

# Relation for Solid–Liquid Coexistence Systems and Its Application to Melting Point Depression of Benzene in Natural Rubber

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A relation that represents “solid–liquid coexistence” curves in binary equilibrium phase diagrams of solvent crystal–noncrystalline polymer systems is deduced on a more general theoretical basis, which is a counterpart of the Flory–Huggins equation representing a solution curve. The relation deduced is expressed as a function of concentration in terms of the interfacial free energy and crystal size. Next, on this relation basis, a melting point depression analysis is made by using certain experimental results on lightly chemically cross-linked NR–benzene systems whose degree of chemical crosslinking is so small that they can be regarded as uncross-linked systems. The relation is revised when considering an elastic term by chain entanglements in the good solvent and a certain concentration–temperature dependent polymer–solvent interaction parameter. Consequently, in the higher concentration range, part of the previous data of crystal size determined from X-ray fit fairly well within the upper and lower limits of the data points calculated from the relation revised.

## Introduction

One of the objectives of this article is to provide a more general background of a temperature–composition relation for “solid–liquid coexistence” curves in equilibrium phase diagrams for solvents in noncrystalline polymers, based on the Flory–Huggins (FH) solution theory.<sup>1,2</sup> Another is to attempt to explain, using the relation deduced, a melting point depression for the solution systems including lightly chemically cross-linked systems that can rather behave as an uncross-linked system. For this aim, reliable experimental data for benzene in a lightly chemically cross-linked natural rubber (NR) will be analyzed by making appropriate modifications introducing several specific effects other than the crystallinity factors.

Experimental solution (or binodal) curves shown in phase diagrams have been frequently compared with theoretical curves represented by the FH equation on the colligative basis<sup>1–3</sup>

$$(1/T_m - 1/T_m^\circ)(h_o/R) = -[\ln(1 - \phi) + (1 - 1/x)\phi + \chi\phi^2] \quad (1)$$

where  $T_m$  is the melting temperature of the system,  $T_m^\circ$  is the bulk melting temperature of the pure solvent,  $h_o$  is the bulk heat of fusion of the solvent,  $x$  and  $\phi$  are the polymerization degree and the volume fraction of the polymer, respectively, and  $\chi$  is the polymer–solvent interaction parameter. In many cases, eq 1 has fitted well experimental results, within the probable limits of experimental error, on an uncross-linked system or even a lightly chemically cross-linked system,<sup>4–8</sup> and thus this formula is sufficiently effective for a fairly wide variety of such binary systems. On the other hand, one can find another available relation that has frequently been used to analyze melting

depressions with varied crystal particle sizes or a solid–liquid interfacial energy of the crystal particles in the pure systems.<sup>9</sup> This relation can basically describe more lowered melting and freezing points of the small particles than those of the bulk solid, which is the so-called Gibbs–Thomson (GT) relation,<sup>5,9–13</sup>

$$(1/T_m - 1/T_m^\circ)(h_o/R) = q\sigma_o/\zeta_o RT_m \quad (2)$$

Here  $\sigma_o$  is the interfacial energy,  $\zeta_o$  is the crystal size, and  $q$  is the shape factor (e.g.,  $q = 2$  for cylindrical crystals, and  $q = 4$  for cubic or spherical crystals), and the  $h_o$  which represents the bulk heat of fusion is assumed to remain constant over a small range of  $(T_m^\circ - T_m)$ . However, it is inconvenient to use eq 2 to deal with mixtures because it is not a function of composition. As a consequence, eqs 1 and 2 have independently been applied to many cases of crystallizing mixtures.

A convenient form of solid–liquid coexistence curves, combined between the FH mixing and GT crystallinity terms (hereafter the FH–GT equation), is also known

$$(1/T_m - 1/T_m^\circ)(h_o/R) = -[\ln(1 - \phi) + (1 - 1/x)\phi + \chi\phi^2] + q\sigma_o/\zeta_o RT_m \quad (3)$$

Needless to say, this relation is a counterpart of eq 1 which represents the reversible equilibrium process between melting and crystallization. Insofar as authors know, however, almost no consideration of this equation has been given to practical uncross-linked systems, except that Jackson and McKenna<sup>5</sup> stated that chemically cross-linked network systems could probably be described by eq 3. Equation 3 can straightforwardly be derived, according to general thermodynamics, from phase equilibrium conditions between the chemical potential based on the FH solution concept and that for the crystal phase. On the other hand, this study which can consequently derive eq 3

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will make its character clearer in considering crystallinity and interfacial factors in a more general treatment.<sup>14</sup> One is that the interfacial factor expressed as a specific parameter will also become clearer, which was not sufficiently described yet in the previous treatment.<sup>14</sup> Another is that two ways will be shown in the theoretical introduction of the FH and GT terms; i.e., in both cases of equilibrium and nonequilibrium crystal size.<sup>15–17</sup> The two final equations derived in such two ways will be found to coincide with each other. This implies that the same form may be applied to either experimental systems regarded as being at equilibrium or those close to equilibrium with sufficiently developed crystal size; thus, this convenience may close the gap between ideal and realistic analyses.<sup>15</sup>

Recently, more reliable values of solid–liquid surface energy have become known of more kinds of low molecular weight substances.<sup>13,18</sup> Therefore, it becomes possible to apply eq 3 to an analysis of melting depression data regarding changes in crystal size with concentration and the effectiveness of eq 3 can be examined in comparison with size data from X-ray or other experimental measurements.<sup>10–12</sup> Further, Jackson and McKenna<sup>5</sup> performed freezing and melting tests of benzene in NR mixtures using differential scanning calorimetry (DSC) and reviewed the behavior. They measured both the melting and freezing point depressions over a wide range of concentration under an equilibrium condition. A great discrepancy between their experimental melting and freezing curves could then be reconfirmed to be principally due to a large degree of undercooling. Particularly, the observed melting data for lightly cross-linked samples fitted well a FH theoretical curve as well as an uncross-linked solution that can keep the colligative property. In contrast, highly cross-linked samples still showed a greater disagreement between experimental results and the FH curve.<sup>5</sup> This appears to show that even the weakly chemically cross-linked systems can behave like an uncross-linked solution due to a fairly small number of chemical junctions present; thus, most parts of free chains appear to play a leading role in melting depression. As a result, the chemically cross-linked part is thought not to have influenced the observed data. It should be remarked that this study does not attempt to explain such an anomalous depression issue but to find main factors for melting point depression of uncross-linked concentrated solutions comprised of long polymer chains with a good solvent.

In most cases, the behavior of practical systems is affected with several effects other than those by crystallization. For example, swelling of polymers in good solvents is an additional effect, as has been introduced in dilute or semidilute polymer solution theories or treatments for the networks.<sup>1,2,19,20</sup> Also, even if such effects are not large enough, these should be taken into account because these accumulated ones may lead to a large result that cannot be neglected. In this context, this article will take into account three principal additional effects via the application of chain elasticity by swelling, a temperature and composition dependent  $\chi$ , and the entanglement concept that has become useful in describing the properties of concentrated polymer solutions.<sup>19,20–27</sup> Equation 3 will be revised then by introducing these effects. The revised equation will be used further to analyze the recent, reliable, experimental data of melting depression of benzene in a natural rubber (NR).<sup>5,13</sup>

## Theoretical Background

**Model and Gibbs Free Energy of Fusion.** In this section, eq 3 for a polymer solution containing equilibrium or nonequi-

librium sized solvent crystals is more generally derived. The solution model for this derivation is shown in Figure 1 where the solvent crystal phase labeled A coexists with the polymer solution phase labeled B. The crystals in this solution system consist of bundles of crystal sequences of size  $\xi_o$ , which are of an extended-chain molecular type. A lattice theory for this solid–liquid coexistence model has only been previously developed by Hoei et al.,<sup>14</sup> and basic equations were calculated so that any polymer segments were excluded from the crystal phase, underlying the FH solution theory. Also, it can experimentally be shown that this model may suit practical systems such as NR–benzene solutions. For example, Oikawa and Murakami<sup>28</sup> verified the presence of the NR–benzene solution phase in the temperature range of 223–283 K by nuclear magnetic resonance spectroscopy (NMR). Jackson and McKenna<sup>5</sup> obviously found that the glass-transition temperature ( $T_g$ ) of one NR–benzene mixture of polymer volume fraction 0.559 was lower by ca. 10 °C than  $T_g$  of the pure bulk NR (~205 K). This was attributed to the presence of liquid benzene in the solidifying system. Arndt and Zander also concluded from measurements of the spin–spin relaxation time of proton by NMR that an unfrozen solvent remained left in swollen systems up to around  $T_g$  because of the great motion of polymer chains contained.<sup>12</sup>

In the lattice theory, a Gibbs free energy of fusion ( $\Delta G_m$ ), from which can be started for deriving basic temperature–composition equations which arrive finally at eq 3, was expressed as a function of the crystal size ( $\xi_o$ ) and degree of crystallinity ( $\omega_o$ ), and the specific parameter ( $D_o$ ) that will be associated later with the interfacial free energy of the crystal end. The Gibbs free energy of fusion, expressed in moles, is written as

$$\Delta G_m/N_o = \omega_o(h_o - s_oT) RT\{\chi[\omega_o\phi^2/(1 - \omega_o\phi_o)] + \Gamma(\phi_o; \omega_o, \xi_o)\} \quad (4)$$

Here

$$\begin{aligned} \Gamma \equiv & [1 + (\phi/x\phi_o)(V_o/V)] \times \\ & \ln\left\{\phi_o \frac{[1 + (\phi/x\phi_o)(V_o/V)](1 - \omega_o\phi_o)}{(\phi/x\phi_o)(V_o/V) + \phi_o(1 - \omega_o)}\right\} + \\ & (\omega_o/\xi_o)(\xi_o - 1) \ln\{\phi_o(\xi_o - \omega_o)[\xi_o - \omega_o(\xi_o - 1)]/\xi_o^2\} + \\ & (\omega_o/\xi_o) \ln(D_o\phi_o) \quad (4') \end{aligned}$$

and  $N_o$  is the total number of solvent molecules in the system,  $\phi$  and  $\phi_o$  are the volume fractions of polymer and solvent, respectively,  $V_o$  and  $V$  are the molar volumes of a solvent molecule and a polymer repeating unit, respectively,  $h_o$  and  $s_o$  are the molar heat and entropy of fusion, respectively,  $x$  is the ratio of the molar volumes of the polymer and solvent, and  $\chi$  is the polymer–solvent interaction parameter. From eq 4, the equilibrium conditions of variables  $\xi_o$  and  $\omega_o$  can be given by calculating  $\partial\Delta G_m/\partial\xi_o = 0$  and  $\partial\Delta G_m/\partial\omega_o = 0$ , respectively. Then, these give the following equations<sup>14</sup>

$$\begin{aligned} \ln D_o = & -\frac{\omega_o^2(\xi_o - 1)(\xi_o - 2)}{(\xi_o - \omega_o)[\xi_o - \omega_o(\xi_o - 1)]} + \\ & \ln\left[\frac{\xi_o - \omega_o}{\xi_o} \frac{\xi_o - \omega_o(\xi_o - 1)}{\xi_o}\right] \quad (5) \end{aligned}$$

and

$$\begin{aligned} (1/N_o)(\partial \Delta G_m / \partial \omega_o) &= h_o - s_o T + RT[\chi[\phi/(1 - \omega_o \phi_o)]^2 + \\ &\quad \frac{\phi[1 - (1/x)(V_o/V)][(\phi/x)(V_o/V) + \phi_o]}{(1 - \omega_o \phi_o)[(\phi/x)(V_o/V) + (1 - \omega_o)\phi_o]} + \\ &\quad \ln\{\phi_o(\xi_o - \omega_o)[\xi_o - \omega_o(\xi_o - 1)]/\xi_o^2\} + (1/\xi_o) \ln(D_o \phi_o) - \\ &\quad \{\omega_o(\xi_o - 1)[\xi_o^2 - 2\omega_o(\xi_o - 1)]/\{\xi_o(\xi_o - \omega_o)[\xi_o - \\ &\quad \omega_o(\xi_o - 1)]\} \} \quad (6) \\ &= h_o - s_o T + RT[\chi[\phi/(1 - \omega_o \phi_o)]^2 + \\ &\quad \frac{\phi[1 - (1/x)(V_o/V)][(\phi/x)(V_o/V) + \phi_o]}{(1 - \omega_o \phi_o)[(\phi/x)(V_o/V) + (1 - \omega_o)\phi_o]} + \\ &\quad \ln\{\phi_o(\xi_o - \omega_o)[\xi_o - \omega_o(\xi_o - 1)]/\xi_o^2\} - \\ &\quad \omega_o(\xi_o - 1)/[\xi_o - \omega_o(\xi_o - 1)] = 0 \quad (6') \end{aligned}$$

It is noted that eq 6' is obtained by eliminating  $\ln D_o$  term in eq 5. Also, the term of eq 5, which will be related to the interfacial energy of crystal end as stated later, takes zero (i.e.,  $D_o = 1$ ) when  $\omega_o = 0$ , and this condition implies disappearance of the interface. Thus, from eq 5, the physically significant parameter values can reasonably be in the range of  $0 < D_o \leq 1$  with the condition  $\xi_o \geq 2$ .  $\xi_o = 2$  means the minimum size that crystallites may take. In the next part, the use of eq 6 will give a temperature-composition relation of fusion for equilibrium crystallinity.

**Equilibrium Crystal Size.** To deduce a solid-liquid coexistence equilibrium relation involving the interfacial parameter, there can be two ways to proceed to this purpose. One is a case taken for equilibrium crystal size and another for nonequilibrium crystal size. The former case is described below and the latter in the subsequent part. Now, if  $V_o \ll V_x$  for simplicity, then from eq 6, a temperature-composition relation involving the interfacial parameter is given by

$$\begin{aligned} (1/T - 1/T_m^\circ)(h_o/R) &= -\chi[\phi/(1 - \omega_o' \phi_o)]^2 - \\ &\quad \phi/[1 - \omega_o' \phi_o(1 - \omega_o')] - (1 - 1/\xi_o') \ln\{\phi_o(\xi_o' - \omega_o') \\ &\quad [\xi_o' - \omega_o'(\xi_o' - 1)]/\xi_o'^2\} - (1/\xi_o') \ln(D_o' \phi_o) + \\ &\quad \{\omega_o'(\xi_o' - 1)[\xi_o'^2 - 2\omega_o'(\xi_o' - 1)]/\{\xi_o'(\xi_o' - \omega_o')[\xi_o' - \\ &\quad \omega_o'(\xi_o' - 1)]\} \} \quad (7) \end{aligned}$$

where  $T_m^\circ$  defined as  $h_o/s_o$  is the equilibrium melting temperature for the pure solvent crystals in the absence of a polymer component and prime marks signify equilibrium values of  $\omega_o$  and  $\xi_o$ .  $h_o(T) \sim h_o(T_m^\circ)$  and  $s_o(T) \sim s_o(T_m^\circ)$  are also assumed. Equation 7 can reduce obviously to the FH equation under the limiting conditions  $\omega_o' = 0$  and  $D_o' = 1$  (implying that the interface vanishes) and  $T = T_{me}$ . Here it is important for the FH equation to be certainly deduced and several extra terms involved in eq 6' (also in eq 6) are of less significance. When the theory<sup>14</sup> was constructed by approximately calculating entropy parts, such extra terms were inevitably accompanied due to the complicatedness of the system, as mentioned earlier.

Another way of putting  $\omega_o' = 0$  and thus  $T = T_{me}$  can reduce eq 7 to

$$(1/T_{me} - 1/T_m^\circ)(h_o/R) = -[\ln(1 - \phi) + (1 - 1/x)\phi + \chi\phi^2] - (\ln D_o')/\xi_o' \quad (8)$$

where  $h_o(T_m^\circ) \sim h_o(T_{me})$  is assumed. Then, if comparing eq 8

formally with eq 3,  $D_o'$  can be apparently connected with the interfacial factor; namely,  $D_o' = \exp(-2\sigma_o'/RT_{me})$ . Thus, another limiting equation which expresses the equilibrium form of eq 3 can be given by

$$(1/T_{me} - 1/T_m^\circ)(h_o/R) = -[\ln(1 - \phi) + (1 - 1/x)\phi + \chi\phi^2] + 2\sigma_o'/\xi_o' RT_{me} \quad (8')$$

**Nonequilibrium Crystal Size.** In this case, one has to revert to eq 4 (and eq 4') that represents the free energy change of fusion of the systems, and that involves the crystallinity factors  $\omega_o$  and  $\xi_o$  as these stand. If  $x$  is large, then eq 4 is given by

$$\begin{aligned} \Delta G_m/N_o &= \omega_o h_o(1 - T/T_m^\circ) + RT\{\chi[\omega_o \phi^2/(1 - \omega_o \phi_o)] + \\ &\quad \ln[(1 - \omega_o \phi_o)/(1 - \omega_o)] + (\omega_o/\xi_o) \ln(D_o \phi_o) + \\ &\quad (\omega_o/\xi_o)(\xi_o - 1) \ln\{\phi_o(\xi_o - \omega_o)[\xi_o - \omega_o(\xi_o - 1)]/\xi_o^2\} \} \quad (9) \end{aligned}$$

Further, if  $\omega_o$  is small, eq 9 becomes, when expanding with respect to  $\omega_o$  and neglecting the higher order terms of  $\omega_o$ ,

$$\Delta G_m/m_o \xi_o = h_o(1 - T/T_m^\circ) + RT\{\chi\phi^2(1 + \omega_o \phi_o) + \phi + \ln(D_o \phi_o) - [1 - (1/\xi_o)]\omega_o\} \quad (10)$$

Then,  $\Delta G_m = 0$  is the thermodynamic condition that the system becomes most stable so that eq 10 yields

$$(1/T - 1/T_m^\circ)(h_o/R) = -\{\chi\phi^2(1 + \omega_o \phi_o) + \phi + \ln \phi_o + [1 - (1/\xi_o)]\omega_o\} - (\ln D_o)/\xi_o \quad (11)$$

If setting  $\omega_o = 0$  and thus  $T = T_{mu}$ ,  $D_o = D_{ou}$ , and  $\xi_o = \xi_{ou}$ , then

$$(1/T_{mu} - 1/T_m^\circ)(h_o/R) = -(\chi\phi^2 + \phi + \ln \phi_o) - (\ln D_{ou})/\xi_{ou} RT_{mu} \quad (12)$$

where the added subscripts (<sub>u</sub>) signify nonequilibrium values before  $\xi_o$ 's reaching the equilibrium values and the approximation  $h_o(T_m^\circ) \sim h_o(T_{mu})$  is assumed. This equation results in the same form as eq 8 after the extra terms are eliminated. Again, by comparing eq 12 with eq 3,  $D_o = \exp(-2\sigma_o/RT)$  (where  $\sigma_o$  is the interfacial free energy of the crystal end) may be redefined as well as is done in the equilibrium case. Namely, the nonequilibrium form of eq 3 can be expressed as

$$(1/T_{mu} - 1/T_m^\circ)(h_o/R) = -(\chi\phi^2 + \phi + \ln \phi_o) + 2\sigma_{ou}'/\xi_{ou}' RT_{mu} \quad (12')$$

It is noted that it is the point for eq 12' to result in the FH-GT type expression so that the extra terms involved in eqs 10 and 11 are minor, as well as in the previous case.

### Analysis for NR-Benzene Uncross-Linked Systems

**Additional Factors.** A single polymer chain should be affected by elastic properties caused by a larger molecular expansion (i.e., swelling) in a good solvent. On the other hand, according to the viscoelastic studies, intermolecular entanglement couplings have been taken into account as a topological interaction in uncross-linked (bulk, melt, or concentrated) systems comprised of long chains.<sup>20-23,26,27</sup> This suggests the entanglement couplings may constrain the thermal motion of polymer chains in the physical network space. Hence the elastic action caused by such entanglement coupling systems in a good solvent should be considered in uncross-linked systems. Thus,



the entanglement couplings could be one of effective factors in the melting point depression of uncross-linked concentrated systems.

Recently, it was pointed that several sophisticated concepts of rubber elasticity,<sup>24,25</sup> based on the constraint of fluctuations of the chemical junctions and network chains, were basically equivalent to the entanglement concept which can also be described by the "tube" model.<sup>21,26,27</sup> Thus, in general, chemically cross-linked systems would involve a chain-trapped or -constrained network situation. Simply, the reticulation density  $\nu$  of such networks may be assumed as the sum of the chemically cross-linked and entanglement network densities (represented by  $\nu_X$  and  $\nu_N$ , respectively).<sup>22</sup> However, the former density of experimental systems dealt with in this study will be smaller than the latter one, to the indistinguishable extent between the numbers of chemical and physical junction points. Therefore, we have only to mention the entanglement term, but will introduce a more general relation related even with the chemical cross-links. Because this relation could be useful in knowing to what extent of chemical cross-linking the colligative properties can be kept. Further, unlike the fixed chemical junction density, the entanglement density would depend perhaps on concentration, as will be stated later in detail.<sup>20–22</sup> The relation also would suggest to what extent of the chemical junction density the concentration dependence begin vanishing.

As is well-known, NR–benzene system is one of good solvent systems and the solvent in NR works as a good solvent down to fairly low temperature. This will further be supported by  $\chi$  values estimated in a low temperature region, as will be shown later in more detail. Thus, the systems may be affected by the elastic effects by swelling even in such temperature range. Such elastic action that is exerted to polymer chains may simply be introduced into eq 3, according to the additivity principle of free energy; i.e., this practical introduction is possible through the use of a conventional procedure from the Flenkel–Flory–Rehner swelling model, based on the Gaussian affine network model, where the Flory–Rehner (FR) elastic term may be added only to the FH mixing term.<sup>2,25,29,30</sup> Although the FR term originally involved only the chemical cross-link density, the density may be assumed to be replaced by the reticulation density as stated earlier,<sup>22</sup>

$$\nu = \nu_X + \nu_N = \nu_X + (d/M_e)T_e \quad (13)$$

Here  $\nu_X$  and  $\nu_N$  are the elastically effective chemical and entanglement network densities, respectively,  $T_e$  is the probability that an entanglement is trapped, which is in the range  $0 \leq T_e \leq 1$ ,  $d$  is the density of polymer, and  $M_e$  is the average molecular weight between entanglement coupling points.  $\nu_X$  may be assumed to be on the affine basis, and the primary molecular weight before cross-linked may also be assumed to be very large (i.e., the effect of free ends is neglected). On the other hand,  $\nu_N (= (d/M_e)T_e)$ <sup>22</sup> is similar to the conventional relationship in terms of a molecular weight ( $M_e$ ) between chemical junctions (i.e.,  $\sim d/M_e$ ).<sup>2</sup> Thus, it is possible to estimate the entanglement term of eq 13 because  $M_e$  can be calculated using experimental plateau values of relaxation modulus determined from the dynamic measurements on uncross-linked bulk systems, and  $M_e$  data of several kinds of polymers were already obtained, including a hevea rubber or a polyisoprene that would be applicable to the present study.<sup>21,22</sup>

The present study is concerned with uncross-linked concentrated systems and thus  $\nu_N$  would have to be corrected so as to be consistent with a composition dependence of  $M_e$ . It was previously predicted that entanglements per chain would

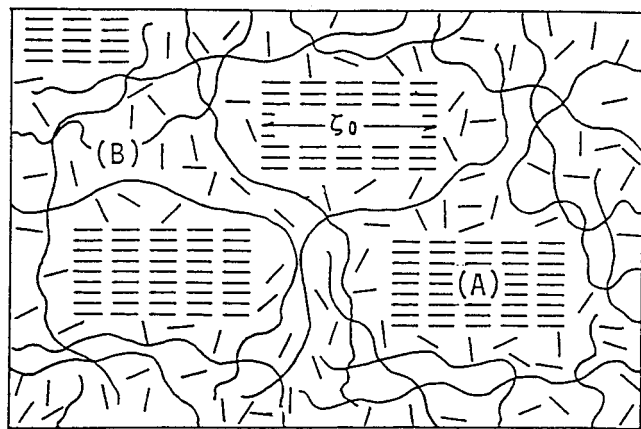
decrease with dilution.<sup>20</sup> Recently, a relation as a function of  $M_e$  and the polymer fraction of polymer  $\phi$  has been given by<sup>22,23</sup>

$$M_e(\phi) = M_e/\phi^{j-1} \quad (2.1 < j < 2.3) \quad (14)$$

Here  $j$  is the composition exponent depending slightly on the polymer species. This relationship was obtained from the measurements of concentration dependence of shear modulus as a function of  $M_e$ . Combining  $\nu$  of eq 13 (i.e.,  $d(1/M_e + T_e/M_e(\phi))$ ) with eq 14 may evaluate approximate overall elastic effects by swelling for the concentrated systems involving the chemically and physically constrained points. This concept will be considered to express a more general equation for melting point depression on such systems, as will be stated later.

Next, the interaction parameter  $\chi$ , included in the FH part of eq 3, has to be redefined as a function of temperature and composition. This is attributed to the changes in solvent quality in the fairly wide measurement ranges of temperature and composition as shown in ref 5. Studies of  $\chi$  on rubber mixtures were performed by several researchers.<sup>25,31–34</sup> However, both concentration and temperature dependence of  $\chi$  specialized for NR–benzene uncross-linked mixtures seems to have been established only by Maron et al.<sup>34</sup> Their  $\chi$  expression (hereafter  $\chi_M$ ) for NR–benzene uncross-linked solutions, based on a Hildebrand type theory (introducing the concept of "effective volume"<sup>35</sup> similar to "free volume"<sup>1,2</sup>) that is alternative to the FH solution theory. The  $\chi_M$  showed excellent agreement with experimental data for the systems over the full concentration range.<sup>35</sup> Also, they suggested then the signs of unentanglement up to concentrations of at least  $\phi = 0.2$ .<sup>34a,35</sup> This information will be used later for discussion.

**Jackson–McKenna Data.** Brief comments are made, because the experimental data obtained by Jackson and McKenna<sup>5,13</sup> are fully used for a FH–GT based analysis in this section. First, their results fit well a FH equilibrium curve ( $(T_m - \phi)$  curve) for  $\chi = 0.43$  (for benzene),<sup>5,10</sup> regardless of those for lightly cross-linked mixtures, as will be stated again later. Therefore it can be said that the network chain systems of  $\phi$  are still under the swelling equilibrium. According to them, the  $\phi$  is that at swelling equilibrium in an excess of benzene. Thus the mixtures maintain property of a noncrystalline and uncross-linked polymer solution; i.e., the network chain length ( $M_c$ ) is very large ( $M_c = 21\,800$ ). Thus the chemical junctions may be assumed to be undistinguishable from entanglement coupling points; i.e., the number of chemical junctions must be much less than that of entanglement couplings. Further, even if the mixtures of  $\phi$  are under nonequilibrium conditions, a similar analysis may be permitted through the use of eq 12' of nonequilibrium type. Second, their measurements on the mixtures cover a fairly wide concentration range that are suitable for the FH solution analysis. This is essential for a wide range of crystal size analysis. Also, the  $M_e$  value was determined stoichiometrically from the relationship for peroxide-curing NR as was given by Wood.<sup>36</sup> The most reliable value of solid–liquid interfacial energy for the benzene solvent is to be used. Recently, it was independently measured by the controlled pore glass method using DSC.<sup>13</sup> The energy value was determined from the melting peaks and heats of fusion of the pure solvent confined in the homogeneous pores of various sizes through the use of the GT equation, eq 2. Thus the use of the energy value is consistent methodologically with the present analytical procedure. As a consequence, they estimated  $15.7 \times 10^{-7} \text{ J cm}^{-2}$  as a new value and found that the conventional values were underestimated.



**Figure 1.** Schematic representation of a crystalline solvent in a noncrystalline polymer system: (A) a solvent crystal and (B) a solution phase consisting of polymer and solvent molecules.

**TABLE 1: Values of Interaction Parameter for Benzene in NR, Estimated from Equation 15**

$\phi^a$ (°C)	$T_m^a$ (°C)	$\Delta T^b$	$\chi_M$
0.134	5.00	0.20	0.400
0.381	4.43	1.07	0.403
0.396	0.82	4.68	0.406
0.437	1.25	4.25	0.406
0.519	-1.73	7.23	0.410
0.543	-3.01	8.51	0.412
0.562	-5.99	11.49	0.416
0.572	-6.20	11.70	0.416
0.647	-10.24	15.74	0.424
0.722	-15.77	21.27	0.437

<sup>a</sup> Data extracted from  $T_m$ - $\phi$  plot by Jackson and McKenna.<sup>5</sup> <sup>b</sup>  $T_m^\circ = 278.5$  K.

As stated earlier, we employ Maron's relationship of  $\chi$  specialized for NR-benzene uncross-linked systems, which is given by

$$\chi_M = k - s\phi_0 \quad (15)$$

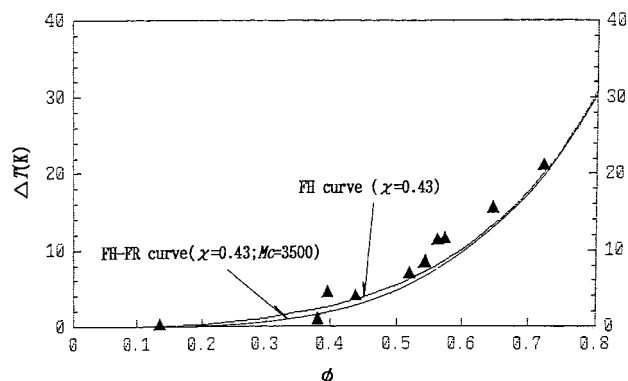
Here

$$k = (0.14 - 0.15\phi + 0.04\phi^2 - 0.24\phi^3) + (74.54 + 44.72\phi - 11.93\phi^2 + 71.56\phi^3)/T_m \quad (16)$$

and

$$s = (-0.15 + 0.08\phi - 0.72\phi^2) + (44.72 - 23.86\phi + 214.68\phi^2)/T_m \quad (17)$$

Because  $x$  is very large in entanglement network systems, the above  $1/x$  term is negligible. Thus, it is convenient in the present study that the  $\chi$  in eq 3 has only to be simply replaced by  $\chi_M$ . As stated earlier, the quality of benzene in NR becomes poorer at lower temperatures, but there are several evidences to indicate that the solvent molecules keep still mobility even at temperatures lower than the frozen points of the systems, and thus the solvent-crystallized polymer solution model illustrated in Figure 1 may be justified to apply to the NR-benzene crystalline systems. Table 1 demonstrates changes in  $\chi_M$  calculated with the data of  $\phi$ ,  $T_m$ , and  $\Delta T$  ( $=T_m^\circ - T_m$ ), according to eq 15, which were extracted from the report presented by Jackson and McKenna.<sup>5</sup> Ten data points of  $\Delta T$  against  $\phi$  could then be clearly read among all of the thirteen points, which are so enough for an analysis over a wide range



**Figure 2.** Plot of  $\Delta T$  vs  $\phi$  for lightly cross-linked NR-benzene systems, where the solid lines are calculated from FH and FH-FR equations with  $\chi = 0.43$  and  $M_c = 3500$ . (▲) Data reproduced from Jackson-McKenna<sup>5</sup> for the  $M_c = 21\,800$  rubber.

of  $\phi$ . Of these points, however, only one point for  $\phi = 0.134$  was unclear: its value of  $\Delta T$  was observed as zero, although the original graph was magnified enough to be able to read. Regardless of this status, one may assume approximately  $\Delta T = 0.1$ – $0.2$  when considering the general limitation of precision from a plotter and other reasons. Thus we have fixed at most  $\Delta T = 0.2$ . As seen from Table 1, it seems sufficiently reasonable that the  $\chi_M$  values become somewhat higher as  $T_m$  becomes lower, and all the mixture samples obviously keep “good solvent” systems within the temperature-composition range.

**Melting Point Depression Equation.** Figure 2 indicates excellent reproducibility of the extracted McKenna-Jackson's data points (▲) near a FH curve (represented by eq 1) depicted as  $\chi = 0.43$ , compared with the original figure shown in ref 5. Necessary parameter values are assigned as  $T_m^\circ = 278.5$  K and  $h_o = 547.3$  J/mol.<sup>5,13</sup> Apparently, the FH curve is also in good agreement with the McKenna-Jackson's data points within error, judged from their scatter around the curve. It should be noted that another FH type (or FH- $\chi_M$ ) curve (but not shown in Figure 2), plotted by replacing the  $\chi$  with the above  $\chi_M$ , can fit well the extracted data points as well. This is because of the small changes in  $\chi_M$  within the temperature range as shown in Table 1. As seen from Figure 2, another curve designated as FH-FR curve, close to the FH curve for  $\chi = 0.43$ , will be mentioned later.

To introduce swelling effects for chemical and/or entanglement network systems to eq 3, it has been already stated that the conventional FR procedure may be applicable to the present study on un- or lightly cross-linked systems and the conventional cross-linking density required in the conventional FR term would be replaced by the reticulation density  $\nu$ ; i.e., a new FR term can be redefined through  $\nu$ . According to the “tube” model, even if the tube space filled with solvent molecules is frozen, the crystal produced in the whole space can be partitioned into small crystal pieces that may cause an appreciable magnitude of  $\Delta T$ .<sup>10–13,37,38</sup> In the present analysis, the elastic effects by swelling can be introduced through the  $\nu$ , while the partition (or “mesh”)<sup>37</sup> effects that may dominate the crystal size may be evaluated through the GT part in eq 3 with the interfacial energy term. From rheological measurements, a molecular weight between the entanglement coupling points ( $M_e$ ) has also been estimated for various polymers.<sup>23,24</sup> For hevea rubbers,  $M_e = 6100$  and  $3500$  at  $25$  °C and  $-30$  °C, respectively, and for a polyisoprene,  $M_e = 5100$  at  $25$  °C. These are bulk data and thus in the case of solution systems, a concentration correction is needed. A concentration dependence of  $M_e$  is already known elsewhere,<sup>24</sup> which shows in general that  $M_e$  increases (i.e., the

**TABLE 2: Estimated Values of Crystal Size for Benzene in Lightly Cross-Linked Natural Rubber, According to Equations 2, 3,<sup>a</sup> and 18**

$\phi^b$	$T_m^b$ (°C)	$\Delta T$ (°C)	GT [ $\zeta_o'$ (nm)]	FH-GT- $\chi_M$ [ $\zeta_o'$ (nm)]	FH-GT-FR- $\chi_M$ ( $M_c = 21\,800$ )		
					$T_e = 0$ [ $\zeta_o'$ (nm)]	$M_c = 3500$ [ $M_c(\phi)$ ]	$T_e = 1$ [ $\zeta_o'$ (nm)]
0.134	5.00	(0.20)	(315.5)	(6015.2)	(1175.7)	(>21800)	(1175.7)
0.381	4.43	1.07	147.4	negative	negative	10116	negative
0.396	0.82	4.68	33.7	85.6	80.1	9696	69.8
0.437	1.25	4.25	37.1	368.0	282.6	8700	178.8
0.519	-1.73	7.23	21.8	204.5	175.2	7201	122.2
0.543	-3.01	8.51	18.5	148.1	132.2	6852	98.5
0.562	-5.99	11.49	13.7	48.2	46.4	6597	41.3
0.572	-6.20	11.70	13.5	53.0	50.8	6470	44.6
0.647	-10.24	15.74	10.0	63.2	60.2	5650	50.9
0.722	-15.77	21.27	7.4	103.9	96.3	5008	72.9

<sup>a</sup> Equation 3 replaced by  $\chi_M$ . <sup>b</sup> Data extracted from  $T_m$ - $\phi$  experimental plots by Jackson and McKenna.<sup>5</sup>

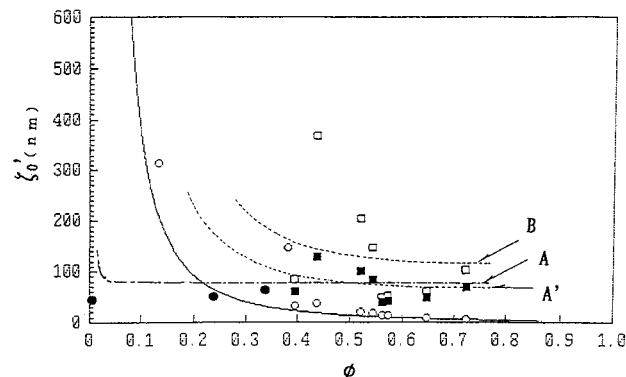
entanglement density decreases) with increasing dilution.<sup>20</sup> Consequently, for the present analysis, a full relevant relation (or the FH-GT-FR- $\chi_M$  equation) based on eq 3 can readily result:

$$(1/T_m - 1/T_m^0)(h_0/R) = -[\ln(1 - \phi) + \phi + \chi_M \phi^2 + dv_o(1/M_c + T_e/M_c(\phi))(\phi^{1/3} - \phi/2)] + 4\sigma_o'/\zeta_o'RT_m \quad (18)$$

where  $M_c(\phi) \sim M_c/\phi^{1.1}$  from eq 14, assuming  $j = 2.1$ ,  $d$  is the density of polymer at  $T_m$ ,  $v_o$  is the molar volume of solvent, and  $(1/x)$  term in eq 3 disappears because  $x$  is very large in the present systems. Equation 18 consists of three parts: the first corresponds to the FH mixing term, the second the FR elastic term, and the last the crystallinity term of the GT type. The  $T_e$  implies the extent of restriction by entanglements per network chain between chemical junctions, or per free chain in uncross-linked systems. In the case of uncross-linked systems,  $M_c$  represents a molecular weight of the primary polymer component. If  $M_c$  is less than the critical molecular weight,  $T_e = 0$  (implying there are no effective entanglement couplings). And for a lower molecular weight than this  $M_c$ ,  $T_e \neq 0$ . In the case of  $T_e = 1$ , the FR term in eq 18 takes a maximum that implies the largest efficiency by entanglements. Now that a  $T_e$  value is unknown for the present NR mixture systems, only trends have to be examined by assigning either  $T_e = 0$  or 1. In addition, a temperature dependence of  $M_c$ , which is said to be insensitive due to interactions of a topological character,<sup>22</sup> is not yet known also; thus, this article adopts  $M_c = 3500$  which was estimated at the lower temperature (i.e., -30 °C). This would be more appropriate in analyzing the data of melting point depression in the temperature range as shown in Table 1.

As seen again in Figure 2, the FH curve for  $\chi = 0.43$  is positioned slightly above the FH-FR curve which is calculated as  $\chi = 0.43$ ,  $T_e/M_c = 1/3500$ , and  $M_c = 21\,800$ , according to the FH-FR equation without the GT term of eq 18. The slight difference in  $\Delta T$  shows a fairly small contribution by the FR term. However its small effect is not negligible in the present analysis. Because the FH-FR curve is also in reasonable agreement with Jackson-McKenna's data points within their scattering range, to nearly the same extent as the FH curve is so. Such a FH-FR analysis considers only the additional elastic effect by entanglements, while the FH-GT-FR- $\chi_M$  equation, eq 18, makes possible more detailed evaluations that can involve the effects of crystal size (or mesh size  $\zeta_o'$ ) through the interfacial energy ( $\sigma_o'$ ).

Table 2 shows all numerical values of  $\zeta_o'$  and  $M_c(\phi)$  calculated considering the same extracted data as in Table 1, according to eq 2, the revised version of eq 3 (or the FH-GT- $\chi_M$  equation), and eq 18, which were used for making the



**Figure 3.** Plot of  $\zeta_o'$  (nm) vs  $\phi$  for lightly cross-linked NR-benzene systems, where broken line A' and B are the best-fitting curves for the data points in Table 2, symbolized by  $\blacksquare$  and  $\square$ , respectively, according to the FH-GT-FR- $\chi_M$  equations for  $T_e/M_c = 1/3500$  and  $T_e = 0$  on the  $M_c = 21\,800$  basis. Dash-dot line A is best fitted with both Boonstra's<sup>10</sup> data ( $\bullet$ ) and other data ( $\blacksquare$ ) in Table 2. Solid line, fitted with GT data ( $\circ$ ) in Table 2, is calculated from the GT equation, smoothed with  $\Delta T$  and  $\phi$  data points extracted from the single FN- $\chi_M$  curve.

corresponding plots as seen in Figure 3. In Figure 3, the GT curve shown by a solid line is only the theoretical reference curve to see variabilities in data points due to the FH and/or FR terms to be added to the GT base. To depict a smooth curve for the reference curve, fairly many data points of  $\zeta_o'$  and  $\phi$  were calculated with those of  $\Delta T$  and  $\phi$ , according to eq 3. The data source of  $\Delta T$  and  $\phi$  was independently sorted from a single theoretical curve (not shown here) of  $\Delta T$  against  $\phi$  plotted, according to the FH- $\chi_M$  equation which is a function of  $\phi$  and  $T_m$ . The value of  $\sigma_o'$  is assigned as  $15.7 \times 10^{-7}$  J cm<sup>-2</sup>. Then, the individual  $\zeta_o'$  values ( $n = 10$ ) represented by the symbol ( $\circ$ ) in Figure 3, were estimated from the individual experimental values of  $\phi$  and  $\Delta T$  in Table 2 (or Table 1), according to the GT equation (eq 2). Obviously, the individual data points fits very well the reference curve, except the point for  $\phi = 0.381$ . Thus such a result will be useful to the following analysis for the solid-liquid systems. It is should noted that the large deviation of the  $\phi = 0.381$  point from the reference curve seems to be due to such experimental difficulties as involved in a sample preparation. As shown in Table 2, furthermore, the  $\zeta_o'$  value calculated as  $T_e = 0$  is assigned for a value under the assumption of  $T_e/M_c = 1/3500$ . This is because the  $M_c(\phi)$  value for  $\phi = 0.134$  is much larger than  $M_c = 21\,800$ .

Here, it is significant to show which was better between the reference (FH- $\chi_M$ ) curve and the conventional FH curve for  $\chi = 0.43$  in the analysis for NR-benzene mixtures. However, this comparison is not shown in Figure 3. Consequently, the FH- $\chi_M$  curve was then a better fit through the GT data points



(○) in the overall range of  $\phi$  than the FH curve shifted adversely in the higher range of  $\phi$ . Thus this status supports additionally the use of  $\chi_M$  in this study.

Curve A' and B in Figure 3 show the best fitting plots for two sets of the data points from Table 2 indicated by the symbols (■) and (□) in Figure 3, calculated according to the FH-GT-FR- $\chi_M$  equation for  $T_c/M_c = 1/3500$  and the FH-GT- $\chi_M$  equation, respectively. Also, curve A will be described in the following section. Attention should be here paid to the calculated values of  $\xi_o'$  for  $\phi = 0.381$  in Table 2; i.e., they take all negative values. This implies that even a slight experimental error which arises from this kind of measurements reflects very sensitively on a calculated results of  $\xi_o'$  involving the FH term.

From Figure 3 and Table 2, we conclude as follows: (1) Obviously, the large scatter of the data points can be attributed to the FH mixing term by dilution of free polymer chains with a solvent. However, the mean crystal size ( $n = 8$  without the data for  $\phi = 0.134$ ) of the FH-GT-FR- $\chi_M$  curve (A') is significantly ca. 37% smaller than that of the FH-GT- $\chi_M$  curve (B). This difference is large enough and is not negligible. As a result, the FR term will be reasonable for analysis. (2) One may suppose that the GT data points seem to have a crossover region of  $\phi$  at around 0.1–0.2, as they could fit the GT reference curve in the lower  $\phi$  range. If curves A' and B run almost parallel with the GT curve, then the curves appear to have certain broader crossover regions at around  $\phi = 0.2$  and 0.2–0.3, respectively, when seeing that the sizes estimated at  $\phi = 0.134$  is drastically changed. These will be concerned with the entanglement condition with concentration, as mentioned further in the following section. The concentration of  $\phi \sim 0.2$  that unentanglement begins, as estimated by Maron et al.,<sup>34</sup> seems to coincide with that in the crossover region of curve A'. However, this should be ascertained gaining more experimental information to explain the status. (3) Briefly, the crystal size can approximately be represented as  $\xi_o' \sim [\Delta T/T_m^o - (\text{mixing term}) + (\text{elastic term})]^{-1}$  from eq 18, which consists of the negative mixing term and the positive elastic term. This shows that the crystal size tends to increase with increasing value of the mixing term and to decrease with increasing value of the elastic term (i.e., with decreasing mesh size).

### Comparison with Observed Data of Crystal Size

To verify the analytical results of crystal size in the above section, it is necessary to compare with some other observed results of crystal size. However, there seems to be almost no such size data directly observed by X-ray or others in the mixtures. This is certainly due to too much difficulties to detect them skillfully, for example, by X-ray. For comparative analysis, helpful data seem to be limited to the minimum size data determined from X-ray, as reported by Boonstra, Heckman, and Taylor.<sup>10</sup> Consequently, they obtained  $\xi_o > 100$  nm for the pure benzene, and then  $\xi_o = 46$  nm and ca. 64 nm when  $\phi = 0.01$  and 0.34 in uncross-linked NR-benzene mixtures, respectively. Also,  $\xi_o = \text{ca. } 57$  nm for another sample of  $\phi = 0.24$ . This must be lightly cross-linked, as commented by Jackson and McKenna.<sup>5</sup> These three data points are indicated by the symbol (●) in Figure 3. If excluding Boonstra's result for  $\phi = 0.01$ , the two other size data appear to be in reasonable agreement with the FH-GT-FR- $\chi_M$  data (■) within the scattering range of the data points around curve A and the concentration range seems to be limited to  $\phi > 0.3$ –0.4. Consequently, the introduction of the elastic effects by entanglements through the aid of the FR term on the FH-GT basis may be permitted. Arguments for  $\phi < 0.3$ –0.4 will be made later. It should be

noted that, to estimate the FR term, no corrections of density and molar volume of two components on temperature were done and the observed values at room temperature were used. This is because they can be compensated by each other.

The dimension of a single polymer coil in a good solvent can be estimated by the use of Flory's relationship  $\langle r^2 \rangle^{1/2} \sim n^{3/5}$  where  $n$  is the number of segments. From this relationship, a coil size range corresponding to the entanglement molecular weight range of  $M_e(\phi) = 5000$ –10000, seen in Table 2, may be estimated to be within the range ca. 7–10 nm when two isoprene monomers are taken as one segment.<sup>2,19</sup> This larger expansion than that estimated from the Gaussian coil dimension formula ( $\sim n^{1/2}$ ) seems close to the corresponding GT crystal sizes, especially in the higher  $\phi$  region, as exhibited in Table 2. On the other hand, the crystal size data estimated with the use of the FH-GT-FR- $\chi_M$  equation in Table 2 (or Figure 3) are affected by the FH and FR terms. Also, the larger crystal sizes estimated for the  $M_c(\phi)$  is obviously close to the size data reported by Boonstra et al.<sup>10</sup> Consequently, the crystal sizes estimated seem to be much larger than the network spatial dimensions estimated from the above formulas, which may play a key role in melting point depression. This might be because the mobile (or slidable) entanglement coupling points and free midchains permit the larger growth of benzene crystallites in the frozen process. This reason will be clarified in the future by making a comparison between coil sizes observed under the unfrozen and frozen conditions.

Finally, for the lower concentration range  $\phi < 0.3$ –0.4, we discuss through curve A' seen in Figure 3 as follows. Curve A was plotted so as to be best fitting with the Boonstra's three data points indicated by the symbol (●) plus the FH-GT-FR- $\chi_M$  data points (■). De Gennes<sup>19</sup> described the presence of a threshold concentration ( $\phi^*$ ) at which polymer chains begin to interpenetrate, corresponding to a close packing of the coils; namely,  $\phi^* \sim n^{-4/5}$  where  $n$  is polymerization degree; thus,  $\phi^*$  can be defined as the crossover between the respective nonentangled and entangled regimes  $\phi < \phi^*$  and  $\phi > \phi^*$ . When  $n$  is of the rough order between 10 and  $10^2$ , which corresponds to the hypothesized molecular weight range between 3500(= $M_c$ ) and maximal 21 800(= $M_c$ ) with and without entanglement couplings, respectively,  $\phi^*$  can be estimated as the order between  $10^{-1}$  and at least  $10^{-2}$ , according to the above relation. Thus, although Boonstra's data of 46 nm and ca. 64 nm falls within this range of  $\phi^*$ , it is still uncertain that a crossover in curve A may appear in the  $\phi$  range of the order of 0– $10^{-1}$ . If one found where the crossover was, the effects by entanglements would become clearer. To ascertain this, it will be preferable to obtain more experimental data points covering the  $\phi$  range of 0–0.4; together with the additional data points, a connectivity with curve A must be more clearly described.

### Conclusions

For the first aim, a reasonable temperature–composition relation for solid–liquid coexistence curves as a counterpart for the FH melting curves has consistently been obtained, based on a more general theory.<sup>14</sup> The resulting form (the FH-GT equation, eq 3) has been found to coincide with the combination of the FH equation (eq 1) with the GT equation (eq 2), which enables one to analyze more thermodynamic information involving the crystal size and interfacial energy of the solvent crystal. The FH and GT classical equations have independently been experimentally verified on polymer solutions and one component solid systems, respectively, while so far there have been no such a relation to go upon. Furthermore, it has been

stated that the model<sup>14</sup> in the theory for a crystalline solvent in a noncrystalline polymer is applicable to practical systems from several experimental facts.<sup>5,12,21,22</sup>

For the other aim, the FH–GT basic relation deduced has been revised, as stated below, and applied to certain reliable data of melting point depression for benzene in a lightly cross-linked NR which could fit the FH melting curve.<sup>5</sup> Also, the most recent reliable data of the interfacial energy, determined elsewhere from a newly developed experimental method by DSC,<sup>13</sup> has been used for this study. By the use of this data, a consistent analysis of a concentration dependence of crystal size has become possible. Although the backbone in this study is the FH–GT equation, it is necessary in general to hypothesize other reasonable factors so as to explain experimental results for most of real systems. In this study, an analysis of the melting point depression behavior on the NR–benzene systems was conducted by the relevant relation eq 18 (the FH–GT–FR– $\chi_M$  equation) introducing the FR term in eq 3. Thus the elastic contribution by entanglements can be evaluated for the uncross-linked systems, or lightly cross-linked ones without almost no effects by the chemical junctions.

We need to briefly refer to the requisite that the part of FH–FR– $\chi_M$  in eq 18 must be zero for swelling equilibrium at normal temperature more than  $T_m$ . This was examined by estimating  $\phi$  value as the equilibrium degree of swelling for a completely swollen system at the temperature. In fact, this estimate showed  $\phi \sim 0.179$  at 23.6 °C for  $M_c \sim 21\,800$ , while Jackson–McKenna gave  $\phi = 0.158$  at this temperature. Also, it was assumed that  $T_e = 1$  and  $M_e = 6100$  at 25 °C for hevea rubber, as shown in the previous section. This result (i.e., the deviation of ca. 10%) can said to be rather fairly good if considering such a rough estimate.

Consequently, a crystal size analysis by the use of eq 18 involving the multiple effects has been partly able to explain the results of crystal size detected by X-ray on the similar systems.<sup>10</sup> As seen from Table 2 or Figure 3, it should be noted that this explanation has been satisfactory within the restricted concentration range higher than  $\phi = 0.3$ – $0.4$ . In contrast, for the lower concentration range of  $\phi < 0.3$ – $0.4$ , further detailed remeasurements for the crystal sizes are required. Together with the additionally gained data points, a connectivity with curve A will become clearer.

As stated in the introduction section, on the other hand, there is another unsettled issue attempting to explain the anomalous behavior of melting point depression for networks which are chemically cross-linked enough.<sup>5,10–12,28,37,38</sup> Jackson–McKenna<sup>5</sup> have also made clearer that the melting point depression of NR–benzene systems of  $M_c \sim 3000$  cannot be described by the FH relationship. It is still unclear at or around what value of  $M_c$  this relationship starts breaking down. Our analysis by eq 18 will become helpful to systems of the critical  $M_c$  or more, while in the more highly cross-linked case the entanglement effect should not be considered on systems swollen in solvent, as suggested by McKenna.<sup>39</sup> And to explain the swelling behavior of such systems, particular attention has been paid to their network elasticity and cross-linking density dependent  $\chi$  and many analyses have been made by seeing applicability of the Frenkel–Flory–Rehner (FFR) hypothesis, i.e., of the additivity (or separability) of free energy terms by mixing and by dry rubber elasticity.<sup>5,29,30,32,33,40–43</sup> With these studies, subsequent further ones will elucidate such melting point anomalous depression issue and also the entanglement effects on systems cross-linked in solutions will be an important subject in this area of study.<sup>39</sup>

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