Concentration fluctuations induced by orientation fluctuations in polybutadiene–4-cyano-4′-*n*-octyl-biphenyl mixtures

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The changes in concentration fluctuations of polymer–liquid crystal (LC) binary mixtures with temperature were investigated by small-angle X-ray scattering in their one-phase region and in the isotropic state of the LC. The concentration fluctuations consist of two modes: an OZD mode expressed by the Ornstein–Zernike–Debye equation with a correlation length ξ and a DB mode expressed by the Debye–Buche equation with a correlation length l. The temperature dependence of the OZD mode exhibits critical phenomena similar to common binary mixtures. Under the condition where the LC molecules are oriented by an electric field, the OZD mode is insensitive to the orientation while the DB mode is enhanced perpendicular to the orientation direction. These results indicate that the DB mode is induced by the orientation of the LC molecules.

1. Introduction

It is well known that the scattering intensity of binary mixtures in the one-phase region is described by the Orstein–Zernike–Debye (OZD) equation. Analyses with the OZD equation yield two parameters, the scattering intensity at the scattering vector $\mathbf{q} = 0$, $I(0)$, and the correlation length ξ. Their temperature dependences are described by the three-dimensional (3D) Ising model (Stanley, 1971). The critical phenomena of polymer solutions also have been extensively investigated and the temperature dependences of $I(0)$ and ξ in polymer solutions obey the 3D Ising model (Kuwahara *et al.*, 1971). Although polymer–liquid crystal (LC) mixtures are kinds of polymer solutions, polymer–LC mixtures have another order parameter in terms of orientation of the LC molecules in addition to concentration, and the phase transition behaviour, such as the isotropic nematic transition, depends on the orientation of the LC molecules. Thus, the phase behaviour and the critical phenomena of polymer–LC mixtures become more complicated than those in other common polymer solutions. The phase diagrams of polymer–LC mixtures have been investigated extensively. Experimental studies of the phase diagrams have shown that a nematic isotropic transition of the LC occurs as well as a liquid–liquid phase transition between the polymer and the LC (Ahn *et al.*, 1992; Benmouna *et al.*, 2000; Dubault *et al.*, 1980; Kronberg *et al.*, 1978; Matsuyama *et al.*, 2000; Shen & Kyu, 1995; Smith, 1993). Several authors predicted the phase diagrams theoretically by combining Flory–Huggins theory for isotropic mixing of two components with Malser–Saupe theory for nematic interactions (Holyst & Schick, 1992; Matsuyama & Kato, 1996).

In a previous paper (Takenaka *et al.*, 2006), we investigated the critical phenomena of a polystyrene (PS)–LC (4-cyano-4′-*n*-octyl-biphenyl, 8CB) mixture by small-angle X-ray scattering (SAXS) in the one-phase region of the mixture and the isotropic state of the LC. We found that the concentration fluctuations consist of two modes characterized by the Ornstein–Zernike–Debye equation with a correlation length ξ (OZD mode) and the Debye–Buche equation with a correlation length l (DB mode). The temperature dependence of the OZD mode exhibits critical phenomena similar to common binary mixtures. Under the condition where the LC molecules are oriented by an electric field, the OZD mode is insensitive to the orientation while the DB mode is enhanced perpendicular to the orientation direction.

In this study, we will show that these two modes can be also observed in a polybutadiene (PB)/8CB mixture and that the DB mode is induced by orientation fluctuations of 8CB.

2. Experimental

The weight-averaged molecular weight M_{w} of PB is 2.61×10^5 g mol^{-1} with a heterogeneity index of 1.04. The volume fraction of PB, ϕ_{PB}, studied here was 0.10. We prepared the specimen by solvent casting at 343 K from toluene solution. The cloud point of this mixture is 330.0 K and the nematic isotropic transition temperature of 8CB in the mixture is 314.0 K. We measured SAXS for this mixture at 350.0, 340.5, 331.0 and 330.2 K, where the LC is in an isotropic state in one phase of this mixture. SAXS experiments were conducted at the BL45XU beamline, Spring-8 (Fujisawa *et al.*, 2000). We used a CCD camera with an image intensifier (Amemiya *et al.*, 1995). The X-ray wavelength λ was 0.11 nm. The SAXS patterns were corrected for the background, air and the transmittance, and then circularly averaged for further analysis.

To clarify the effects of the orientation fluctuations on the concentration fluctuations of the mixture, we applied an electric field to the mixture to align the orientation fluctuations and investigated how the SAXS patterns were affected. We used a cell having a pair of electrodes and sandwiched the sample between the electrodes. SAXS patterns were measured under the application of 800 V mm^{-1}.

3. Results and discussion

Fig. 1 shows the SAXS scattering intensity $I(q)$ plotted as a function of the magnitude of the scattering vector q [$= (4\pi/\lambda)\sin(\theta/2)$] at 350 K
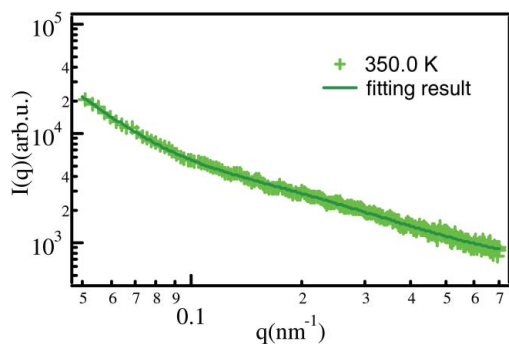
Figure 1
The scattering intensity $I(q)$ is plotted as a function of q at 350.0 K. The solid lines correspond to the fitting with equation (1).

with θ being the scattering angle. Like the case of the PS–8CB mixture, the scattering intensity of PB–8CB exhibits an upturn at $q <$ 0.1 nm^{-1} and can not be described by the OZD equation alone. According to the previous result, the whole scattering profile can be expressed by a linear combination of the Debye–Buche (DB) equation and the OZD equation,

$$I(q) = \frac{I_{DB}(0)}{(1 + q^2 l^2)^2} + \frac{I_{OZD}(0)}{(1 + q^2 \xi^2)} + I_{TDS}, \qquad (1)$$

where l and ξ are correlation lengths for the DB and OZD equations, respectively. I_{TDS} is the thermal diffuse scattering of the mixture. Thus, we fitted the experimental data of the PB–8CB mixture using equation (1) with $I_{DB}(0)$, l, $I_{OZD}(0)$, ξ, and I_{TDS} being variables. The solid lines in Fig. 1 are the result of fitting with equation (1). The fitting result indicates equation (1) can describe the experimental data well, which agrees with previous results for PS–8CB. Although we do not show it here, equation (1) can also describe the scattering profiles at the other temperatures well. Fig. 2 shows the temperature dependences of $I_{OZD}(0)$ and ξ obtained by fitting with equation (1). We found the critical phenomena in the parameters $I_{OZD}(0)$ and ξ. We found $I_{OZD}(0)$ and ξ are expressed by

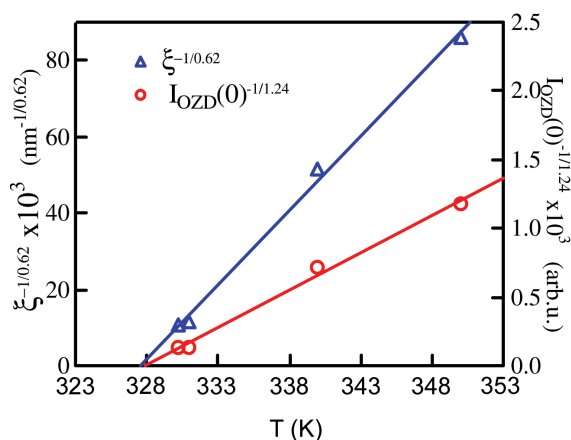$$\xi \sim (T - T_S)^{-0.62} \qquad (2)$$

and

Figure 2
$I_{OZD}(0)^{-1/1.22}$ (open triangles) and $\xi^{1/0.62}$ (open circles) are plotted as a function of T. The linear relationship in the plots indicates that the temperature dependences of $I_{OZD}(0)$ and ξ can be described by a 3D Ising model. The lines merge at $T_S =$ 327.3 K on the T axis.

$$I_{OZD}(0) \sim (T - T_S)^{-1.22}, \qquad (3)$$

where T is the temperature and T_S is the spinodal temperature of PB–8CB, which is estimated to be 327.3 K. These temperature dependences indicate that the OZD mode originates from the osmotic compressibility for the liquid–liquid phase transition between PB and 8CB. Fig. 3 shows the temperature dependences of $I_{DB}(0)$ and l. $I_{DB}(0)$ and l do not show any critical phenomena and are almost independent of temperature except near the spinodal temperature of PB–8CB for the liquid–liquid phase transition. This fact indicates that the DB mode at larger wavelengths is independent of the osmotic compressibility.

We assumed that the orientation fluctuations of the LC molecules may induce the DB mode of the concentration fluctuations. Thus, we applied an electric field to the PB–8CB mixture and investigated how the electric field affects the concentration fluctuations. The electric field induces the alignment of the LC molecules along the electric field and we can expect that the DB modes become anisotropic if the orientation fluctuations affect the concentration fluctuations. Fig. 4 shows the effects of the electric field on the two-dimensional SAXS patterns of PB–8CB at 350.0 K. The scattering pattern at 0 V mm^{-1} is isotropic while the scattering pattern at 800 V mm^{-1} is elongated perpendicular to the electric field direction, indicating that the electric field enhances the concentration fluctuations perpendicular to its direction. This enhancement is due to the alignment of the orientation of 8CB molecules. Fig. 5 shows the scattering intensity $I_{\parallel}(q)$ parallel to the electric field and $I_{\perp}(q)$ perpendicular to the electric field direction at 350.0 K and 800 V mm^{-1} as a function of q. We also plotted the scattering intensity $I_0(q)$ at 0 V mm^{-1} in the same figure. As for $I_{\perp}(q)$, the enhancement of the scattering intensity is observed in $I_{\perp}(q)$ at $q <$ 0.1 nm^{-1}, while $I_{\perp}(q)$ is almost identical with $I_0(q)$ at $q >$ 0.1 nm^{-1}. Each solid line is the fitting result of experimental data with equation (1). The fitting results yielded $l_{\perp} =$ 33.7 nm, $l_{\parallel} =$ 30.0 nm, $l_0 =$ 31.8 nm, $\xi_{\perp} =$ 5.0 nm, $\xi_{\parallel} =$ 4.8 nm and $\xi_0 =$ 5.0 nm, where $\perp$, $\parallel$ and 0 denote perpendicular, parallel and 0 V mm^{-1}, respectively. $l_{\perp}$ is larger than $l_{\parallel} \simeq l_0$ while ξ is independent of the electric field, indicating that the DB mode perpendicular to the electric field is enhanced but that the OZD mode is insensitive to the electric field. This enhancement is the proof that the DB mode stems from the orientation fluctuations of the LC molecules.

We have investigated the temperature dependence of the scattering intensity on the electric field. Fig. 6 shows the effects of the electric field on the two-dimensional SAXS patterns of the PB–8CB mixture at 330.2 K. The scattering pattern at 0 V mm^{-1} is isotropic
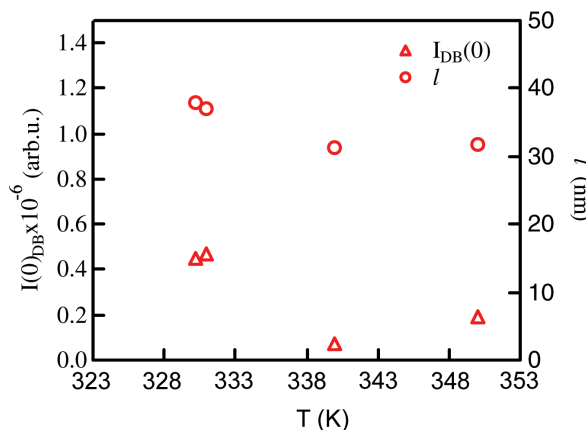

Figure 3
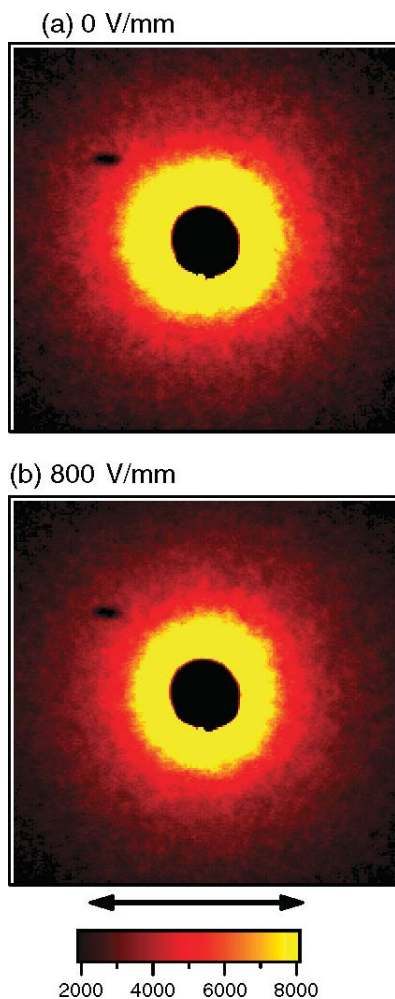$I_{DB}(0)$ (open triangles) and l (open circles) are plotted as a function of T.

Figure 4
Two-dimensional SAXS patterns of PB–8CB at 0 V mm^{-1} (a) and 800 V mm^{-1} (b) for 350.0 K. The direction of the electric field is indicated by the arrow. The scattering pattern at 0 V mm^{-1} is isotropic while the scattering pattern at 800 V mm^{-1} is elongated in the direction perpendicular to the electric field.

Figure 6
Two-dimensional SAXS patterns of PB–8CB at 0 V mm^{-1} (a) and 800 V mm^{-1} (b) for 330.2 K. The direction of the electric field is indicated by the arrow. The scattering pattern at 0 V mm^{-1} is isotropic while the scattering pattern at 800 V mm^{-1} is elongated in the direction perpendicular to the electric field.

while the scattering pattern at 800 V mm^{-1} is elongated perpendicular to the electric field direction. However, the anisotropy of the scattering pattern at 330.2 K is smaller than that at 350.0 K. This is
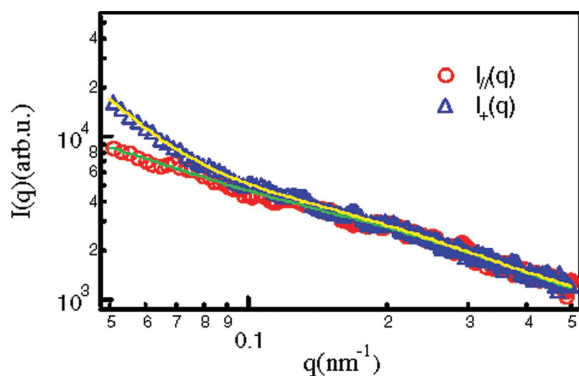
because the contribution of the OZD mode to the scattering intensity at 330.2 K becomes more influential than that at 350.0 K.

The SAXS intensity depends on the electron density difference and the orientation fluctuations themselves cause the electron density fluctuations since the volume of one LC molecule depends on its orientation, like the electron density difference between amorphous and crystalline regions in crystalline polymers. As already shown in a previous paper, we have derived the following scattering function for orientation fluctuations from the free energy functional (Matsuyama *et al.*, 2000):

$$S_{\rm S}(q) = \frac{S(0)}{1 + q^2\kappa^2}. \tag{4}$$

Here κ is the correlation length for orientation fluctuations defined by

$$\kappa = \left(\frac{L_1 + 2L_2/3}{f_{\rm SS}}\right)^{1/2}, \tag{5}$$

where $L_1 = b^2/8$, $L_2 = b^2/2$, and $f_{\rm S}$ is the second derivative of the free energy and is equal to $1 - T_{\rm NI}/T$ with b and $T_{\rm NI}$ being the molecular size of an LC molecule and the nematic isotropic temperature of the LC (Fukuda, 1999), respectively. Using $b = 2$ nm, $T_{\rm NI} = 315$ K and $T =$

Figure 5
Scattering intensities $I_\parallel(q)$ (open circles) parallel to the electric field and $I_\perp(q)$ (open triangles) perpendicular to the electric field at 350.0 K and 800 V mm^{-1} are plotted as a function of q. The solid lines correspond to the fitting with equation (1).
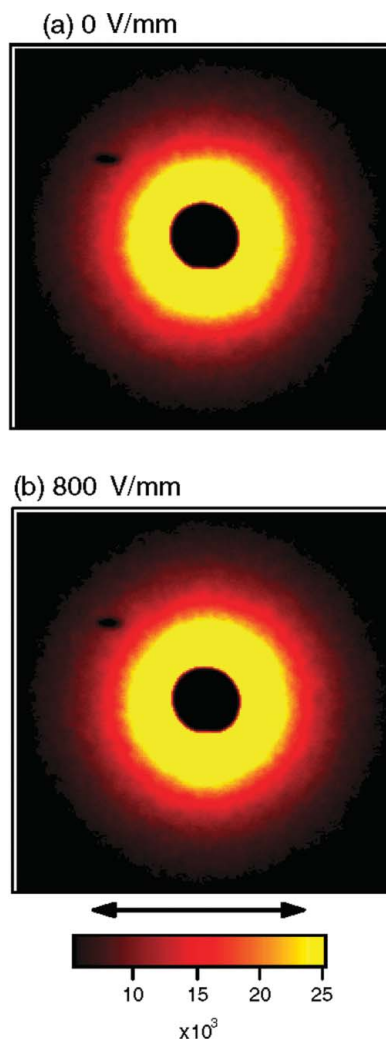
350 K, we obtained $\kappa = 4.3$ nm. This value is much smaller than $l_0 = 29.8$ nm. Moreover, the scattering function is of the OZD form and does not agree with the DB form obtained experimentally. Thus we need to consider other effects induced by orientation fluctuations. We speculate that the larger scale concentration fluctuations may be induced by orientation fluctuations. Matsuyama (2003) calculated the polymer swelling ratio in polymer–LC mixtures as a function of the orientation-dependent interactions between LC molecules under good solvent conditions. He found that a flexible polymer condensed with the orientation-dependent interactions [see Fig. 2 in Matsuyama (2003)]. Thus even though orientation fluctuations are activated thermally, the orientation fluctuations induce the concentration fluctuations. These orientation effects can explain the anisotropic enhancement of concentration fluctuations perpendicular to the electric field since the attractive interaction perpendicular to the alignment direction of the LC molecules is stronger than that parallel to the alignment direction. Further consideration of the coupling between the concentration and orientation fluctuations in critical phenomena in polymer–LC mixtures will be needed.

4. Conclusion

We investigated the critical phenomena of PB–8CB mixtures by using SAXS to explore the coupling effects between concentration and orientation fluctuations of the LC. We found two modes of concentration fluctuations characterized by an OZD mode with correlation length ξ and a DB mode with correlation length l in PB–8CB binary mixtures. The temperature dependence of the OZD mode exhibits 3D Ising critical phenomena like common binary mixtures. The DB mode does not show any critical exponent. Under the conditions where the LC molecules are oriented by an electric field, the OZD mode is insensitive to the orientation and the temperature dependences of $I_{OZD}(0)$ and ξ under the electric field are identical with those without the electric field. On the other hand, the DB mode is enhanced perpendicular to the orientation direction by the electric field. We calculated the correlation length induced by orientation fluctuations of LC itself from the free energy functional of polymer–LC systems and found the calculated correlation length is much shorter than the experimental results. These results agree with the previous results for PS–8CB, indicating that the induction of the concentration fluctuations by orientation fluctuations is universal irrespective of the kind of polymer.

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