1}. On decreasing the strain from 500%, the stress rapidly reached zero and the sample bent. The dotted line in the figure connects the point of the maximum applied strain of 500% and the point of the equilibrated remaining strain of 330% determined for the sample relaxed at 100°C. The WAXD patterns taken for the original unstrained sample (a), the sample elongated at a strain of 500% and the sample unloaded and relaxed after the elongation (c) are shown in the insets. The elongation direction is along the horizontal.

liquid-like packing of the mesogens is concentrated on the meridional line upon stretching the elastomer in the equatorial direction, and it is somewhat spread in the azimuthal direction for the relaxed sample. In the small-angle region of the WAXD patterns for the oriented samples, weak streaks with a spacing of 15.5 Å, which corresponds to the average repeat length of the polymer chain, appear on the equatorial line. The nematic order parameter, S, estimated from the intensity distribution of the outer halo on the azimuthal angle by applying Hermann's method [10] is 0.86 and 0.48 for the stretched and relaxed elastomers, respectively. Fairly high value of S for the stretched elastomer is reasonable, but S for the relaxed one is still high, which can be expected for the conventional nematics. Thus, we know that stretching of the nematic elastomer results in the monodomain structure which is maintained in the unloaded and relaxed sample.

Thermoelastic measurement was performed for the monodomain nematic elastomer obtained as described above. Change of sample length in the nematic director direction by heating and cooling cycles in the nematic temperature range between 80°C and 150°C was detected by TMA with a slight tensile force of 0.1 mN applied to the sample. Figure 3 shows the relative length L/L_0 and the temperature against time. Here, L_0 is the sample length at 150°C determined at the beginning of the measurement. The elastomer was expanded along the nematic director on cooling and contracted reversibly on heating in the nematic LC state. The degree of expansion or contraction was about 45% in the temperature range of 80 to 150°C. Heating the monodomain nematic elastomer up to the isotropic liquid state resulted in irreversible contraction to the initial length L_0.

The most interesting result is that the WAXD patterns observed simultaneously with the reversible distortion showed S of the monodomain elastomer to be 0.48 (±0.02) independent of L/L_0. This temperature

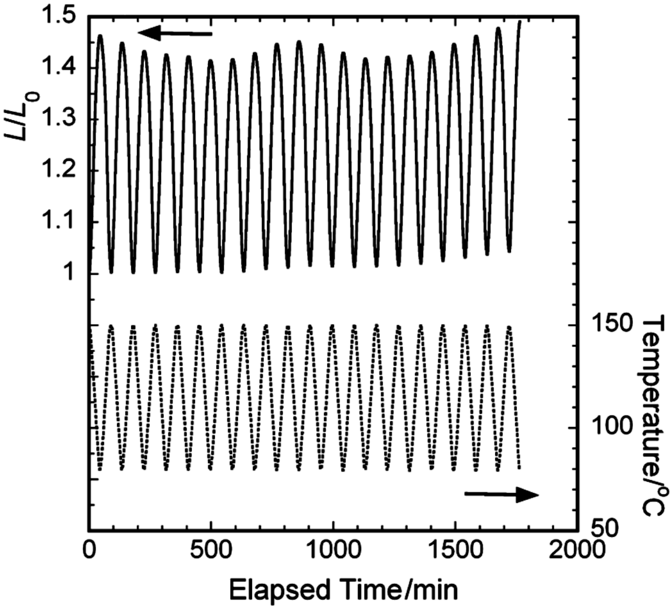


FIGURE 3 Repeatability of the change of the relative length (L/L_0) of the oriented nematic elastomer by heating and cooling cycles between 150 and 80°C at a rate of 2°C min^{-1}.

independence of S is likely attributed to the selected temperature range for measurement fairly lower than T_{NI}. Thus, we reach the short conclusion that the monodomain nematic elastomer increased and decreased its length by 45% along the nematic director without changing the degree of molecular orientation. This is in marked contrast to the experimental results for the monodomain side-chain nematic elastomer whose S is proportional to L/L_0 upon spontaneous distortion [11–13]. In this system with a constant orientational order, the polymer chain connecting the two successive cross-link points must change its configuration so as to decrease (or increase) the number of chains in the cross-sectional area on cooling (or heating).

Such a change of chain configuration is expected if the polymer chain includes the hairpin folds where the chain executes abrupt reversals. According to theoretical debates on the chain configuration in the nematic LC field, the hairpin probability is proportional to the Boltzmann factor, $\exp(-U_{\mathrm{h}}/k_{\mathrm{B}}T)$, where $U_{\mathrm{h}} = 2\sqrt{3aS\varepsilon}$ is the hairpin energy, ε the elastic bend constant of the polymer chain and a the LC field coupling constant [3,4]. Then, the number of hairpin folds along the chain increases (or decreases) as the temperature increases (or decreases), and hence the distance between the cross-link points along the nematic director decreases (or increases) (see Fig. 4). This trend coincides with the results observed here. Similar reversible change of the chain configuration has been observed in the SANS study of semiflexible nematic main-chain polyesters, poly(4,4′-dioxy-2,2′-dimethyl-azoxybenzene alkanedioyl)s with decamethylene and undecamethylene units included as spacers [6].

The temperature dependence of the length of the nematic elastomer is given by

$$\ln(L/L_0) = \frac{U_{\mathrm{h}}}{k_{\mathrm{B}}T} + \mathrm{const} \qquad (2).$$

A linear relationship is then expected between $\ln(L/L_0)$ and T^{-1} and the value of U_{h} can be determined from the slope of the line. In Figure 5, L/L_0 is plotted on a logarithmic scale against the reciprocal absolute temperature. Although the linear relationship is not observed over the entire experimental temperature range, U_{h} is interestingly comparable to that obtained from the SANS experiment. The SANS data have been obtained in a limited temperature range from $T/T_{\mathrm{NI}} = 0.978$ to 0.907, where T_{NI} is the isotropization temperature in the unit of K [6], and the obtained value of U_{h} is $9.2 \times 10^{-21} \sim 1.6 \times 10^{-20}$ J. Our value is 1.9×10^{-20} J, as estimated in the temperature range from 403 K ($T^{-1} = 2.48 \times 10^{-3}\,\mathrm{K}^{-1}$) to 423 K ($T^{-1} = 2.36 \times 10^{-3}\,\mathrm{K}^{-1}$)

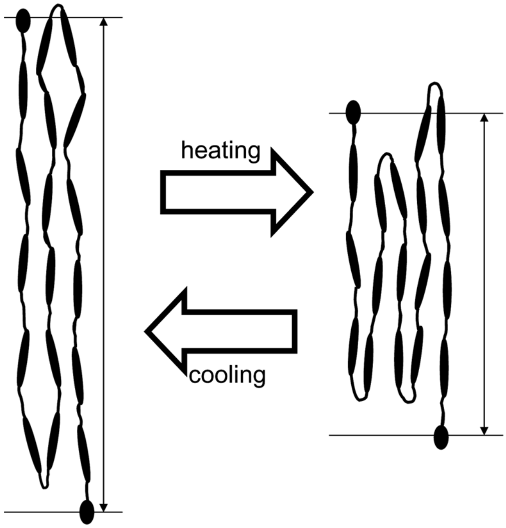


FIGURE 4 Change in the configuration of the polymer chain connecting two successive cross-linking points on heating or cooling as indicated by arrows.

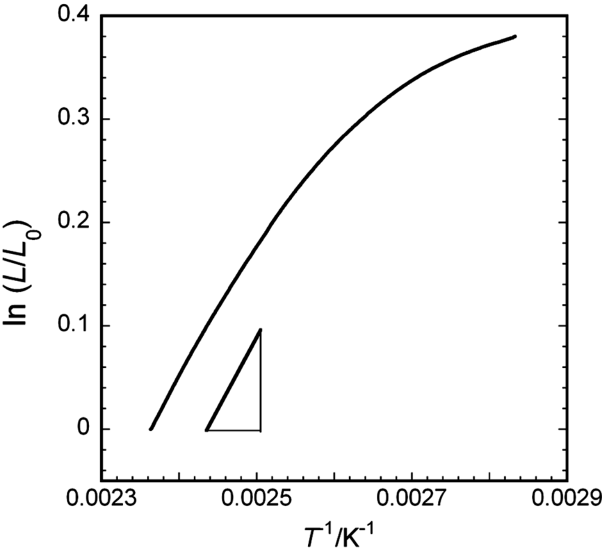


FIGURE 5 Plots of logarithmic relative length (L/L_0) against the reciprocal of the temperature for the nematic elastomer. The data plotted here was obtained in the second cooling process (with elapsed time from 90 to 135 min) (see Fig. 3). The slopes of the solid and dotted straight lines give U_{h} of 1.9×10^{-20} J and 3.5×10^{-21} J, respectively.

(T/T_{NI} range from 0.912 to 0.869). The correspondence is very good, supporting that the distortion of the nematic elastomer is attributed to the change of the chain configuration of the main-chain nematic LC polymer. The value of ln (L/L_0) becomes smaller than that expected theoretically with increasing T^{-1}, in other words, the increase in the length of the elastomer on cooling is not as much as that expected theoretically. This may be due to the delay in the change of the macroscopic shape caused by the increase in viscosity with decreasing temperature. However, the temperature dependence of L/L_0 at $T^{-1} > 0.00276\,\mathrm{K}^{-1}$ ($T < 362\,\mathrm{K}$) gives U_{h} of $3.5 \times 10^{-21}\,\mathrm{J}$, which is still comparable to that from the SANS data.

4. CONCLUSION

In conclusion, the oriented nematic elastomer of the cross-linked main-chain LC polyester expands and contracts reversibly along the orientation direction on decreasing and increasing the temperature, respectively. The shape change takes place with a constant orientational order. Then, this characteristic thermoelastic behavior was attributed to the variation of the polymer chain configuration including hairpin folding, the probability of which is proportional to the Boltzmann factor of hairpin energy. The hairpin energies deduced from the temperature dependence of the distortion of nematic elastomer are ranged from $1.9 \times 10^{-20}\,\mathrm{J}$ to $3.5 \times 10^{-21}\,\mathrm{J}$, which are similar to those estimated from the SANS data for other nematic semi-flexible main-chain polyesters.

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