

# Compatibility studies of blends of a thermotropic liquid crystalline polymer and flexible chain polymers by application of Flory's lattice theory

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## Abstract

Flory's lattice theory has been applied to the polymer blends containing a thermotropic liquid crystalline polymer (LCP) and flexible chain polymers. The phase behavior of blends of a thermotropic LCP and a flexible chain polymer at melt processing temperature can be evaluated by two quantitative parameters: the polymer–polymer interaction parameter ( $\chi_{12}$ ) and the degree of disorder ( $y/x_1$ ). From the results of the model calculation, it has been found that the miscibility is increased with the increase of the degree of disorder ( $y/x_1$ ) of the LCP and with the decrease of the degree of polymerization ( $x_1m$  and/or  $x_2$ ). The simulated spinodal curve of ternary polymer blends containing a thermotropic LCP and two flexible chain polymers has been calculated using the lattice theory. When three pairs of binary polymer blends are immiscible, the coexistence curve of the three phases appears for the ternary blend having similar values of  $\chi_{ij}$  among component polymers. When the LCP is immiscible with two flexible chain polymers, and also when the two flexible chain polymers are miscible with each other, the strong effect of anisotropy of the LCP is observed in the simulated spinodal curve. When three pairs of binary polymer blends are miscible, a phase separation is also observed due to the  $|\Delta\chi|$  effect. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Polymer blends; Liquid crystalline polymer; Polymer–polymer interaction parameter

## 1. Introduction

Liquid crystalline polymers (LCPs) are known to have high modulus and unique properties of the formation of lyotropic solutions or thermotropic melts [1–8]. The blending of a thermotropic LCP with various flexible chain polymers has been of interest in recent years [9–32]. The incorporation of a thermotropic LCP to the flexible chain polymers may result in the improvement of mechanical strength and processibility of the flexible chain polymers. On these points of view, many investigators have studied the blends of a thermotropic LCP with flexible chain polymers such as poly(ether imide) (PEI) [9–14], poly(ether ether ketone) (PEEK) [14–20], polysulfone [21,22], polycarbonate (PC) [23–29], poly(ethylene terephthalate) [30,31], and a copolymer of tetrafluoroethylene and hexafluoro-propylene [32].

Flory [33] proposed a modified lattice theory in order to

investigate the phase equilibrium in solutions of tobacco mosaic virus (TMV) particles. He incorporated the anisotropy of the TMV into the original lattice theory [33]. In the modified lattice theory [33], the free energy of mixing ( $\Delta G_m$ ) was given as a function of mole numbers, axial ratio of TMV particles ( $x_1$ ), disorientation factor ( $y$ ) and the intermolecular interaction parameter ( $\chi_{12}$ ) between TMV and solvent. Subsequently, Flory and coworkers [34–39] applied the theory to lyotropic polymer solutions. Intermolecular interaction was deliberately neglected in the theory [34–39]. In our previous work [14,23], we have applied the lattice theory to the blends of a thermotropic liquid crystalline polymer and flexible chain polymers such as PEI, PEEK, and PC, and reported the equilibrium degree of disorder ( $y/x_1$ ) and the polymer–polymer interaction parameter ( $\chi_{12}$ ) of the blend at melt processing temperature.

The miscibility between a thermotropic LCP and a flexible chain polymer at melt processing temperature is an important factor for understanding the physical properties of the blend. For the blend of a thermotropic LCP and a flexible chain polymer, it has been reported that there are some miscible pairs [17], partially miscible pairs [9,14,23],

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and immiscible pairs [21,22]. However, there are few theories in the literature that describe the miscibility of the blends of a thermotropic LCP and a flexible chain polymer. Therefore, we hope to describe the miscibility of the blends of a thermotropic LCP and flexible chain polymers at melt processing temperature by using two quantitative parameters: the polymer–polymer interaction parameter ( $\chi_{12}$ ) and the degree of disorder ( $y/x_1$ ).

In this work, we apply Flory's lattice theory to the blends of a thermotropic LCP and a flexible chain polymer in order to evaluate the polymer–polymer interaction parameter ( $\chi_{12}$ ) and predict the miscibility limit. In this paper, we have derived the Gibbs free energy of mixing ( $\Delta G_m$ ) of the blend containing a thermotropic LCP and a flexible chain polymer from the lattice theory. Also the miscibility limits (spinodal curve at constant temperature) of the binary and ternary blends containing a thermotropic LCP and flexible chain polymers have been calculated by the proposed equations from the lattice theory.

## 2. Theory

### 2.1. Gibbs free energy of mixing ( $\Delta G_m$ )

Flory and coworkers [34–39] developed the lattice theory in which the orientation of the LCP is considered in lyotropic solutions. This lattice theory can be applied to the blend systems containing a thermotropic LCP. The thermotropic LCP can be treated as a freely jointed chain comprising  $m$  rod-like segments of the same length, such as the lyotropic LCP treated in Flory's work [39]. For the binary blend of a flexible chain polymer and a thermotropic LCP, the blend can be treated as a fictitious ternary blend system composed of a vacant cell (0), the LCP (1), and a flexible chain polymer (2). The fraction of the vacant cell is limited to zero. In this work, the configurational partition function is obtained as follows:

$$Z_M = \left[ \frac{[n_T - n_1(mx_1 - my)]!}{(n_T - x_1mn_1)!n_1!n_T^{n_1(my-1)}} \right] \times \left[ \frac{(n_T - x_1mn_1)!z_2^{n_2}}{(n_T - x_1mn_1 - x_2n_2)!n_2!n_T^{n_2(x_2-1)}} \right] [y^{2mm_1}] \quad (1)$$

where  $n_T = n_0 + n_1mx_1 + n_2x_2$ ,  $m$  is the number of freely rotating joints in the submolecule,  $x_1$  the axial ratio of each of the  $m$  rods comprising the molecule,  $x_2$  the contour length of the flexible chain polymer (the molar volume of the repeating unit of the flexible chain polymer is regarded as 1),  $y$  denotes the disorientation [34];  $y = x_1 \sin \phi$ ,  $\phi$  is the angle to the domain axis of the LCP, and  $z_2$  is the internal configurational partition function for the flexible chain polymer [39]. The first and second brackets in Eq. (1) are combinatorial parts of the LCP and the flexible chain polymer, respectively. The last bracket in Eq. (1) is the orientational part. The orientational part can be given

more exactly by Flory–Ronca theory [40,41]. However, we adopt an approximated value of the orientational part in the configurational partition function for simplicity, which will be discussed in this work. The limit of complete disorder is  $y = x_1$  in this work. When the LCP has a completely ordered structure, the orientation factor ( $y$ ) has a unit value. When the fraction of a vacant cell is limited to zero, then Eq. (1) reduces to:

$$Z_M = \frac{[n_2x_2 + ymn_1]!y^{2mm_1}z_2^{n_2}}{n_1!n_2!(n_1mx_1 + n_2x_2)^{n_1(my-1)+n_2(x_2-1)}} \quad (2)$$

Introducing Stirling's approximation, one can obtain the entropy of mixing from Eq. (2). Adding the residual contribution to the Gibbs free energy of mixing [42,43], we can obtain Eq. (3) after some rearrangement:

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12} \phi_1 \phi_2 (x_1 mn_1 + x_2 n_2) + \Delta g_{\text{orient}} \quad (3)$$

where

$$\Delta g_{\text{orient}} = n_1 m_1 y_1 \ln \left( \frac{y_1}{x_1} \right) - (x_2 n_2 + m y n_1) \times \ln \left[ \frac{(x_2 n_2 + m y n_1)}{(x_1 m n_1 + x_2 n_2)} \right] + n_1 (m_1 \ln y_1^2 - m_1 y_1 + 1) - n_1 (m \ln y^2 - m y + 1)$$

where  $n_i$  is the number of moles of the  $i$ th component ( $i, j = 1, 2$  and  $i \neq j$ ),  $\chi_{12}$  the polymer–polymer interaction parameter, and  $\phi_i$  the volume fraction of component  $i$ . Subscripts 1 and 2 denote polymers 1 and 2, respectively.  $y_1$  and  $y$  are the orientation factors of the LCP in pure state and in blended state, respectively, and  $m$  the number of flexible joints of the LCP. In fact,  $\Delta g_{\text{orient}}$  is composed of some part of combinatorial contribution and the orientational contribution in Eq. (3). In this work, the pure LCP is treated as a perfectly ordered polymer at melt state:  $y_1 = m_1 = 1$  in Eq. (3).

When the LCP has a completely disordered structure (i.e.  $y = y_1 = x_1$ ),  $\Delta g_{\text{orient}}$  becomes zero in Eq. (3). Then Eq. (3) is reduced to the well-known Flory–Huggins equation.

### 2.2. Polymer–polymer interaction parameter ( $\chi_{12}$ )

At equilibrium, the entropy may be maximized with the variation of the disorientation factor ( $y$ ). Therefore, the equilibrium disorder can be obtained by equating  $\partial \ln Z_M / \partial y$  to zero [34] as follows:

$$\exp\left(\frac{-2}{y}\right) = 1 - \phi_1 \left(1 - \frac{y}{x_1}\right) \quad (4)$$

The chemical potential of component  $i$  is obtained as the partial derivative of Eq. (3) with respect to  $n_i$ . Then the chemical potential of components 1 and 2 are given by Eqs. (5) and (6) after the substitution of Eq. (4) to the

derivative of Eq. (3), respectively:

$$\frac{\Delta\mu_1}{RT} = \ln\left(\frac{\phi_1}{x_1}\right) + \phi_1 x_1 m \left(\frac{y}{x_1} - \frac{1}{x_1 m}\right) + \phi_2 x_1 m \left(1 - \frac{1}{x_2}\right) + 2m(1 - \ln y) + x_1 m \chi_{12} \phi_2^2, \quad (5)$$

$$\frac{\Delta\mu_2}{RT} = \ln \phi_2 + \phi_1 x_2 \left(\frac{y}{x_1} - \frac{1}{x_1 m}\right) + \phi_1 (1 - x_2) + \frac{2x_2}{y} + x_2 \chi_{12} \phi_1^2. \quad (6)$$

Similarly, the chemical potential of the isotropic phase can be obtained by Eqs. (7) and (8), when  $y = x_1$ :

$$\frac{\Delta\mu_1}{RT} = \ln\left(\frac{\phi_1}{x_1}\right) + \phi_1 (x_1 m - 1) + \phi_2 x_1 m \left(1 - \frac{1}{x_2}\right) - 2m \ln x_1 + x_1 m \chi_{12} \phi_2^2, \quad (7)$$

$$\frac{\Delta\mu_2}{RT} = \ln \phi_2 + \phi_1 x_2 \left(1 - \frac{1}{x_1 m}\right) + \phi_1 (1 - x_2) + x_2 \chi_{12} \phi_1^2. \quad (8)$$

At equilibrium, the chemical potential of each component must be the same in both phases. Denoting the anisotropic phase by a single prime and the isotropic phase by a double prime, respectively, we have Eq. (9) for the LCP (component 1):

$$\Delta\mu'_1 = \Delta\mu''_1. \quad (9)$$

Then, we can obtain Eq. (10) from Eqs. (5), (7), and (9):

$$\ln\left(\frac{\phi'_1}{\phi''_1}\right) + \phi'_1 x_1 m \left(\frac{y}{x_1} - \frac{1}{x_1 m}\right) - \phi''_1 (x_1 m - 1) + x_1 m \left(1 - \frac{1}{x_2}\right) (\phi'_2 - \phi''_2) + 2m \left[1 + \ln\left(\frac{x_1}{y}\right)\right] + x_1 m \chi_{12} (\phi_2'^2 - \phi_2''^2) = 0. \quad (10)$$

Similarly, we have Eq. (11) for the flexible chain polymer (component 2):

$$\Delta\mu'_2 = \Delta\mu''_2. \quad (11)$$

Then we can obtain Eq. (12) from Eqs. (6), (8), and (11):

$$\ln\left(\frac{\phi'_2}{\phi''_2}\right) + \phi'_1 x_2 \left(\frac{y}{x_1} - \frac{1}{x_1 m}\right) - \phi''_1 x_2 \left(1 - \frac{1}{x_1 m}\right) + (x_2 - 1) (\phi'_2 - \phi''_2) + \frac{2x_2}{y} + x_2 \chi_{12} (\phi_1'^2 - \phi_1''^2) = 0. \quad (12)$$

If the volume fractions in each conjugate phase can be determined experimentally, the polymer–polymer interaction parameter ( $\chi_{12}$ ) and the degree of disorder ( $y/x_1$ ) can be calculated by Eqs. (4), (10), and (12) in equilibrium condition. The volume fractions in each phase have been

determined from the experimentally measured glass transition temperatures ( $T_g$ s) of the blends as reported in our earlier papers [14,23,44,45].

### 2.3. Miscibility limit of polymer blends

Eq. (3), which is expressed as the number of moles and volume fraction of each component can be expressed as a function of just the blend composition as follows:

$$\tilde{G} = \frac{\phi_1}{x_1 m} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2 + \chi_{12} \phi_1 \phi_2 + \Delta\tilde{g}_{\text{orient}} \quad (13)$$

where

$$\Delta\tilde{g}_{\text{orient}} = \frac{\phi_1}{x_1 m} \ln\left(\frac{1}{x_1 m}\right) - \left[1 - \phi_1 \left(1 - \frac{y}{x_1}\right)\right] \ln\left[1 - \phi_1 \left(1 - \frac{y}{x_1}\right)\right] - \frac{\phi_1}{x_1 m} (m \ln y^2 - my + 1).$$

The miscibility limit of the binary polymer blend containing a thermotropic LCP is obtained at the spinodal of Eq. (13):

$$\frac{\partial^2 \tilde{G}}{\partial \phi_i^2} = 0. \quad (14)$$

For the binary polymer blends containing a thermotropic LCP, the spinodal relationship is obtained as Eq. (15) after the substitution of Eq. (13) into Eq. (14):

$$\frac{1}{\phi_1 x_1 m} + \frac{1}{\phi_2 x_2} - 2\chi_{12} - \frac{(1 - (y/x_1))^2}{[1 - \phi_1(1 - (y/x_1))]} = 0. \quad (15)$$

For the ternary polymer blends containing a thermotropic LCP, the Gibbs free energy of mixing is obtained as Eq. (16):

$$\tilde{G} = \frac{\phi_1}{x_1 m} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2 + \frac{\phi_3}{x_3} \ln \phi_3 + \chi_{12} \phi_1 \phi_2 + \chi_{23} \phi_2 \phi_3 + \chi_{31} \phi_3 \phi_1 + \Delta\tilde{g}_{\text{orient}}. \quad (16)$$

For the ternary polymer blend containing a thermotropic LCP, the spinodal relationship is obtained as Eq. (18) after the substitution of Eq. (16) into Eq. (17):

$$\frac{\partial^2 \tilde{G}}{\partial \phi_1^2} \frac{\partial^2 \tilde{G}}{\partial \phi_1 \partial \phi_2} - \left[ \frac{\partial^2 \tilde{G}}{\partial \phi_1 \partial \phi_2} \right]^2 = 0, \quad (17)$$

$$x_1 m \phi_1 + x_2 \phi_2 + x_3 \phi_3 - 2[x_1 m x_2 (\chi_1 + \chi_2) \phi_1 \phi_2 + x_2 x_3 (\chi_2 + \chi_3) \phi_2 \phi_3 + x_3 x_1 m (\chi_3 + \chi_1) \phi_1 \phi_3] + 4x_1 m x_2 m_3 (\chi_1 \chi_2 + \chi_2 \chi_3 + \chi_3 \chi_1) \phi_1 \phi_2 \phi_3 - \frac{(1 - (y/x_1))^4}{[1 - \phi_1(1 - (y/x_1))]^2} \left[ 2 + \frac{\phi_3}{\phi_2} \right] = 0 \quad (18)$$

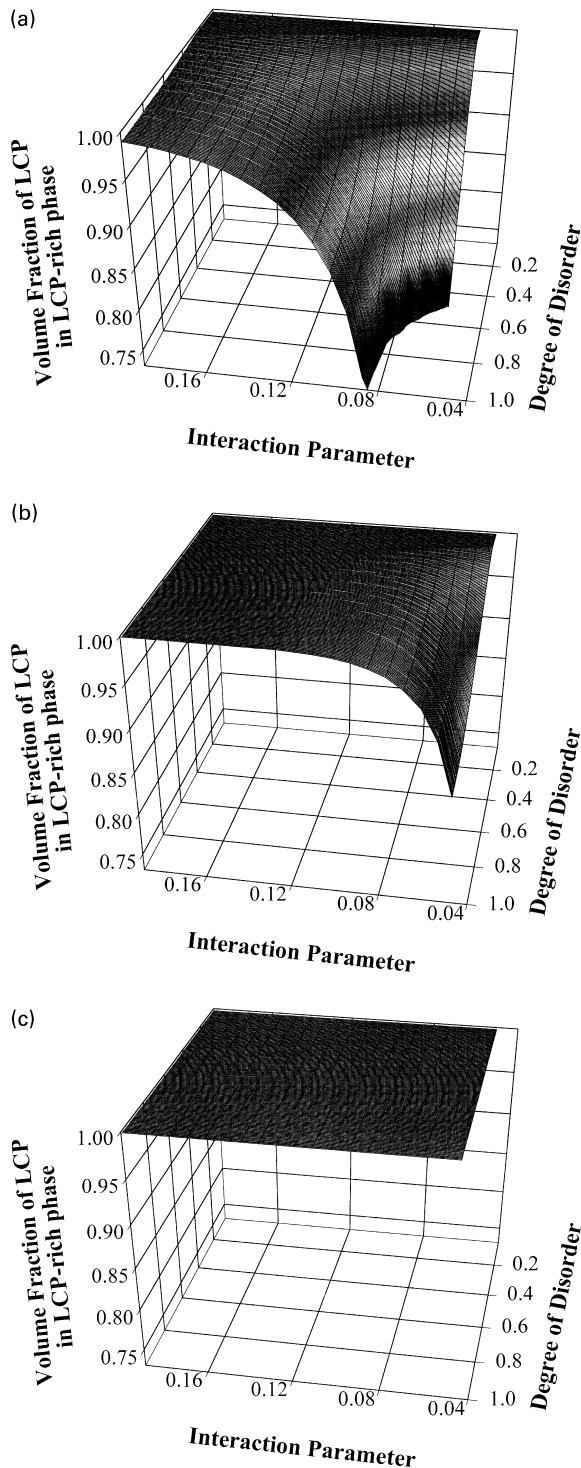


Fig. 1. Model calculation of polymer–polymer interaction parameter ( $\chi_{12}$ ) with degree of disorder ( $y/x_1$ ) and apparent volume fraction ( $\phi$ ): (a)  $x_1m = x_2 = 25$ ; (b)  $x_1m = x_2 = 50$ ; (c)  $x_1m = x_2 = 100$ .

where

$$\chi_i = \frac{\chi_{ij} + \chi_{ik} - \chi_{jk}}{2}$$

Apart from the last term, Eq. (18) is similar to the spinodal

relationship of the Flory–Huggins equation in the work of Su and Fried [46], which described the miscibility of polymer blends containing three isotropic polymers. In Eq. (18), it is worth noting that the LCP phase becomes an isotropic phase when  $y/x_1 = 1$ , then the last term of Eq. (18) becomes zero. Therefore, Eq. (18) can be used in the polymer blends containing the LCP as well as polymer blends containing only isotropic polymers. Also, the effect of anisotropy of the LCP on the miscibility of ternary polymer blends can be estimated using Eq. (8) by varying the  $y/x_1$  values. The detailed description of Eqs. (15) and (18) is introduced in Section 3.

### 3. Results and discussion

#### 3.1. Model calculation of the polymer–polymer interaction parameter ( $\chi_{12}$ )

A model calculation of  $\chi_{12}$  using Eqs. (10) and (12) is shown in Fig. 1. In Fig. 1(a), the apparent volume fraction of component 1 in the component-1-rich phase ( $\phi_1$ ) is set equal to the apparent volume fraction of component 2 in the component-2-rich phase ( $\phi_2$ ). The components 1 and 2 denote the LCP and the flexible chain polymer, respectively. The degree of polymerization of components 1 ( $x_1m$ ) and 2 ( $x_2$ ) is set equal to 25. From Fig. 1(a), we can see that  $\chi_{12}$  is decreasing with the decrease of  $\phi_1$  at a certain degree of disorder ( $y/x_1$ ). Also we can see that  $y/x_1$  is increasing with the decrease of  $\phi_1$  at a certain value of  $\chi_{12}$ . From this result, it can be surmised that the ordering of the LCP is inhibited by the flexible polymer that is dissolved in the LCP-rich phase. In order to see the molecular weight dependency of the miscibility of a LCP and a flexible polymer, component polymers having various degrees of polymerization are used in Eqs. (10) and (12).

In Fig. 1(b) and (c) are shown the results of a model calculation when  $x_1m$  and  $x_2$  are set equal to 50 and 100, respectively. From Fig. 1, it is predicted that the miscibility is increased with the increase of the degree of disorder and with the decrease of the degree of polymerization at a certain value of  $\chi_{12}$ . From these results, it is suggested that the two quantitative parameters,  $\chi_{12}$  and  $y/x_1$ , can be

Table 1

Apparent volume fraction ( $\phi$ ), degree of disorder ( $y/x_1$ ), and polymer–polymer interaction parameter ( $\chi_{12}$ ) of the 0.7 weight fraction LCP blends

Blend	$\phi_1^a$	$\phi_2^a$	$y/x_1^b$	$\chi_{12}^c$	References
LCP–PC	0.9875	0.8671	0.80	0.074	[23]
LCP–PEI	0.9893	0.9785	0.76	0.182	[14]
LCP–PEEK	0.9643	0.9658	0.92	0.066	[14]

<sup>a</sup> Single prime and double prime denote LCP-rich phase and flexible chain polymer-rich phase, respectively. Subscripts 1 and 2 denote LCP and flexible chain polymer, respectively.  $\phi_1' = 1 - \phi_2'$  and  $\phi_2'' = 1 - \phi_1''$ .

<sup>b</sup> Degree of disorder of LCP in amorphous phase.

<sup>c</sup> All  $\chi_{12}$  values are calculated by Eqs. (4), (10), and (11).

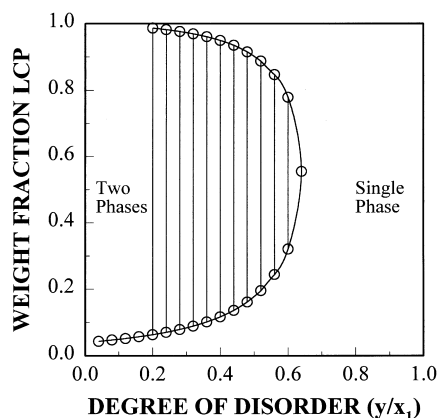


Fig. 2. Spinodal curve of the binary polymer blend containing a thermotropic LCP and a flexible chain polymer with various values of degree of disorder ( $y/x_1$ ) of the LCP:  $\chi_{12} = 0$  and  $x_1 m = x_2 = 25$ .

used to estimate the miscibility of the blends containing a thermotropic LCP. In our early studies of blends of LCP with polycarbonate (PC), poly(ether imide) (PEI), and poly(ether ether ketone) (PEEK) [14,23], we have reported  $\chi_{12}$  and  $y/x_1$  for the blends of LCP–PC, LCP–PEI, and LCP–PEEK, and the values are shown in Table 1.

### 3.2. Miscibility of binary polymer blends

For a binary polymer blend containing a thermotropic LCP and a flexible chain polymer, the miscibility limit which is a spinodal curve at constant temperature has been calculated by Eq. (15) at  $\chi_{12} = 0$  and  $x_1 m = x_2 = 25$ , and the result is shown in Fig. 2. In Fig. 2, the flexible chain polymer appears to be miscible with a thermotropic LCP when the degree of disorder ( $y/x_1$ ) of a thermotropic LCP is higher than 0.63, which is defined as a critical degree of disorder  $((y/x_1)_c)$ . However, there is phase separation when  $y/x_1 < (y/x_1)_c$  in Fig. 2. For a binary polymer blend having a negative value of  $\chi_{12}$ , the miscibility limit has also been calculated by Eq. (15) and the result is shown in Fig. 3,

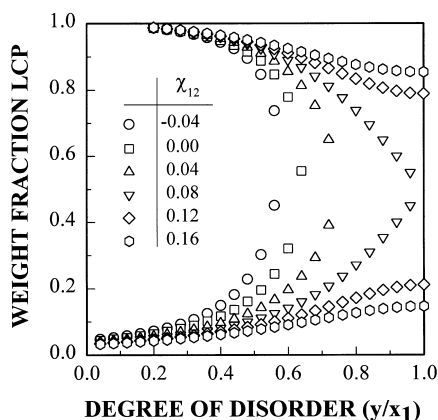


Fig. 3. Spinodal curves of the binary polymer blend containing a thermotropic LCP and a flexible chain polymer with various values of  $y/x_1$  and  $\chi_{12}$ :  $x_1 m = x_2 = 25$ .

which is found to be similar to the result shown in Fig. 2. For the flexible–flexible chain polymer blends, it is well known that the component polymers are miscible when  $\chi_{12} \leq 0$  [47]. By comparing the results of a thermotropic LCP and flexible chain polymer blends (Fig. 2) and flexible–flexible chain polymer blends with regard to  $\chi_{12}$  and  $y/x_1$ , both  $\chi_{12}$  and  $y/x_1$  should be considered in order to find the miscibility in the blend of a thermotropic LCP and a flexible chain polymer. Here, it is worth noting that the anisotropy of a thermotropic LCP disappears when  $y/x_1 = 1$  in Eqs. (3) and (15).

In Fig. 3, the miscibility limit of a binary polymer blend containing a thermotropic LCP and a flexible chain polymer has been calculated by Eq. (15) with various values of  $\chi_{12}$ . In Fig. 3, we can see that the critical degree of disorder  $((y/x_1)_c)$  is increased with the increase of  $\chi_{12}$ . Also, we can see that the critical degree of disorder  $((y/x_1)_c)$  becomes 1.0 when  $\chi_{12} = 0.08$  in Fig. 3. This result suggests that  $\chi_{12} = 0.08$  is the critical polymer–polymer interaction parameter  $((\chi_{12})_c)$  of a thermotropic LCP and a flexible chain polymer blend in the case when  $x_1 m = x_2 = 25$ . The critical polymer–polymer interaction parameter  $((\chi_{12})_c)$  can also be determined by Eq. (19). Eq. (19) can be obtained from the contact point of the spinodal and binodal of Eq. (3):

$$(\chi_{12})_c = \frac{1}{2}(x_1 m^{-1/2} + x_2^{-1/2})^2. \quad (19)$$

Eq. (19) is similar to the result of Scott and Tompa [42,43] for the flexible–flexible chain polymer blend.

At this point, the miscibility of the binary polymer blend containing a thermotropic LCP and a flexible chain polymer can be summarized as follows: when  $\chi_{12} > (\chi_{12})_c$ , phase separation is always observed in any value of the degree of disorder ( $y/x_1$ ). When  $\chi_{12} < (\chi_{12})_c$ , phase separation is also observed at  $(y/x_1) < (y/x_1)_c$ . When  $\chi_{12} < (\chi_{12})_c$  and  $(y/x_1) > (y/x_1)_c$ , the homogeneous phase is observed at all blend compositions.

The effect of the degree of polymerization on the miscibility limit of the binary polymer blends containing a

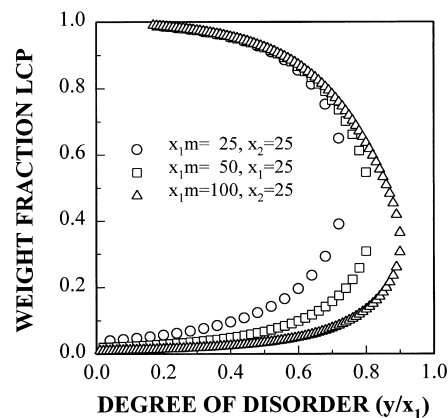


Fig. 4. Effect of the degree of polymerization of a thermotropic LCP on the miscibility of the blends with degree of disorder ( $y/x_1$ ):  $\chi_{12} = 0.04$  and  $x_2 = 25$ .

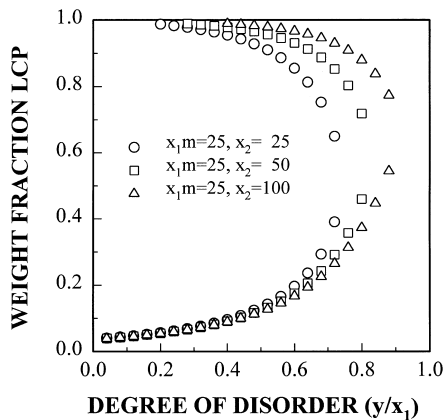


Fig. 5. Effect of the degree of polymerization of a flexible chain polymer on the miscibility of the blends with degree of disorder ( $y/x_1$ ):  $\chi_{12} = 0.04$  and  $x_{1m} = 25$ .

thermotropic LCP and a flexible chain polymer has been examined by Eq. (15). In Fig. 4, the effect of the degree of polymerization ( $x_{1m}$ ) of the LCP component on the miscibility of the blends is shown at constant  $x_2$  ( $x_2 = 25$ ) and  $\chi_{12}$  values ( $\chi_{12} = 0.04$ ). In Fig. 4, the  $(y/x_1)_c$  is shown to increase with the increase of the degree of polymerization of the LCP ( $x_{1m}$ ). This result suggests that the miscibility is decreased with the increase of  $x_{1m}$ , which is the general description of the miscibility of the polymeric blends. In Fig. 5, the effect of the degree of polymerization of the flexible chain polymer ( $x_2$ ) on the miscibility of the blends is shown at constant  $x_{1m}$  ( $x_{1m} = 25$ ) and  $\chi_{12}$  values ( $\chi_{12} = 0.04$ ). In Fig. 5, the  $(y/x_1)_c$  is shown to increase with the increase of the degree of polymerization of a flexible chain polymer ( $x_2$ ), which is similar to the result of Fig. 4.

### 3.3. Miscibility of ternary polymer blends

For a ternary polymer blend containing a thermotropic LCP and two flexible chain polymers, the miscibility limit (spinodal curve at constant temperature) has been calculated by Eq. (18). Model calculations have been performed for

four cases of the polymer blend systems, which are summarized in Table 2. Case I is the ternary polymer blend system in which all component polymers are immiscible with each other such that  $\chi_{12} > (\chi_{12})_c$ ,  $\chi_{23} > (\chi_{23})_c$ , and  $\chi_{13} > (\chi_{13})_c$ . Case II is the ternary polymer blend system in which a thermotropic LCP(1) is immiscible with a flexible chain polymer(2) such that  $\chi_{12} > (\chi_{12})_c$ ; a flexible chain polymer(2) is miscible with a flexible chain polymer(3) such that  $\chi_{23} < (\chi_{23})_c$ ; and a thermotropic LCP(1) is miscible with a flexible chain polymer(3) such that  $\chi_{13} < (\chi_{13})_c$  and  $y/x_1 > (y/x_1)_{c,13}$ . Case III is the ternary polymer blend system in which a thermotropic LCP(1) is immiscible with a flexible chain polymer(2) such that  $\chi_{12} > (\chi_{12})_c$ ; a flexible chain polymer(2) is miscible with a flexible chain polymer(3) such that  $\chi_{23} < (\chi_{23})_c$ ; and a thermotropic LCP(1) is immiscible with a flexible chain polymer(3) due to the anisotropy of the LCP such that  $\chi_{13} < (\chi_{13})_c$  and  $y/x_1 < (y/x_1)_{c,13}$ . Case IV is the ternary polymer blend system in which all component polymers are miscible separately such that  $\chi_{12} < (\chi_{12})_c$ ,  $\chi_{23} < (\chi_{23})_c$ ,  $\chi_{13} < (\chi_{13})_c$ ; and  $y/x_1 > (y/x_1)_{c,12}$  and  $y/x_1 > (y/x_1)_{c,13}$ .

In the calculations we have used arbitrary values of  $\chi_{ij}$  and  $y/x_1$  that satisfy the conditions suggested in Table 2, since we hope to present only qualitative features of the miscibility of the ternary polymer blends containing a thermotropic LCP. The spinodal curves for Case I have been calculated by Eq. (18). Spinodal curves for the (Case I) systems having equal values of  $\chi_{ij}$  are shown in Fig. 6, where  $y/x_1 = 0.3$ . In Fig. 6, the two miscibility gaps appear along the sides of the triangle and the closed curve appears in the center of the triangle diagram. These results are similar to the calculation results of Su and Fried [46] for the ternary polymer blend containing three flexible chain polymers. The central miscibility gap may be ascribed to the coexistence of three phases, since three critical points appear in this curve. The three critical points indicate three phases having identical chemical potential. The three critical points appear in the direction of the angular points indicating each component-rich phase in the ternary blends. We have calculated the spinodal curves for the various values of  $\chi_{ij}$  of Case I. The coexistence curve of the three

Table 2

Conditions of polymer–polymer interaction parameter ( $\chi_{12}$ ) and degree of disorder ( $y/x_1$ ) in four different cases of ternary blend systems for the calculation of spinodal curves

Case	Binary blend			Results <sup>a</sup>
	LCP(1) + Flexible(2)	Flexible(2) + Flexible(3)	LCP(1) + Flexible(3)	
Case I	Immiscible, $\chi_{12} > (\chi_{12})_c$	Immiscible $\chi_{23} > (\chi_{23})_c$	Immiscible $\chi_{13} > (\chi_{13})_c$	Fig. 6
Case II	Immiscible, $\chi_{12} > (\chi_{12})_c$	Miscible, $\chi_{23} < (\chi_{23})_c$	Miscible, $\chi_{13} < (\chi_{13})_c$ , $y/x_1 > (y/x_1)_{c,13}$	Fig. 7
Case III	Immiscible, $\chi_{12} > (\chi_{12})_c$	Miscible, $\chi_{23} < (\chi_{23})_c$	Immiscible, $\chi_{13} > (\chi_{13})_c$ , $y/x_1 < (y/x_1)_{c,13}$	Fig. 8
Case IV	Miscible, $\chi_{12} < (\chi_{12})_c$ , $y/x_1 > (y/x_1)_{c,12}$	Miscible, $\chi_{23} < (\chi_{23})_c$	Miscible, $\chi_{13} < (\chi_{13})_c$ , $y/x_1 > (y/x_1)_{c,13}$	Fig. 9

<sup>a</sup> All results have been calculated by Eq. (18).

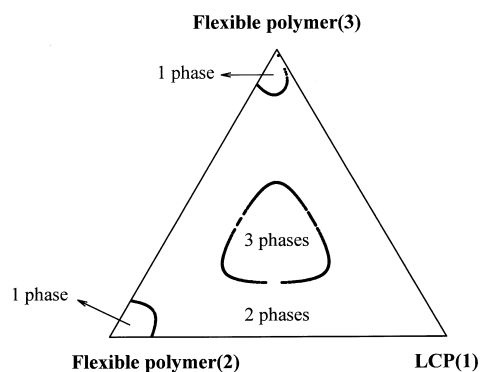


Fig. 6. The spinodal curves for the ternary polymer blend containing a thermotropic LCP and two flexible chain polymers:  $x_1 m = x_2 = x_3 = 50$ ,  $(\chi_{ij})_c = 0.04$ ,  $(y/x_1) = 0.3$ ,  $\chi_{12} = \chi_{23} = \chi_{13} = 0.09$  (Case I).

phases has appeared only for the systems having similar values of  $\chi_{ij}$ .

The spinodal curves for Cases II and III are presented in Figs. 7 and 8, respectively. The same values of  $\chi_{ij}$  have been used in Figs. 7 and 8. The value  $y/x_1 = 0.8$  is used for Fig. 7 and  $y/x_1 = 0.1$  for Fig. 8. In Figs. 7 and 8, the critical degree of disorder  $(y/x_1)_{c,13}$  is 0.72. Therefore a thermotropic LCP(1) and a flexible chain polymer(3) are miscible in Fig. 7 and immiscible in Fig. 8. In Fig. 8, we can see that the spinodal curve is bent near the axes of components 1 and 3. The bent curve is not seen in Fig. 7. The bent curve shown in Fig. 8 may be due to the strong effect of anisotropy ( $y/x_1 = 0.1$ ) of the LCP compared to the anisotropy ( $y/x_1 = 0.8$ ) of the LCP in Fig. 7. The spinodal curve shown in Fig. 8 is similar to the phase diagram of the ternary blends of poly(ether ether ketone)–poly(ether imide)–LCP, which is reported qualitatively by thermal analysis [48].

One would expect a concave surface of Gibbs free energy of mixing for a fully miscible ternary system. However, a hump may appear in the surface of Gibbs free energy of mixing with a phase separation. For this case, there are compositions that satisfy the equality of Eq. (18), which are the inflection points of the surface of Gibbs free energy

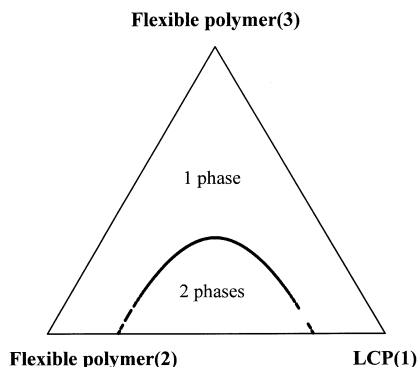


Fig. 7. The spinodal curves for the ternary polymer blend containing a thermotropic LCP and two flexible chain polymers:  $x_1 m = x_2 = x_3 = 50$ ,  $(\chi_{ij})_c = 0.04$ ,  $(y/x_1)_{c,13} = 0.72$ ,  $\chi_{12} = 0.06$ ,  $\chi_{23} = 0.0003$ ,  $\chi_{13} = 0.0001$  and  $y/x_1 = 0.8$  (Case II).

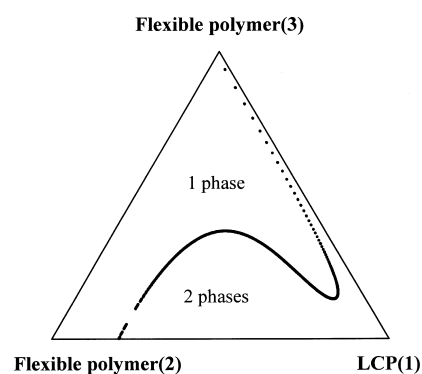


Fig. 8. The spinodal curves for the ternary polymer blend containing a thermotropic LCP and two flexible chain polymers:  $x_1 m = x_2 = x_3 = 50$ ,  $(\chi_{ij})_c = 0.04$ ,  $(y/x_1)_{c,13} = 0.72$ ,  $\chi_{12} = 0.06$ ,  $\chi_{23} = 0.0003$ ,  $\chi_{13} = 0.0001$  and  $y/x_1 = 0.1$  (Case III).

of mixing. In Eq. (18), we can also see the compositions with three negative  $\chi_{ij}$  values satisfying the equality. This may be caused by small difference in  $\chi_{ij}$  values, which is the so-called  $|\Delta\chi|$  effect [46,49]. In Fig. 9, the spinodal curves have been calculated for Case IV where  $y/x_1 = 0.8$ . In Fig. 9, we can see a phase separation curve in the central region. The phase separation may be due to the effect, since all component polymers are miscible with each other.

From the results of Figs. 1–9, it is suggested that the proposed Eqs. (3)–(19) are consistent quantitatively with the miscibility behavior of the binary and ternary polymer blends containing a thermotropic LCP and a flexible chain polymer at melt processing temperature. The two quantitative parameters, the polymer–polymer interaction parameter ( $\chi_{12}$ ) and the degree of disorder ( $y/x_1$ ), can be used to estimate the miscibility of the blend of a thermotropic LCP and flexible chain polymers.

#### 4. Conclusions

In the blends of a thermotropic LCP and flexible chain

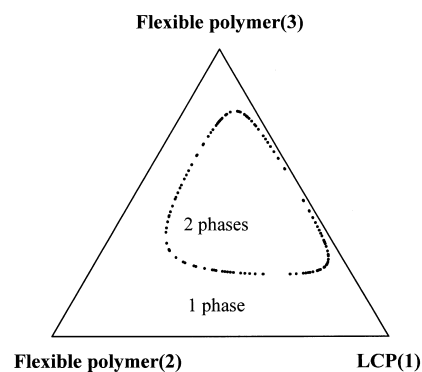


Fig. 9. The spinodal curves for the ternary polymer blend containing a thermotropic LCP and two flexible chain polymers:  $x_1 m = x_2 = x_3 = 50$ ,  $(\chi_{ij})_c = 0.04$ ,  $y/x_1 = 0.8$ ,  $\chi_{12} = -0.5$ ;  $(y/x_1)_{c,12} = 0.3$ ,  $\chi_{23} = -0.2$ ,  $\chi_{13} = 0.02$  and  $(y/x_1)_{c,13} = 0.78$  (Case IV).

polymers, miscibility has been predicted from the model calculation by the application of Flory's lattice theory. From the results of the model calculation, it has been predicted that the miscibility is increased with the increase of the degree of disorder ( $y/x_1$ ) of the LCP and with the decrease of the degree of polymerization ( $x_1m$  and/or  $x_2$ ). In addition, the phase behavior of the blend of the LCP and a flexible chain polymer at melt processing temperature may be evaluated by the two quantitative parameters: the polymer–polymer interaction parameter ( $\chi_{12}$ ) and the degree of disorder ( $y/x_1$ ).

From the results of a binary polymer blend containing the LCP and a flexible chain polymer, it has been predicted that phase separation occurs for any value of degree of disorder ( $y/x_1$ ) at  $\chi_{12} > (\chi_{12})_c$ . When  $\chi_{12} < (\chi_{12})_c$ , phase separation is also predicted at  $y/x_1 < (y/x_1)_c$ . When  $\chi_{12} < (\chi_{12})_c$  and  $y/x_1 > (y/x_1)_c$ , a homogeneous phase is predicted at all blend compositions.

From the results of ternary polymer blends containing the LCP and two flexible chain polymers, it can be concluded that the miscibility of the ternary blends can be estimated by the application of Flory's lattice theory. When three binary polymer blend pairs are immiscible, the coexistence curve of the three phases has appeared for the ternary blends having similar values of  $\chi_{ij}$  between component polymers. When the LCP is immiscible with two flexible chain polymers and the two flexible chain polymers are miscible with each other, the simulated spinodal curve is bent near the axes of components 1 and 3. This is due to the strong effect of anisotropy of the LCP. When three pairs of binary polymer blends are miscible, a phase separation is also observed due to the  $|\Delta\chi|$  effect.

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