Study of Molecular Interactions in the Photopolymerization-Induced Phase Separation of Liquid Crystal and Polymers

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We studied the influence of polymer molecular weight on molecular interactions between a liquid crystal (LC) and a polymer during phase separation of the LC and the polymer. The critical temperature for the phase separation increased with increasing polymer molecular weight. The critical temperatures that we obtained were compared with theoretical values calculated for the Flory-Huggins free energy. As a result, it was clarified that parameter D, which denotes the molecular interaction between the LC and the polymer in the Flory-Huggins interaction parameter χ, increased with increasing polymer molecular weight. This result suggests that the large interaction between the LC and the polymer decreases as the polymer molecular weight increases and that the interaction finally becomes saturated. The change in the molecular interaction was quantified by measuring the mixing enthalpy using a differential scanning calorimeter.
Key words: phase separation, molecular interaction, Flory-Huggins free energy, LC, polymer

1. INTRODUCTION

A phase separation of a liquid crystal (LC) and a polymer is induced by polymerizing a monomer in the LC. This is because the critical temperature of the phase separation increases with increasing the polymer molecular weight[1]. We consider that an increase in the polymer molecular weight may influence the molecular interaction between the LC and the polymer.

Historically, changes in critical temperature due to changes in the polymer molecular weight have been studied experimentally and theoretically through a phase diagram[2,3]. The measured critical temperature has also been compared with the calculated temperature obtained by the Flory-Huggins theory etc. However, there are very few reports in which the molecular interaction, (namely, the Flory-Huggins interaction parameter χ), has been studied through an evaluation of the critical temperature.

It has recently been found that the morphology of a polymer dispersed in LC can be controlled by the molecular interactions between the LC and the polymer, such as phase separation with molecular alignment[4]. Therefore, studying the influence of polymer molecular weight on molecular interactions is very important if we wish to understand the dynamics of photopolymerization-induced phase separation and to create functional devices in the future.

In this study, we investigated the relationships between the polymer molecular weight and molecular interactions. The dependence of the χ parameter on the polymer molecular weight was estimated by comparing the experimental and theoretical value using the phase diagram. The theoretical value was calculated by using the Flory-Huggins theory. The enthalpy was also measured by using a differential scanning calorimeter. The dependence of the molecular interaction on the polymer molecular weight was discussed on the base of van der Waals force between the LC and the polymer.

2. FABRICATION OF THE LC/POLYMER SYSTEM

The LC and the polymer material that we used were a nematic LC (MJ911421 from Merck, phase transition temperature: nematic phase $\rightarrow$ 157°C $\rightarrow$ isotropic phase) and a linear polymer (polystyrene from either Polyscience Inc. or Chemco). The molecular weight of the polystyrene varied from 300 to 200,000. The polymer materials having low polydispersity ratio less than 1.1 were employed for applying to theoretical model based on single molecules.

The LC/polymer systems were formed by a solvent-induced phase separation method[5] as follows. The LC and the polymer (total weight: 50mg) were stirred in a solvent (chloroform from Wako, 250mg) until all of the materials were uniformly mixed. The LC/polymer systems were then obtained by evaporation of the solvent. The concentration ratio of the LC to the polymer was changed in steps of 10wt% to obtain different products.

3. DEPENDANCE OF CRITICAL TEMPERATURE ON POLYMER MOLECULAR WEIGHT

Estimation of the critical temperature of the LC/polymer system was achieved by observation of the system using a polarizing microscope (OPTIPHOTO2-POL, Nikon). Sample cells filled with the different systems were obtained as follows. The solvent evaporation process mentioned in section 2 was carried out on a glass substrate onto which spacer particles (10 μ m) had been scattered in advance. Another glass substrate was laminated onto this at 200°C, at which temperature the polymer was completely dissolved in the LC. Cells containing a solution of the various LC/polymer systems with a uniform thickness of 10 μ m were therefore obtained. The sample cells were placed on the stage of a polarizing microscope incorporating a thermostatic system (STC200, Instec). The temperature of the sample cells was then decreased at 3°C/min. from

200 ℃ (solution state) to room temperature and any changes in the system were observed. If phase separation of the LC and the polymer occurred, droplets containing the LC component appeared in the system, and the droplet size expanded with decreasing temperature[6]. The temperature where the droplets appeared in the solution was defined as the critical temperature between mixing and phase separating. As shown in Fig.1, the upper critical solution temperature, (namely, the binodal curve) increased with increasing polymer molecular weight. The behavior of the rise in the binodal curve was dynamic when the difference in molecular weights between the LC and the polymer was comparatively small, but became saturated when the polymer molecular weight was greater than 2,5000. The critical temperature obtained for LC concentrations of 70wt% to 100wt% was almost proportional to the LC concentration when the obtained binodal curve was lower than the phase transition temperature of the pure LC (157℃). This is a particular phenomenon of LC/polymer blends and cannot be confirmed in a conventional polymer blend[7]. It is caused by the alignment free energy of the LC[8].

In the systems composed by the polymer molecular weights of 2,5000 and 200,000, the LC droplets showed the nematic phase even at the temperature higher than the LC phase transition temperature (157 ℃). This phenomenon has been similarly confirmed in the phase diagrams obtained by another systems which were E7 LC/poly(n-butyl acrylate) polymer[9] and E7 LC/NOA65 polymer[10]. In E7/NOA65 system, it has been found that the increase in the phase transition temperature was caused by the change of the composition of the LC droplet from that of the original LC which consists of several LC materials. It is thought that this is because the LC materials had rather different solubility to the polymer. The LC we used also had several LC materials. So it is thought that the phase transition temperature was increased by above factor.
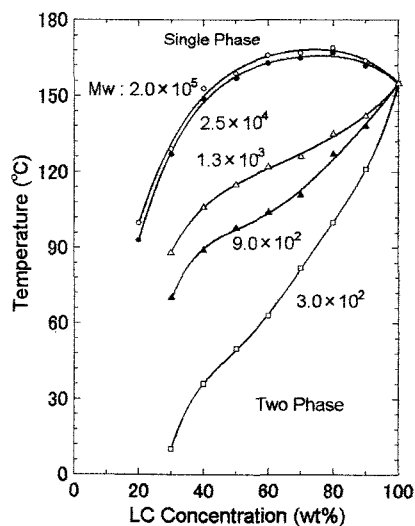

Fig.1 Phase diagrams of LC/polymer systems with varying polymer molecular weights.

4. RELATIONSHIP BETWEEN THE POLYMER MOLECULAR WEIGHT AND THE FLORY-HUGGINS INTERACTION PARAMETER χ

These results were compared with a set of theoretical values. Theoretical phase diagrams can generally be obtained using the total of the Maier-Saupe alignment free energy and the Flory-Huggins mixing free energy[8]. This is because, as mentioned above, the alignment free energy strongly affects the phase behavior in the LC high concentration region. In this study, in order to focus on the interaction parameter χ, the critical temperature of the LC/polymer system was calculated using only the Flory-Huggins free energy. The calculated critical temperature was therefore compared with the experimental value in the low LC concentration region, where the influence of the alignment free energy on the critical temperature is comparatively small.

The Flory-Huggins mixing free energy (ΔG_{mix}) is generally given by

$$\Delta G_{mix} = Nk_B T \left[\chi\phi(1-\phi) + \frac{\phi}{m_1} ln\phi + \frac{(1-\phi)}{m_2} ln(1-\phi) \right], \quad (1)$$

where k_B is the Boltzmann constant and T is the absolute temperature. m_1 is the number of sites occupied by one LC molecule and is defined as 1 in this study. On the other hand, m_2 represents the number of sites occupied by a polymer molecule. We used a value of m_2 that was obtained by dividing the molecular weight of the polymer by that (100) of a styrene monomer. ϕ is the volume fraction of the LC component. N is the total number of sites, i.e., $N = n_1 m_1 + n_2 m_2$, where n_1 and n_2 are the number of LC molecules and polymer molecules respectively. χ is known as the Flory-Huggins interaction parameter. The χ parameter doesn't only contain an enthalpic term but also an entropic term, and is generally assumed to be a function of the reciprocal of the absolute temperature, i.e.,

$$\chi = C + \frac{D}{T}, \quad (2)$$

where C and D are entropic and enthalpic terms respectively. The critical temperature constituting the binodal curve was obtained by a double tangent method where the equilibrium volume fractions of the individual phases fall on the same tangent line of the free energy curve calculated using equation (2)[11]. Fitting of the calculated binodal curve to the experimental values was attempted by changing the χ parameter for the system with a polymer molecular weight of 200,000. When parameters C and D were -2.933 and 1600K, respectively, it was conformed that the calculated binodal curve was nearly in agreement with the experimental values between LC volume fractions $\phi = 0.2$ and $\phi = 0.5$, as shown in Fig.2. In order to estimate the dependence of parameters C and D on the polymer molecular weight, fitting of the calculated binodal curve to the experimental values was attempted at another polymer molecular weight. It was found that the calculated binodal curves approximately agreed with the experimental values for the conditions shown in Table I , and it was also found that parameters C and D changed with the polymer molecular weight. The dependence of parameter D on the polymer molecular weight was then plotted, as shown in Fig.3. It was clarified that parameter D increases as the polymer molecular weight increases. The plots shown in Fig.3 almost agreed with the solid line when expressed as a function of the molecular weight M_W, as follows;

$$D = D_0 \left[1 - \exp\left(-\frac{M_W}{M_0} \right) \right],$$ (3)

where D_0 and M_0 were 1650 K and 1000 respectively.

According to the Flory-Huggins theory, an increase in parameter D implies a decrease in the molecular interaction between the LC and the polymer. However, it cannot be absolutely concluded that the change in the obtained value of parameter D was caused by a difference in the molecular interaction between the LC and the polymer in accordance with the increase in the polymer molecular weight. This is because when parameter D was determined, the alignment free energy was completely neglected, and so a measurement of the mixing enthalpy in the LC/polymer system was attempted to reinforce the above result. If parameter D depends on the molecular interaction, the change in the mixing enthalpy according to the increase in the polymer molecular weight should be similar to the change in parameter D.
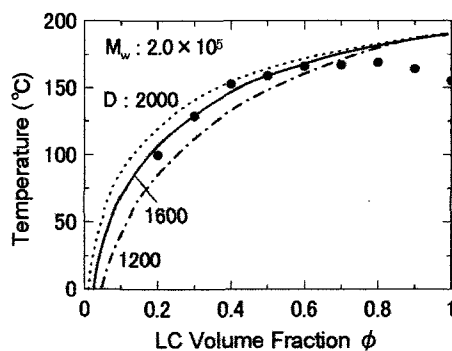

Fig.2 Comparison of the binodal curve and experimental phase separation temperatures (●) of the LC and the polymer. The experimental values have been taken from Fig.1. The calculated solid curve (·······) was obtained for T_C = 190°C, C = -2.933, D = 1600 (K) and m = 2000. The calculated dotted curve (——) was obtained for T_C = 190°C, C = -3.797, D = 2000 (K) and m = 2000. The calculated dot-dash-curve (— · ·) was obtained for T_C = 190°C, C = -2.069, D = 1200 (K) and m = 2000.

Table I

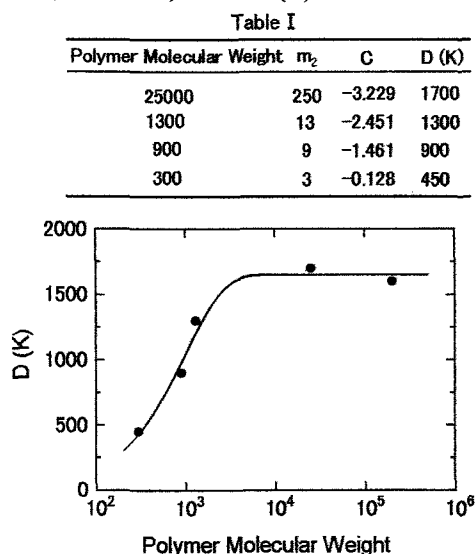| Polymer Molecular Weight	m_2	C	D (K)
25000	250	-3.229	1700
1300	13	-2.451	1300
900	9	-1.461	900
300	3	-0.128	450

Fig.3 Calculated curve (——) obtained by equation (3) and polymer molecular weight dependence of D taken from Table I .

5. DEPENDANCE OF ENTHALPY ON POLYMER MOLECULAR WEIGHT

The mixing enthalpy that was generated by the phase separation was estimated from the changes in the specific heat of the system. Measurement of the specific heat was performed using a DSC (DSC6200 from Seiko Instruments), as follows. A sample of an LC/polymer system (10mg) and a reference material (Al_2O_3, 10mg) were placed into different aluminum pans. An LC/polymer system with an LC concentration of 50wt% was employed. This is because the mixing enthalpy of this system would be larger than that of a system with a different LC concentration, and the change in the enthalpy due to the nematic-isotropic phase transition of the LC caused by mixing or phase separating would be smaller than that of a system with a higher LC concentration. The solvent evaporation process was carried out in the pan to induce a uniform phase separation in the system. After that, the pans were completely covered with an aluminum lid to prevent evaporation of the materials while heating the system. The pans were then placed in the sample chamber of the DSC. In order to measure the change in the specific heat of the system, the temperature of the sample chamber was increased at a heating rate of 20°C/min. from room temperature to 200°C. If mixing of the LC and the polymer components occurs in the system, an endothermic peak appears in the DSC thermal trace. The area under the peak gives an indication of the change in enthalpy.

As a result, an endothermal peak appeared in every system for each different polymer molecular weight, as shown in Fig.4. The temperature of the endothermal peak increased with increasing polymer molecular weight and almost corresponded with the critical temperature shown in Fig.1. Hence it is thought that these endothermal peaks were obtained due to the change from the phase separation state to the solution state. The area under the peak expanded with increasing polymer molecular weight.
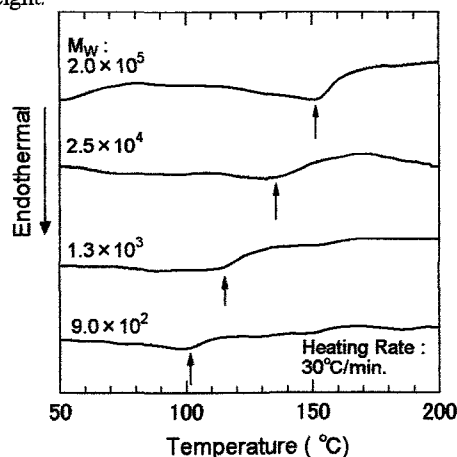

Fig.4 DSC thermal traces of the polymer/LC 1/1 blend with different polymer molecular weights

The endothermal peaks that were obtained include the enthalpy of the phase transition as well as the enthalpy of mixing, and therefore the mixing enthalpy could not be determined directly from the peak. However, it is thought that the enthalpy of the phase transition at high

temperature is smaller than that at low temperature. This is because the alignment order, which depends on the activation of the molecules, decreases with increasing temperature. Therefore this tendency, i.e. the increase in the mixing enthalpy with increasing polymer molecular weight, is maintained or becomes more noticeable when the enthalpy of the phase transition is subtracted from the measured enthalpy. The increase in the mixing enthalpy with increasing polymer molecular weight supports the notion that the change in parameter D had been caused by a molecular interaction between the LC and the polymer.

6. DISCUSSION

It was clarified that the polymer molecular weight affects the molecular interaction between the LC and the polymer. In this section, the factors contributing to the increase in the molecular interaction are discussed. Parameter D is proportional to the energy of the molecular interaction, as follows[1]

$$D \propto \Delta\varepsilon = \varepsilon_{LP} - \frac{\varepsilon_{LL} + \varepsilon_{PP}}{2}, \qquad (4)$$

where the ε terms represent the intermolecular interaction energies for the system components: ε_{PP}, ε_{LL} and ε_{LP} respectively stand for the interaction energies between the polymer-polymer, the LC-LC and the polymer-LC components. Since the ε terms are defined as negative values, the increase in parameter D was caused by a decrease in the absolute value of ε_{LP} and an increase in that of ε_{PP}. This means that the attractive force between the LC and the polymer becomes weaker, and the force between the polymer molecules becomes stronger. This is thought to be due to a change in the intermolecular distance, based on the difference of the molecular motion between the LC and polymer caused by the increase in the polymer molecular weight. Hence the distance between the polymer molecules becomes shorter than that between the LC and the polymer. As a result, the van der Waals forces between the polymers increase, while they decrease between the LC and the polymer.

Though the molecular interaction between the LC and the polymer changes dramatically when the polymer molecular weight is comparatively small, the molecular interaction becomes saturated when the polymer molecular weight reaches a certain level. This is very interesting because it indicates that in the initial stages of photopolymerization-induced phase separation, the molecular behavior of the polymer is strongly influenced by the molecular orientation and movement of the LC. This influence then gradually fades away in accordance with the increasing polymer molecular weight.

Additionally, we have already achieved the fine phase separation of the LC and the polymer by using the photopolymerization-induced phase separation. Namely an amount of impurity included in the LC separated from the polymer was less than 3 wt%[12]. It is thought that this is because the molecular interaction between the polymer molecules was increased by rapidly increasing the molecular weight of the polymer due to the polymerization of the monomer mixed in the LC. As shown in Fig.5, it was actually confirmed that the segregated polymer molecules had comparatively high molecular weights (about 10^4).
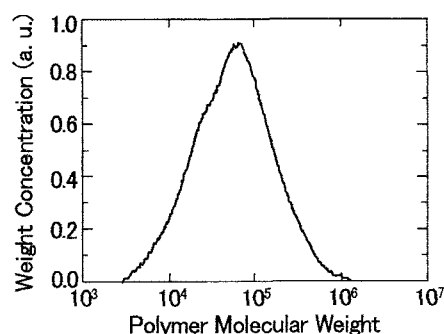

Fig.5 Molecular weight distribution of the segregated polymer

7. CONCLUSION

The influence of the polymer molecular weight on the molecular interaction between the LC and the polymer in the phase separation process was investigated. As a result, parameter D, which denotes the molecular interaction in the Flory-Huggins interaction parameter χ, increased with increasing the polymer molecular weight and finally became saturated. Besides the mixing enthalpy of the system generated by the phase separation also increased with increasing polymer molecular weight. These results indicate that in the photopolymerization-induced phase separation, the large interaction between the LC and the polymer decreases as the polymer molecular weight increases, until the interaction finally saturates. Therefore, it was thought that the change in the molecular interaction between the LC and the polymer with the polymer molecular weight is very important for controlling the polymer structure in the LC.

At next-stage, we will study the influence of the change in the molecular interaction on formed polymer morphology.

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