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## Liquid Crystals

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# Swelling behaviour of poly(butadiene) gels in liquid crystal solvents

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The swelling behaviour of poly(butadiene) gels in four different nematogenic liquid crystalline (LC) solvents has been investigated as a function of temperature ( $T$ ). Microscopy with crossed polarizers reveals that the nematic to isotropic phase transition temperature of the LC solvents inside the gels ( $T_{NI}^g$ ) is slightly lower than that of the surrounding pure LC solvents ( $T_{NI}^o$ ), but the degrees of depression in  $T_{NI}^g$  in each system are comparable regardless of the considerable differences in the degrees of equilibrium swelling ( $Q$ ) at  $T_{NI}^g$  between the various systems. In general,  $Q$  in the isotropic phase is larger than that in the nematic phase, but a unique swelling behaviour of the gel is found in the vicinity of  $T_{NI}$  due to the phase transition of the LC solvents.  $Q$  remains constant in the temperature range of  $T_{NI}^g \leq T \leq T_{NI}^o$  in which the phases of the LCs outside or inside the domain of the gels are different, namely, nematic and isotropic phase, respectively. In addition, a finite abrupt (discontinuous-like) change in  $Q$  is observed at around  $T_{NI}$ . The gels swollen in the LCs, having an ability to interact with the crosslinking points via hydrogen bonding, show a significant thermal hysteresis for the temperature dependence of  $Q$  in the vicinity of  $T_{NI}$ , while no discernible thermal hysteresis is observed for the gels in the LCs incapable of forming hydrogen bonds.

## 1. Introduction

Swelling is an interesting property specific to polymer gels, together with rubber elasticity. The degree of swelling of polymer gels significantly depends on conditions such as the nature of the swelling solvents, temperature, etc., which influence the thermodynamic interaction between the constituent polymer and the solvent. The unique characteristics of swelling phenomena have attracted much attention of physicists, chemists and engineers from both academic and industrial viewpoints [1–5]. The thermodynamics and kinetics of swelling have been extensively investigated both experimentally and theoretically. Most of the earlier studies focused on swelling in conventional isotropic solvents, but a few studies [6–8] on polymer gels swollen in anisotropic solvents, i.e. liquid crystal (LC) solvents have been reported. As pointed out first by Brochard [7], a polymer network swollen in a liquid crystal solvent is theoretically expected to exhibit some unique physical properties originating from the nematic to isotropic phase transition and the nematic character of the LC solvents. Especially, the effect of the nematic to isotropic phase transition of the LC on the degree of equilibrium swelling ( $Q$ ) is an interesting subject, as the phase

transition of the LC (as swelling solvent) from an isotropic to an anisotropic character may considerably change the thermodynamic interaction between the constituent polymer and the LC. It has been reported [3] that some polymer gels show a large discontinuous change in gel volume (called volume phase transition), caused by abrupt changes in thermodynamic interactions in response to small changes in temperature, solvent composition, etc. at certain critical values.

In our previous paper [8], preliminary studies on the nematic to isotropic phase transition and swelling behaviour for a polymer gel swollen in a LC were reported for poly(butadiene) (PB) gels in *p*-ethoxybenzylidene-*p*-*n*-butylaniline (EBBA), a nematic LC. It was observed that the nematic to isotropic phase transition temperature ( $T_{NI}$ ) of EBBA inside the PB gel was slightly lower than that of the surrounding (pure) EBBA. The depression in  $T_{NI}$  of EBBA inside the PB gels was also found to be much smaller in comparison with that of EBBA in the un-crosslinked PB solution with the same PB content. It was also reported [8] that the variation of  $Q$  with temperature was continuous without any anomaly below and above  $T_{NI}$ . Unfortunately, a thorough investigation on the swelling behaviour of the PB gel in the vicinity of  $T_{NI}$  of the LC was not possible because of the undesirable hydrolysis of EBBA in the presence of even trace amounts of moisture. In the present

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study, we have critically investigated the temperature dependence of  $Q$  especially in the close vicinity of  $T_{NI}$  using four chemically stable LC solvents with varying structures. We have demonstrated that the PB gels in the LC solvents show interesting and complex swelling behaviour in the vicinity of  $T_{NI}$  because of the nematic to isotropic phase transition of the LC solvents, and that there are two different  $T_{NI}$  values outside and inside the gels. We have also seen some significant differences in swelling behaviour between LCs with and without the ability to form hydrogen bonds.

## 2. Experimental

### 2.1. Material

The hydroxyl-terminated polybutadiene used as the precursor chain for network formation was obtained from the Aldrich Chemical Co. The quoted mass average molecular mass of the PB was  $6.2 \times 10^3 \text{ g mol}^{-1}$ . Triphenylmethane-4,4'-4''-tri-isocyanate (TPMTI), used as crosslinking agent, was procured from the Sumitomo Bayer Co. The liquid crystals, 4'-octyl-4-biphenyl-carbonitrile (**I**), 4-(*trans*-4-pentylcyclohexyl) benzonitrile (**II**), 4-cyanophenyl 4-heptylbenzoate (**III**) and 4,4'-diheptylazoxybenzene (**IV**), used as swelling solvents, were obtained from the Aldrich Chemical Co. The chemical structures of the LC solvents are shown in figure 1. The LC solvents with a quoted purity of at least 98% were used without further purification.

### 2.2. Sample preparation

The polymer network was prepared by end-linking the hydroxyl-terminated PB with TPMTI in *p*-xylene. The PB concentration was 30 vol %. The pre-gel solution was transferred into an end-capped glass tube with a diameter of *c.* 1 mm. The end-linking reaction was performed at room temperature for 24 h. The resulting

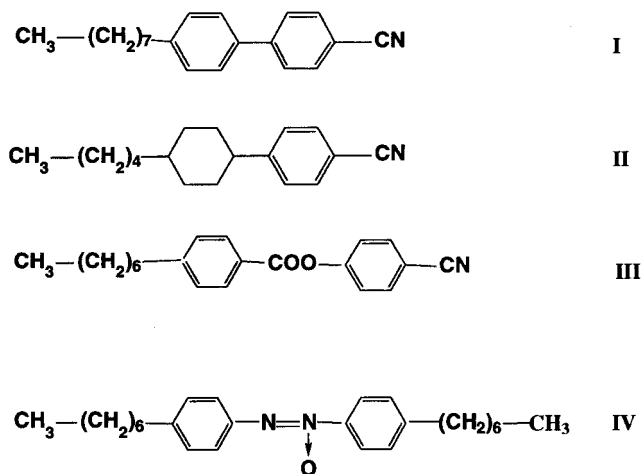


Figure 1. Chemical structures of the liquid crystalline solvents.

chemically crosslinked cylindrical gels were immersed in *p*-xylene for two days and subsequently in toluene for four weeks. The *p*-xylene and toluene were renewed every day in order to wash away residual chemicals or unattached chains. The mass fractions of unreacted materials were found to be less than 5%. The gel samples were completely dried in air and thereafter immersed in the LC solvents in an optical cell at selected temperatures until equilibrium swelling was achieved.

### 2.3. Measurements

The phase and swelling behaviours were examined using a Nikon polarizing optical microscope equipped with a Mettler hot stage FP-82 under a nitrogen atmosphere. The experimental set-up used here is the same as that reported previously [8]. The temperature was controlled with an accuracy of better than  $\pm 0.05 \text{ K}$ . The nematic to isotropic phase transition temperature ( $T_{NI}$ ) of the LC solvent was determined as the temperature at which the nematic texture appears in the cooling process. The error in determination of  $T_{NI}$  was less than  $\pm 0.1$  degree. The surface level of the LC solvents was adjusted to be low enough so that the phases of the LC inside the gels and the boundary of the gel surface were distinctly visible when viewed through the microscope (but high enough to immerse the gel completely). No appreciable change in  $T_{NI}^{\circ}$  was observed throughout the experiments, confirming the chemical stability of the LC solvents used.

The gel samples in the equilibrium swollen state at various swelling temperatures as viewed in the polarizing microscope were photographed, and the diameters of the cylindrical gels at each temperature were measured from the enlarged photographs. The degree of equilibrium swelling ( $Q$ ), defined as the ratio of the gel volumes in the dry ( $V_0$ ) and equilibrium swollen state ( $V$ ), was calculated from the diameter of the gels in the dry ( $d_0$ ) and swollen state ( $d$ ) under the assumption of isotropic swelling using the relationship

$$Q = V/V_0 = (d/d_0)^3. \quad (1)$$

The maximum value of  $d/d_0$  for the entire measurements was only about 2. Therefore the gels remained free without being touched by the surface of the window of the Mettler hot stage and so the isotropic swelling condition prevailed throughout the entire experiment.

## 3. Results

Microscopic observation with crossed polarizers reveals that the LC solvents outside and inside the gels have different nematic to isotropic transition temperatures ( $T_{NI}$ ) for all the systems studied. The LC solvent outside the gel corresponds to the pure LC solvent. The  $T_{NI}$  of the LC inside and outside the gel, designated  $T_{NI}^g$  and  $T_{NI}^{\circ}$ , respectively, are displayed in the table. It

Table. Nematic–isotropic phase transition temperature ( $T_{\text{NI}}$ ) of liquid crystalline solvents outside and inside the poly(butadiene) gel. Determinations made during cooling

Solvent	$T_{\text{NI}}^{\circ}/\text{K}^{\text{a}}$	$T_{\text{NI}}^{\text{g}}/\text{K}^{\text{b}}$
<b>I</b>	313.6	312.9
<b>II</b>	327.3	326.4
<b>III</b>	328.1	327.4
<b>IV</b>	343.5	342.6

<sup>a</sup> Outside gel.

<sup>b</sup> Inside gel.

can be seen that  $T_{\text{NI}}^{\text{g}}$  of all the systems are 0.7–0.9 degree lower than  $T_{\text{NI}}^{\circ}$ . A similar observation was found for PB gels in EBBA liquid crystal as reported previously [8]. In the temperature range  $T_{\text{NI}}^{\text{g}} \leq T \leq T_{\text{NI}}^{\circ}$ , the LCs outside and inside the domain of the gel form two different phases: nematic and isotropic, respectively. The corresponding appearance of the surrounding solvents and gel remain bright and dark, respectively, using crossed polarizers.

The temperature ( $T$ ) dependences of the degree of equilibrium swelling ( $Q$ ) for the PB gels in the different LC solvents are shown in figures 2(a–d). In general,  $Q$  tends to increase with increase in temperature. The magnitude of  $Q$  in the isotropic phase is larger than that in the nematic phase. It is also found that the  $T$  dependences of  $Q$  around  $T_{\text{NI}}$  for all the systems have the following three common features as shown by the insets of figures 2(a–d): (i) the  $Q$ – $T$  curves show plateau regions at around  $T_{\text{NI}}$  with no appreciable change in  $Q$ ; (ii) the plateau regions extend slightly but definitely beyond the temperature region  $T_{\text{NI}}^{\text{g}} \leq T \leq T_{\text{NI}}^{\circ}$ ; (iii) a finite abrupt (discontinuous-like) change in  $Q$  is observed at certain temperatures around  $T_{\text{NI}}$ . These characteristic swelling behaviours are likely to be independent of the swelling ability of the PB gels with LCs, since  $Q$  is observed to be considerably different for all four LC solvents. Compared more critically, however, some significant differences can be pointed out in the above-mentioned three general features for all the systems studied. For simplicity, the gels with four different liquid crystalline solvents can be categorized into two groups according to their observed swelling behaviour in the temperature range  $T_{\text{NI}}^{\text{g}} \leq T \leq T_{\text{NI}}^{\circ}$ . For the gel in LCs **I** and **II**,  $Q$  does not change in the temperature range  $T_{\text{NI}}^{\text{g}} \leq T \leq T_{\text{NI}}^{\circ}$ . On the other hand, for the gel with LCs **III** and **IV**, a finite abrupt volume change is observed between  $T_{\text{NI}}^{\text{g}}$  and  $T_{\text{NI}}^{\circ}$ .

Another striking difference in the swelling behaviour between the two groups is observed in the thermal hysteresis effects of the  $T$  dependence of  $Q$ . The swelling curves in the cooling and subsequent heating process for the systems with LCs **III** and **IV** are shown in figures

3(a) and 3(b), respectively. It can be seen that the  $T$  dependence of  $Q$  shows thermal hysteresis at temperatures near  $T_{\text{NI}}$ , while no significant differences in the  $Q$  values for the cooling and heating processes are observed at temperatures either far above or below  $T_{\text{NI}}$ . In both the gels containing LCs **III** and **IV**,  $Q$  values in the heating process are definitely smaller than those in the cooling process, at temperatures in the vicinity of  $T_{\text{NI}}$ . It should be noted that the swelling curves are reproducible over a number of trial runs, confirming the presence of hysteresis. On the contrary, the system with LC **I** is found to produce the same swelling curve within experimental error, regardless of the direction in which the temperature is varied, as shown in figure 3(c). The system with LC **II** also exhibits no appreciable thermal hysteresis in the swelling curve, although the data are not shown here.

#### 4. Discussion

The slightly lower  $T_{\text{NI}}^{\text{g}}$  compared with  $T_{\text{NI}}^{\circ}$ , commonly observed for all the systems, can be qualitatively explained by taking into account the impurity effects of the polymer backbone of the gels on the phase transition of the LCs. The existence of a non-mesomorphic substance, in general, depresses the  $T_{\text{NI}}$  of LCs [8–11]. However, it is noteworthy that the degrees of depression in  $T_{\text{NI}}^{\text{g}}$  in each system are comparable (0.7 to 0.9 degree) regardless of the considerable differences in  $Q$  values (impurity content) at  $T_{\text{NI}}^{\text{g}}$  for all the systems. For example, the polymer volume fractions in the gels containing LCs **II** and **III** at  $T_{\text{NI}}^{\text{g}}$  are *c.* 0.14 and *c.* 0.49, respectively, corresponding to the minimum and the maximum for the four systems. Here, the polymer volume fractions are calculated using the assumption of volume additivity for the PB and solvents. In our previous communication, we reported that  $T_{\text{NI}}^{\text{g}}$  of the PB gels in EBBA was much higher than  $T_{\text{NI}}$  of the un-crosslinked PB solution of EBBA with the same PB content, i.e.  $T_{\text{NI}}^{\text{g}}$  was not depressed as much as expected from the impurity content [8]. In the present study, the independence of the  $T_{\text{NI}}^{\text{g}}$  values on the polymer volume fraction observed also implies that the depression in  $T_{\text{NI}}^{\text{g}}$  cannot be explained simply in terms of just the impurity effect. Interaction between the LC solvents outside and inside the gel leading to promotion of nematic phase formation inside the gel, if present, may explain the unexpected insensitivity of  $T_{\text{NI}}^{\text{g}}$  to polymer volume fraction for the present systems. This problem is worth investigating further, but is beyond the scope of this present paper.

In the temperature range  $T_{\text{NI}}^{\text{g}} \leq T \leq T_{\text{NI}}^{\circ}$ , the  $T$  dependence of  $Q$  for all the systems shows plateau regions, although a discontinuous-like volume change at certain temperatures is noticed for gels with LCs **III** and **IV**. It is well known that in the absence of any

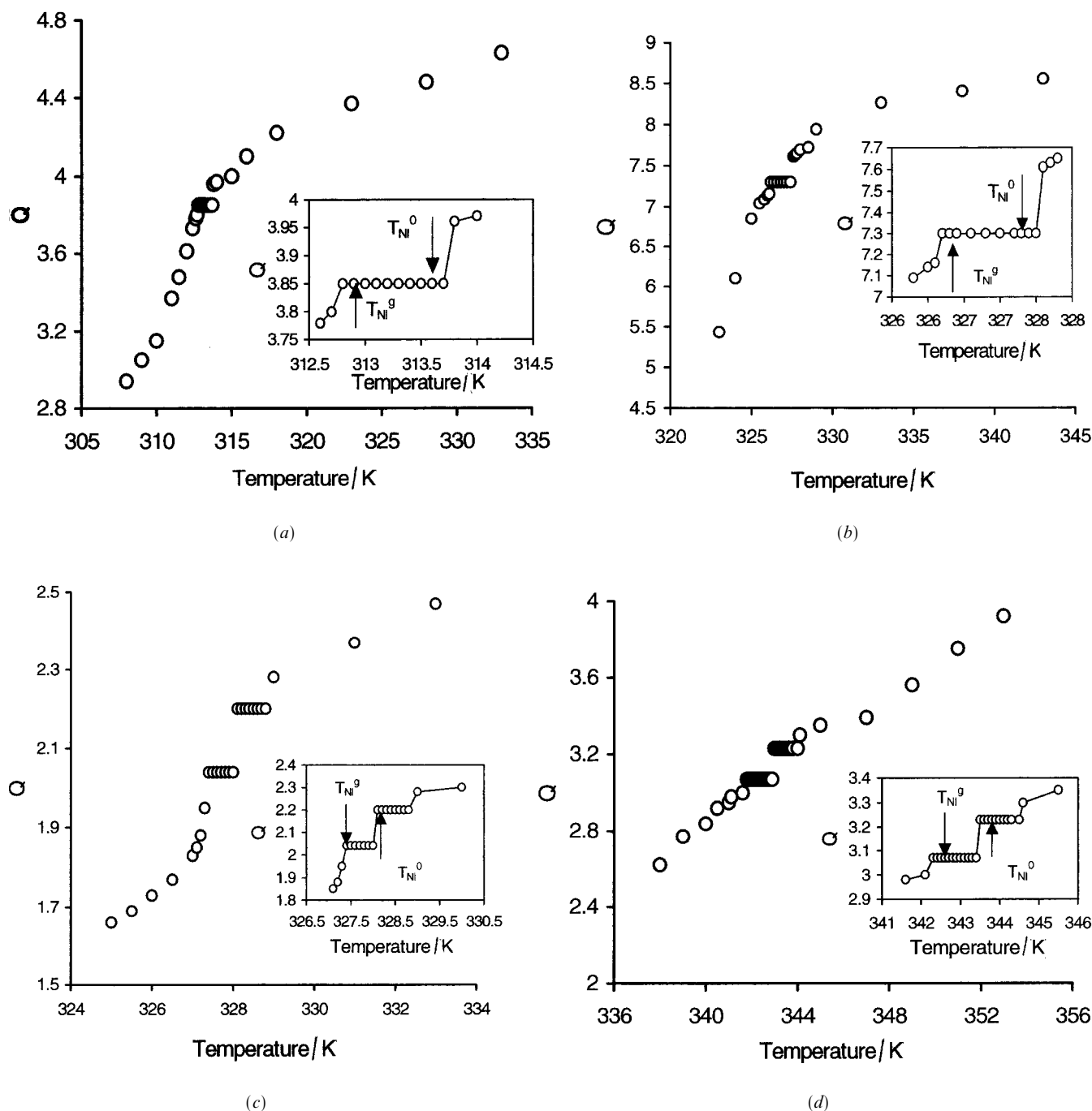


Figure 2. Temperature dependence of the degree of equilibrium swelling ( $Q$ ) of PB gel in (a) 4'-octyl-4-biphenylcarbonitril (I); (b) 4-(trans-4-pentylcyclohexyl)benzonitril (II); (c) 4-cyanophenyl 4-heptylbenzoate (III); (d) 4,4'-diheptylazoxybenzene (IV). The insets relates to the vicinity of the nematic-isotropic transition temperature.

external electric or magnetic field, a LC in the nematic phase forms a so-called poly-domain structure where the direction of the principal axis of orientation (the director) is macroscopically random in space, but a high order of alignment of LC molecules in each domain is maintained [12]. In the temperature range  $T_{NI}^g \leq T \leq T_{NI}^0$  which is characterized by a plateau region for  $Q$ , the LC

solvent inside the gel is isotropic, whereas the solvent outside is in the nematic phase. It appears that such a phase difference prevents the flow of LC solvent between the outside and the inside of the gel and swelling practically stops, showing an almost constant value of  $Q$  with reference to temperature change. It is emphasized that the phase transitions of all the LC solvents used

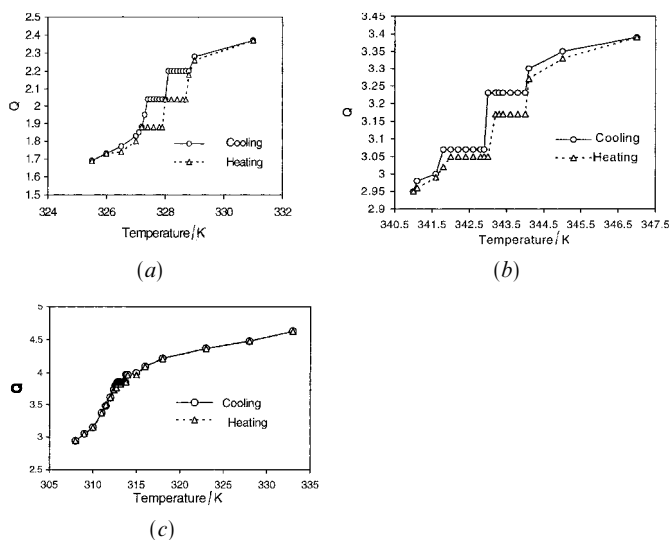


Figure 3. Temperature-swelling curves (heating and cooling) for PB gel in (a) 4-cyanophenyl 4-heptylbenzoate (**III**); (b) 4,4'-diheptylazoxybenzene (**IV**); (c) 4'-octyl-4-biphenyl-carbonitrile (**I**).

occur sharply within a temperature range of less than 0.1 K, convincing us that the almost constant  $Q$  values in the range  $T_{NI}^g \leq T \leq T_{NI}^o$  are not due to the broad transition temperature ranges commonly observed for some commercially available LC solvents. The reason for the discontinuous-like volume change occurring in the range  $T_{NI}^g \leq T \leq T_{NI}^o$  in the systems with LCs **III** and **IV**, which cannot be explained by considering only the phase difference, will be discussed later.

It has been noted that the plateau regions of  $Q$ , for all the systems extend slightly wider than the temperature range  $T_{NI}^g \leq T \leq T_{NI}^o$ . Despite the identity of LC phase inside or outside the gel,  $Q$  remains constant even slightly above  $T_{NI}^o$ , as well as below  $T_{NI}^g$ . This may be due to the critical behaviour of the LC in the close vicinity of  $T_{NI}$ . It is well known that various physical properties of LCs show some pretransitional phenomena in the close vicinity of  $T_{NI}$ , implying that the LC molecules have a local order of spatial correlation even in the isotropic phase [13, 14]. Pretransitional effects have been reported in light scattering, magnetic-, electric-, and flow-birefringence studies [15–18]. The extension of the plateau regions of  $Q$  slightly beyond the temperature region  $T_{NI}^g \leq T \leq T_{NI}^o$  may also be an indication of such pretransitional phenomena of the LC solvents in the close vicinity of  $T_{NI}$ .

The discontinuous-like change in  $Q$  is observed at certain temperatures for all the systems, but the degree of discontinuity is much smaller than that observed in some gels showing a typical volume phase transition. As mentioned before, without application of any external fields, a nematic LC has poly-domain structure where

the anisotropic nature of the LC is macroscopically cancelled out. Accordingly, it is expected that the nematic to isotropic transition does not cause a remarkable change in thermodynamic interaction (affinity) between PB and the LC, as well as in  $Q$ , which is directly related to the thermodynamical interaction. This expectation qualitatively agrees with the experimental results. The slight discontinuity of volume change may be attributed to the screening effect of the poly-domain nematic structure on the anisotropic character of the nematic LC molecules. However, the effect of the formation of the poly-domain nematic structure on the thermodynamic interaction between the PB and LC is still large enough to cause an appreciable, though small, discontinuous-like change in gel volume. Formation of a mono-domain nematic structure, under the application of an external field whereby the LC molecules are macroscopically aligned in a unique direction would be expected to induce a significant change in the thermodynamic interactions leading to a large discontinuous volume change. Swelling in a mono-domain nematic LC solvent using an external electric field is our future subject of study.

The swelling behaviour of the gels with LCs **III** and **IV** is significantly different in two major points from that of the systems containing LCs **I** and **II**: first is the swelling behaviour in the range  $T_{NI}^g \leq T \leq T_{NI}^o$  and second the thermal hysteresis effects on  $Q$ . The probable reason for the different swelling behaviour of the gels with LCs **III** and **IV** compared with the gels with LCs **I** and **II** is a specific interaction between the gel and the solvents via hydrogen bonding. The molecular structures of LCs **III** and **IV**, as shown in figure 1, suggest that intermolecular hydrogen bonding may occur between the hydrogen of  $-NH$  groups in the crosslink points of the gels and the ester carbonyl group ( $-C=O$ ) of **III** or  $-N(=O)N-$  groups of **IV**. LC solvents **I** and **II** are incapable of forming hydrogen bonding with the crosslinking points of the network. It is to be noted that the swelling characteristic of the systems containing **III** and **IV** is qualitatively analogous to that of some gels where hydrogen bonding takes place among the constituent polymer molecules [3, 19, 20]. These hydrogen-bonded polymer gels have been reported to exhibit not only a large discontinuous volume phase transition, but also significant thermal hysteresis in  $Q$  at around the volume phase transition temperature. The chance of formation of hydrogen bonds between the crosslink points leading to aggregation cannot be ruled out, and some reports have mentioned that polyurethanes form aggregates themselves via hydrogen bonding among the urethane groups [21]. In the gels with **III** and **IV**, the formation and disappearance of the local nematic domain and the global poly-domain nematic structures should significantly influence the probability of formation of hydrogen

bonds between the LC and the crosslinking points, as well as the aggregation of the crosslinking points.

In order to confirm the involvement of hydrogen bonding on the swelling behaviour of the gel, it would be necessary to resolve the hydrogen bonding behaviour at different temperatures and FTIR spectroscopy is an effective method of doing this. But the leaching of the LC solvent out of the fully swollen gels during the measurement would be inevitable due to the absence of surrounding LC solvents, and this is a serious obstacle for quantitative FTIR measurements at present.

### 5. Conclusions

We have examined the swelling behaviour of poly-(butadiene) gels swollen in four different nematic liquid crystalline solvents. The nematic to isotropic phase transition temperature of the LCs inside the gels ( $T_{NI}^g$ ) is slightly depressed due to the impurity effects of the polymer backbone relative to that of the surrounding pure LC solvents ( $T_{NI}^o$ ). The degrees of depression in  $T_{NI}^g$  in each system are comparable (0.7 to 0.9 degree) regardless of the considerable difference in polymer volume fraction at  $T_{NI}^g$  between the systems. In general, the degree of swelling ( $Q$ ) increases with increase in temperature, but the nematic to isotropic transition of the LC solvents largely influences the temperature dependence of  $Q$  in the vicinity of  $T_{NI}$ . In the temperature region  $T_{NI}^g \leq T \leq T_{NI}^o$ ,  $Q$  remains unchanged against temperature change probably due to the phase difference of the LCs outside and inside the domain of the gels, namely, nematic and isotropic phase, respectively. An abrupt change (discontinuous-like) in  $Q$  is also observed at certain temperatures around  $T_{NI}$ .

The gels in the LCs capable of forming hydrogen bonds between the crosslinking points show pronounced thermal hysteresis in the temperature dependence of  $Q$  in the vicinity of  $T_{NI}$ , while no appreciable thermal hysteresis is observed for the gels in the LCs without the ability to form hydrogen bonds. This behaviour is qualitatively analogous to that reported for hydrogen-bonded polymer gels [19] where a significant thermal hysteresis was also evidenced in swelling.

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