4084 *Macromolecules* **2009**, *42*, 4084–4089
DOI: 10.1021/ma9004692

Macromolecules
ARTICLE

Polydomain−Monodomain Transition of Randomly Disordered Nematic Elastomers with Different Cross-Linking Histories

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Received March 4, 2009; Revised Manuscript Received April 7, 2009

ABSTRACT: Stretching driven polydomain−monodomain (PM) transitions have been investigated for the two types of polydomain nematic elastomers with different random alignments of the mesogens in the stage of cross-linking. One (I−PNE) is made by cross-linking in the high−temperature isotropic state and then cooling to the nematic state. The other (N−PNE) is directly obtained by cross-linking in the low-temperature polydomain nematic state. They are similar in the order of the induced monodomain as well as the phase transition temperature, but they markedly differ in the process of the PM transitions. The transition in I−PNEs occurs under a very small constant−force condition, and the work of deformation required for forming the monodomain state (W_{PM}) is only a few percent of the initial shear modulus. In contrast, the transition of N−PNEs requires a significantly larger W_{PM}, and the formation proceeds gradually in the wide range of stress. The optical microscopy observation reveals that N−PNEs possess the memory of the initial polydomain texture before cross-linking. The broad PM transition in N−PNEs stems from the memory effect of randomness which results in a robust constraint to the reorientation of local directors.

Introduction

Nematic elastomers are rubbery polymer networks with a sufficient amount of mesogenic groups to induce nematic liquid crystallinity.[1,2] The director configuration of nematic elastomers is strongly influenced by that of nematogens in the stage of cross-linking. Without special care in the stage of cross-linking, the resultant elastomers in the nematic state have a polydomain structure composed of many randomly oriented domains.[3] The polydomain nematic elastomers (PNEs) have no global director but possess local director in each constituent domain with a size of the order of μm. One of the interesting phenomena specific to PNEs is a stretching driven polydomain-to-monodomain (PM) transition: The imposition of sufficiently large uniaxial stress (strain) transforms the polydomain director alignments to the globally aligned monodomain state.[4−8] An initially opaque PNE becomes transparent accompanying the PM transition, because a randomly oriented domain structure leading to strong light scattering changes to a uniformly aligned one transparent to light. A plateau of small stress in the stress−strain curves was often observed in the PM transition. The origin of the plateau stress has been attributed to an indication of almost no cost energy regarding the director rotation specific to nematic elastomers[9,10] or instability stemming from a heterogeneous structural change.[11,12]

The PNEs can be made via two different routes: One (I−PNE) is obtained by cross-linking the mesogenic molecules in the high-temperature isotropic state and then cooling the resultant elastomers to the low-temperature nematic state. The other (N−PNE) is prepared by cross-linking the mesogens in the low-temperature polydomain nematic state. So far little attention has been paid to the effects of such different cross-linking histories on the physical properties of PNEs. Recently, we found that the cross-linking histories significantly affect the strain recovery dynamics of the deformed PNEs after the removal of imposed fields: The N−PNEs exhibited substantially faster strain recovery than the I−PNEs.[13] This result implies that N−PNEs have a memory of the initial director configuration in the stage of cross-linking. The simulation work by Uchida[14] showed that the cross-linking history also has a pronounced effect on the PM transition. In contrast, no systematic experimental survey on this issue has not yet been made. Most of the earlier studies on the PM transition employed I−PNEs as the samples. Quite limited data for the comparison of the PM transition of I−PNEs and N−PNEs are found in the literatures:[5,6] Only the difference in the threshold stress was shown in ref 5, and the cross-linking condition for each stress−strain data is not explicitly described in ref 6. In ref 5, they compared the stretching driven director−reorientation behavior of the nematic elastomers with different cross-linking histories, but most of the data were obtained for the “monodomain” nematic elastomers with global orientation cross-linked under loading. In this paper, we elucidate the difference in the PM transition behavior of N−PNEs and I−PNEs. The cross-linking history effect provides an important basis to understand the physical origin of the plateau stress during the PM transition. Further, this is also expected to give valuable information about the mechanism of the formation of “monodomain” nematic elastomers with permanent global director. The monodomain nematic elastomers realized in laboratories are prepared by cross-linking the mesogenic monomers or polymers in the globally aligned state, which is achieved by mechanical stretching stress,[15] magnetic field,[16] and the alignment force from rubbed sacrificial layers:[17,18] The imprinting of a memory of global director is required in the stage of cross-linking. We also examine the effects of cross-link concentration on the P−M transitions of the two types of PNEs. This information is also significant for the full understanding of the PM transition because the defects such as cross-links in network structure act as a main source of random disorder in PNEs.[10,11]

Experimental Section

Sample Preparation. The side chain type nematic elastomers with polydomain texture were prepared by the methods described elsewhere.[13] The two types of PNEs (I−PNE and N−PNE) were made by photocross-linking the monoacrylate mesogens A-6OCB (Figure 1) and 1,6-hexanediol diacrylate

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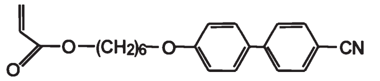

A-6OCB

Figure 1. Chemical structure of A-6OCB.

(cross-linker) with the photoinitiator bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (Irgacure 784) at the two different temperatures. 4-*n*-Hexyloxy-4′-cyanobiphenyl (6OCB) was employed as a miscible nematic solvent to broaden the temperature range of the nematic phase, because A-6OCB exhibits the nematic phase within a narrow range of about 2 °C owing to the high crystallizability. The mixing ratio of A-6OCB and 6OCB was 1:1 by molar ratio, and the transition temperature of the nematic mixture was 50 °C. The cross-linker concentration in feed was 3 or 10 mol %, and the corresponding samples are designated as PNE-3 and PNE-10, respectively. The reactant mixtures were sandwiched by glass plates with a gap of 100 μm. For cross-linking reaction, the glass cell was irradiated using a xenon lamp with emission at a wavelength 526 nm for 30 min in air. It was confirmed by the swelling experiments of the resultant films that 30 min was sufficient for irradiation to saturate the extent of cross-linking reaction. The cross-linking temperatures of I−PNEs and N−PNEs were 90 and 45 °C, respectively. The resultant films were allowed to swell in dichloromethane to wash out the materials which were not incorporated into the networks. The dried films with a thickness of ca. 80 μm were employed as the specimens.

Measurements. Uniaxial stress−strain relations of the specimens were examined by an Orientec Tensilon RTM-500 with a temperature-controllable box. The film specimens with 10 mm × 2 mm × 80 μm were stepwise stretched after the tensile force at each strain was equilibrated. The details of the force equilibration are described in the next section. The IR dichroism measurements for the stretched samples were separately conducted with a custom-built tensile device and an FTIR spectrometer Jasco 4200ST. The details of the IR dichroism measurements were described elsewhere.[19] The elongation was made stepwise in the same manner as in the measurements of the equilibrium stress−strain behaviors. The beam spot on the central part of the specimen remained at the same position during elongation because the specimen was equally stretched from both ends. The absorption band at around 2225 cm^{-1} regarding the stretching vibration of the terminal cyano group along the long axis of the mesogen was employed to evaluate the orientational order of the mesogen. The orientational order parameter (S) is calculated with the absorbances of the incident polarized light parallel and normal to the stretching direction (denoted by $A_\parallel$ and $A_\perp$, respectively) using the relation $S = (A_\parallel - A_\perp)/(A_\parallel + 2A_\perp)$. The quantity S corresponds to the global order parameter because the beam spot (ca. 1 mm in diameter) is substantially larger than the size of individual domain in polydomain textures.

The nematic textures of the samples were observed using a polarized optical microscope Nikon 600POL equipped with a hot stage Mettler FP-82 and a CCD camera Imaging Source DFK41AU02. The equilibrium degree of swelling (Q) in the low-molecular-mass liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (5CB) was measured at 25 °C: $Q = (d/d_0)^3$ where d and d_0 are the dimensions in the fully swollen and dry states, respectively. No anisotropy in swelling was observed due to the polydomain structures without global director. The characteristics of each sample are listed in Table 1.

Table 1. Sample Characteristics

	c_x (mol %)	T_{NI} (K)	Q	W_{PM} (kJ/m^3) $T/T_{NI} = 0.91$	W_{PM} (kJ/m^3) $T/T_{NI} = 0.96$
I−PNE−3	3	378	5.4	2.7×10^{-1}	[a]
N−PNE−3	3	376	5.3	8.4	8.6
I−PNE−10	10	363	3.6	9.8×10^{-1}	1.8×10^{-1}
N−PNE−10	10	365	3.5	9.8	8.7

[a] Not measured.

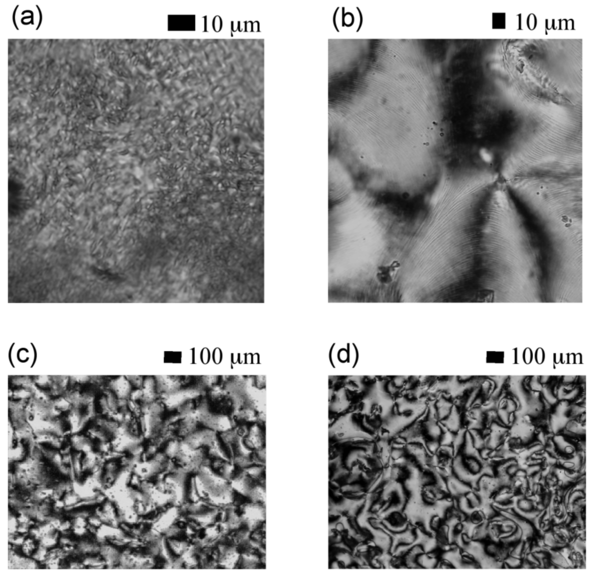

Figure 2. Micrographs of the elastomer films (a) I−PNE−10 and (b) N−PNE−10 between crossed polarizers at 80 °C in the nematic states. The micrographs of the schlieren textures for (c) the nematogen mixture (before cross-linking) confined in the glass cell for photopolymerization and (d) the resultant elastomer film N−PNE−10.

Results

Figure 2a,b shows the micrographs of the elastomer films I−PNE−10 and N−PNE−10 between crossed polarizers at 80 °C in the nematic state, respectively. These correspond to the equilibrium textures obtained after sufficient annealing at the temperature under consideration. Obviously, the average “domain” size (ξ_D) of I−PNE−10 is far smaller than that of N−PNE−10: ξ_D of the former is roughly estimated to be a few micrometer, while that of the latter is about several tens micrometer. We define here the distance between disclinations as ξ_D. Figure 2c,d shows the cross−polarized images of the nematogen mixtures (before cross-linking) confined in the glass cell for photopolymerization and the resultant elastomer film N−PNE−10, respectively. The nematogens before cross-linking and the resultant N−PNE have a similar schlieren texture with almost the same ξ_D, although the nonreactive nematic solvent (ca. 50 vol %) in the nematic mixture is absent in the elastomer film. The texture of N−PNEs was thermally reversible even after repeating the nematic−isotropic transitions. Evidently, the elastomers made in the nematic state possess a memory of the randomness of initial director field before cross-linking.

Table 1 lists the nematic−isotropic transition temperature (T_{NI}) and the degree of equilibrium swelling (Q) for each sample. The values of T_{NI} or Q for I−PNE and N−PNE are almost the same if the cross-linker concentration (c_x) is identical. Küpfer et al. also reported no effect of cross-linking history on T_{NI} for the siloxane based side−chain type PNEs.[5] Davis et al.[20] examined the influence of cross-linking history on T_{NI} for the acrylate based side-chain type PNEs with various lengths of the spacer units $(CH_2)_n$ (alkyl units linking mesogen and network backbone): T_{NI} for the N−PNE with $n = 6$ was slightly (ca. 2 °C) higher but comparable to that for the corresponding I−PNE, although the chemical structures of the mesogens in our and their studies are not the same. A theoretical work[21] predicts that cross-linking in the nematic state produces an elastomer having a higher T_{NI} compared to one cross-linked in the isotropic state.

This agrees with the result in ref 20 for the PNEs with the short spacer length of $n = 2$. These results suggest that the effect of cross-linking history on T_{NI} may be influenced by the strength of coupling between the network backbone and dangling mesogens. No significant difference in Q between I−PNEs and N−PNEs with the same c_x ensures that the amounts of cross-link truly incorporated into the networks are almost the same: The difference in photopolymerization temperature has no appreciable effect on the concentration of elastic chains. An increase in c_x reduces T_{NI}, which is simply attributed to an increase in the number of defects (cross-links) for the formation of nematic state.

Figure 3 displays the nominal stress (σ) as a function of nominal strain (ε) for I−PNE−10 and N−PNE−10 in the isotropic state of $T > T_{\mathrm{NI}}$. The difference in cross-linking history has no effect on the stress−strain relations in the isotropic states. The values of the initial Young's modulus for I−PNE−10 and N−PNE−10 (1.6×10^2 and 1.5×10^2 kPa, respectively) are almost identical. This result ensures again that the amounts of cross-link truly introduced into the two networks have no appreciable difference. The effect of stretching on the global order parameter (S) for the dangling mesogens is also shown in the figure. Almost zero values of S in the entire strain region indicate that the elongation in the isotropic state induces no appreciable reorientation of the dangling mesogens.

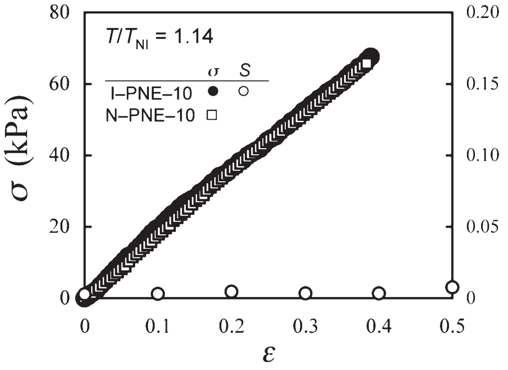

Figure 3. Nominal stress (σ) as a function of nominal strain (ε) for I−PNE−10 and N−PNE−10 in the isotropic state of $T/T_{\mathrm{NI}} = 1.14$. The ε dependence of the global order parameter (S) for the dangling mesogens of I−PNE−10 is also shown.

Figure 4a,b shows the equilibrium $\sigma-\varepsilon$ and $S-\varepsilon$ relations for I−PNE−3 and N−PNE−3 in the nematic states of $T/T_{\mathrm{NI}} = 0.91$, respectively. The $\sigma-\varepsilon$ relations of these two elastomers in the nematic states are considerably different in contrast to the results in the isotropic states. The stress gradually increases with strain without singularity in N−PNE−3, while the $\sigma-\varepsilon$ curves of I−PNE−3 exhibit a definite plateau in the ε region of $0.06 < \varepsilon < 0.19$. The similar differences in I−PNE and N−PNE are observed for the elastomers with a higher cross-linker concentration of $c_x = 10$ mol %, as shown in Figure 5. The curves of I−PNEs show the same features as those reported previously with an initial increase in stress followed by a plateau region and the subsequent stress growth.[2−6] The plateau stresses of I−PNE-3 and I−PNE−10 are 1.8 and 6.3 kPa, respectively. The stretching increases S from zero to a finite plateau value (S_{mono}), which represents the orientational order of the formed monodomain texture. In I−PNEs, S dominantly grows in the strain region exhibiting the plateau stress, and it starts to level off at the end of the plateau region. The saturation of S in N−PNEs occurs at a higher strain (stress) than that for I−PNEs. The appearance of all samples of I−PNEs and N−PNEs changes from opaque to transparent during stretching, which is an indication of the PM transition. Both I−PNEs and N−PNEs recover the initial polydomain state ($S = 0$) after the full release of imposed strain from the monodomain state.

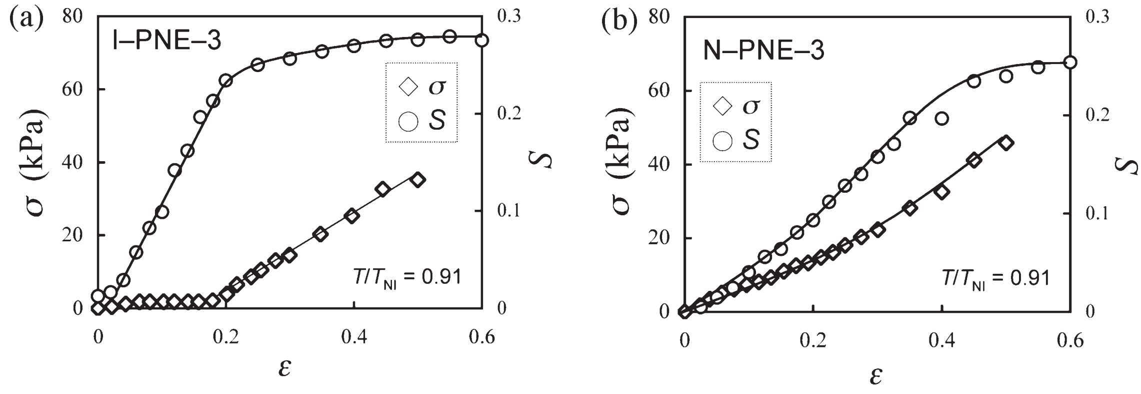

Figure 4. Nominal stress (σ) and global order parameter (S) as a function of nominal strain (ε) for (a) I−PNE−3 and (b) N−PNE−3 in the nematic states of $T/T_{\mathrm{NI}} = 0.91$.

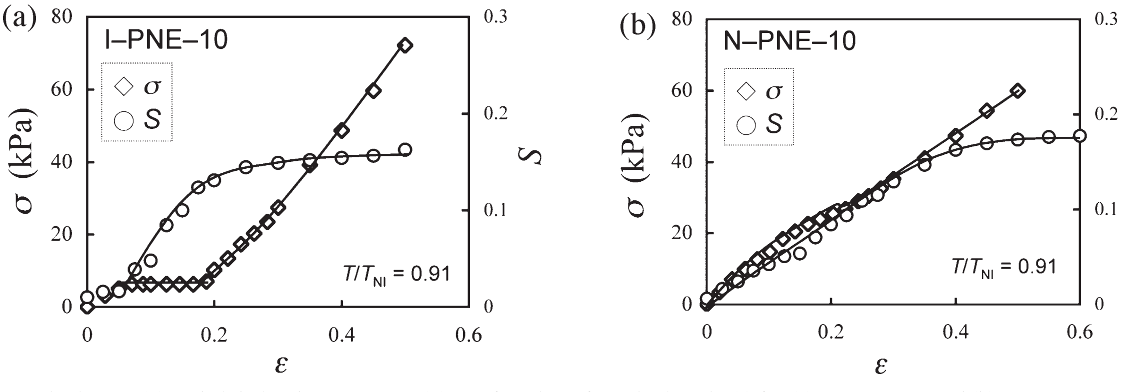

Figure 5. Nominal stress (σ) and global order parameter (S) as a function of nominal strain (ε) for (a) I−PNE−10 and (b) N−PNE−10 in the nematic states of $T/T_{\mathrm{NI}} = 0.91$.

We would like to make some comments on the equilibration of stress. Clark et al.[22] reported that the equilibration of stress in the plateau regime required an extraordinary long time, and the equilibrium stress were only attainable by extrapolation to infinite time. They observed nonuniform necking deformation during stretching. The necking deformation is an indication of mechanical instability and it may be a major origin of very slow stress relaxation. The samples in the present study show no appreciable necking in the whole process of stretching. In addition, the plateau stresses in Figures 4 and 5 are as low as that (ca. 4 kPa) estimated by the extrapolation in their study.[22] These facts support that the stresses obtained here correspond to the equilibrium ones. The equilibration of stress in the plateau regime for I−PNEs required less than a few hours when stretched stepwise. The stress equilibration for I−PNEs in the strain regimes excepting the plateau region and that for N−PNEs in the whole strain region were considerably faster than that for I−PNEs in the plateau regime. The dynamics of stress relaxation in PNEs is also an interesting issue but it is beyond the scope of the present study.

The difference in the P−M transition behaviors of I−PNEs and N−PNEs becomes more obvious in the dependence of S on σ rather than on ε. Figure 6 shows the $S-\sigma$ relations obtained from the $\sigma-\varepsilon$ and $S-\varepsilon$ data in Figures 4 and 5. The order parameter S steeply increases from zero to S_{mono} at a critical nominal stress (σ_c) that corresponds to a plateau stress in Figure 4a or 5a. This trend of I−PNEs was often observed in the literatures.[2−6] The results in Figure 6 indicate that the PM transition in I−PNEs occurs at a nearly constant-force condition: If we conduct the experiments using force as a controllable variable, the specimens are expected to exhibit a spontaneous elongation corresponding to the width of the plateau region in Figures 4 and 5, which is driven by a transition to the monodomain state at a critical force. The stress σ_c increases with c_x. In contrast, the PM transition in N−PNEs exhibits no threshold stress, and S gradually increases in the wide σ range. Interestingly, the cross-linking history has no effect on S_{mono}, although it significantly affects the formation process of monodomain textures. The values of S_{mono} depend on c_x, and S_{mono} increases with decreasing c_x.

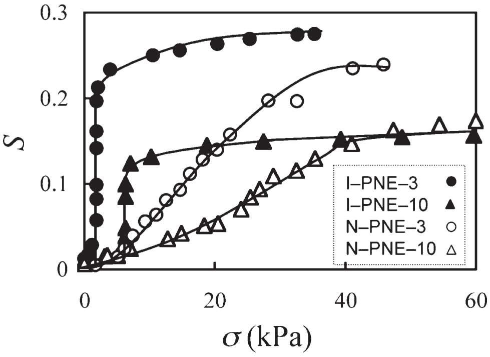

Figure 6. Global order parameter (S) as a function of nominal stress (σ) for I−PNE−3, I−PNE−10, N−PNE−3, and N−PNE−10 at $T/T_{\text{NI}} = 0.91$.

Figure 7 illustrates the temperature (T) effect on the $S-\sigma$ relations for I−PNE-10 and N−PNE-10. No significant difference in S_{mono} at each T is observed between the two elastomers, while S_{mono} decreases with increasing T. In contrast, the T effects in the transition region are considerably different between them: In I−PNE−10, σ_c decreases as T increases ($\sigma_c = 6.3$ and 2.3 kPa at $T/T_{\text{NI}} = 0.91$ and 0.96, respectively), but the $S-\sigma$ relation of N−PNE−10 in the transition regime is almost T independent. Several groups reported the different results for the T dependence of σ_c for I−PNEs: One group[7] observed qualitatively the same trend for the smectic main chain type elastomers as the present study, while the others[4,8] reported almost no dependence. The reason for the different results is unclear, but it should be noticed that the temperature ranges examined in ref 7 and the present study are considerably wider than those in the other groups[4,8] that did not observe a finite dependence: The lowest temperatures in ref 7 ($T/T_{\text{NI}} = 0.86$) and the present study ($T/T_{\text{NI}} = 0.91$) are lower than those in refs 4 and 8 ($T/T_{\text{NI}} = 0.94$ and 0.95, respectively).

Discussions

It is evident from these results that the difference in random alignments of mesogens (polydomain nematic or isotropic state) upon cross-linking has a pronounced effect on the PM transitions of the resultant PNEs. I−PNE undergoes a sharp PM transition at a small critical stress whereas the formation of the monodomain state in N−PNEs gradually proceeds in the wide range of stress. The sharp transition in I−PNEs indicates that the constituent domains concertedly rotate toward the stretching direction at a critical stress. The broad transition in N−PNEs results from the memory effect of the initial disordered alignments of mesogens which is obvious from the similar textures before and after cross-linking (Figure 2). The memory of the initial random alignments gives a robust constraint to the realignment of the individual domains. This memory effect prohibits the uniform director−rotation of the constituent domains, and result in the PM transition proceeding over a wide range of stress. The experimental results clearly indicate that the strongly correlated random structures of N−PNEs needs significantly larger work of deformation for the rotation of the local directors than I−PNEs. A measure of the amount of work required for the monodomain formation (W_{PM}) is simply obtained from the area under the $\sigma-\varepsilon$ curves in the range of $0 < \varepsilon < \varepsilon_e$: ε_e corresponds to the strain where the reorientation is completed, that is, S reaches S_{mono}. In the case of I−PNEs, ε_e is the strain at the end of the plateau regime. Table 1 summarizes W_{PM} for each sample. The values of W_{PM} for N−PNEs are more than 1 order of magnitude larger than those

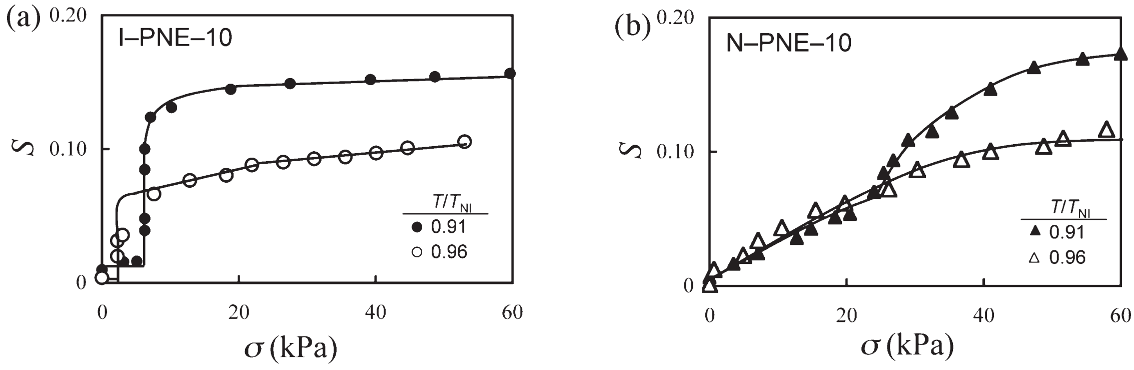

Figure 7. Global order parameter (S) as a function of nominal stress (σ) for (a) I−PNE−10 and (b) N−PNE−10 at $T/T_{\text{NI}} = 0.91$ and 0.96.

for I−PNEs. It should also be noted that W_{PM} of I−PNEs is so small as to be only a few percent of the initial shear modulus (G), which is obtained from the initial slope of the $\sigma-\varepsilon$ curve. Küpfer et al.[5] observed a considerably difference in the stretching driven director−orientation behavior between the monodomain nematic elastomers cross-linked in the isotropic and nematic states under loading. They attributed the difference to a memory effect, that is, an anisotropic orientational distribution of cross-links in the elastomers made in the nematic state. N−PNEs possess the polydomain nematic field before polymerization (Figure 2), and W_{PM} of N−PNEs are almost unaffected by c_x. These results indicate that the memory effect in N−PNEs results from the polydomain nematic field of the mesogens rather than the anisotropic orientational distribution of cross-links. The marked difference in nematic texture between I−PNEs and N−PNEs may also lead to a significant effect on the conformation of the network strands. We need the information about the network structures to discuss this issue.

The simulation work of Uchida[14] predicted that the cross-linking history significantly influences the PM transition behaviors: I−PNEs exhibits a perfectly soft response ($W_{PM} = 0$), that is, the PM transition completes at zero stress ($\sigma_c = 0$); N−PNEs need a finite stress for the transition, and the monodomain formation continuously proceeds in a finite range of stress. These features are qualitatively similar to the experimental results, although a finite threshold stress ($\sigma_c \neq 0$) is observed in the real I−PNEs. In ref 14, the nonsoft PM transition of N−PNEs was attributed to the strong dehomogenization of the spatial distribution of elastic free energy which was caused by the memory of the initial mesogen orientation.

Another interesting aspect of the memory effect of randomness in N−PNEs is observed in the T dependence of W_{PM}. As can be seen in Table 1, W_{PM} for N−PNEs is insensitive to T. In other words, W_{PM} for N−PNEs is not appreciably affected by the local order parameter (S_{local}) for the individual domains at the temperature for elongation, because S_{local} increases with decreasing T. Furthermore, the effect of c_x on W_{PM} for N−PNEs is also small, as observed in Table 1. This is because the distance between neighboring cross-links (ξ_c) is much smaller than the size of local nematic domains (ξ_D): $\xi_D/\xi_c > 10^4$. These results imply that the strength of the memory of randomness in N−PNEs is mainly governed by S_{local} at the temperature for cross-linking (T_{prep}). The influence of T_{prep} on W_{PM} provides important information about this issue, but the photocross-linking at precisely controlled temperature was difficult in the vicinity of T_{NI} where S_{local} is appreciably temperature−dependent because the heat of light irradiation was not negligibly small. In our previous study,[13] no difference in the strain recovery dynamics was observed for the two N−PNEs made at the temperatures lower than T_{NI} by 5 and 17 °C. This is probably due to the small difference in S_{local} at the two temperatures, which are considerably far from T_{NI}.

The PM transition of the "ideal" I−PNEs are theoretically expected to need no energy cost ($W_{PM} = 0$).[14] A finite W_{PM} observed for the real I−PNEs indicates the presence of a finite potential required for the onset of the uniform rotation of local directors. The effects of T and c_x on W_{PM} give important basis about the physical origin of the finite W_{PM}. Fridrikh et al.[10] theoretically derived the simple expression of σ_c by considering the elastic energy cost which results from the size mismatch in the domains boundary region between the initially misaligned domains:

$$\sigma_c \approx G(r-1) \tag{1}$$

where G and r are the shear modulus and the parameter for the anisotropy of network strands, respectively. The parameter r is related to S_{local} as $r = (1 + 2S_{local})/(1 - S_{local})$.[1] The validity of eq 1 was discussed using σ_c of several polydomain nematic elastomers,[10] but it has not yet been examined from the viewpoint of the dependence of σ_c on T and c_x. Table 2 summarizes σ_c and G for I−PNEs. The values of G were estimated from the initial Young's modulus (E), that is, the initial slope of the stress−strain curve, using $E = 3G$ for incompressible materials. A decrease in T leads to an increase in σ_c. This trend is qualitatively explained by eq 1, because r increases with decreasing T as a result of an increase in S_{local}, whereas the T dependence of G is sufficiently small in the T range of interest. Equation 1 also qualitatively explains the c_x dependence of σ_c. If the literature value of r ($\approx$1.1) for polyacrylate−based nematic elastomers[10] is employed in eq 1 at $T/T_{NI} = 0.91$ (sufficiently far from T_{NI}), the resultant values of σ_c for the elastomers with $c_x = 3$ and 10 mol % are 1.0 and 3.0 kPa, respectively, each of which is not much different from the corresponding experimental value (1.8 and 6.3 kPa, respectively) in spite of the crudity of the estimations.

Table 2. Characteristics of I−PNEs

	$T/T_{NI} = 0.91$		$T/T_{NI} = 0.96$	
	σ_c (kPa)	G (kPa)	σ_c (kPa)	G (kPa)
I−PNE−3	1.8	10	[a]	[a]
I−PNE−10	6.3	30	2.3	31

[a] Not measured.

The values of S_{mono} in the present study, which are as large as 0.3, are relatively small compared to those in the previous studies. This is mainly attributed to the small chain anisotropy ($r \approx 1.1$) specific to the acrylate-based nematic elastomers, and a modest coupling between the alignments of the dangling mesogens and network backbone originating from the relatively long spacer (six methylene units). The main features of the cross-linking history effects on the PM transtions revealed in the present study should be universal for general PNEs independently of the chemical structures of the mesogens and network backbone.

Summary

The stretching−induced PM transition behaviors markedly depend on whether the mesogen is cross-linked in the high-temperature isotropic state or low−temperature polydomain nematic state. The transition of the former (I−PNE) occurs at a very small constant−force condition. The latter (N−PNE) needs a substantially larger energy for the formation of the monodomain texture, and the formation gradually proceeds over the wide range of stress. The main features of the effects of cross-linking history on the PM transitions qualitatively agree with the results in a simulation work.[14] N−PNEs show almost the same polydomain nematic texture as the nematogens before cross-linking, while the domain size of I−PNEs is much smaller than that of N−PNEs. The broad transition of N−PNEs originates from the memory effect of randomness regarding the initial mesogen alignment upon cross-linking which results in a robust constraint to the reorientation of local directors. The energy required for the monodomain formation for N−PNEs is almost independent of the temperature for stretching as well as cross-linker concentration. These results imply that the memory effect is mainly governed by the state of random orientation upon cross-linking (i.e., cross-linking temperature). The work of deformation required for the PM transition of I−PNEs is very small: It is only a few percent of the shear modulus. The required work increases with an increase in cross-linker concentration as well as a decrease in temperature for stretching. These trends are qualitatively explained by the existing theory.[10]

Note Added after ASAP Publication. This article was published ASAP on May 6, 2009. Two values in Table 1 have been modified. The correct version was published on May 8, 2009.

Acknowledgment. The authors would like to thank Ryo Mashita for his assistance in tensile experiments. The authors also appreciate the cooperation of Prof. Kenichi Yoshikawa in Kyoto University in the preliminary observation of nematic texture. The authors also thank Dr. Nariya Uchida in Tohoku University for helpful discussions. This work was partly supported by a Grant-in-Aid on Priority Area "Soft Matter Physics" (No. 19031014) and a Grant-in-Aid for Scientific Research (B; No. 16750186) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. This research was also supported in part by the Global COE Program "International Center for Integrated Research and Advanced Education in Materials Science" (No. B-09) of MEXT of Japan, administrated by the Japan Society for the Promotion of Science.

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