

Lattice model of living polymerization. II. Interplay between polymerization and phase stability

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Representative spinodal curves and polymerization lines for the equilibrium polymerization of linear polymers in a solvent have been calculated using a Flory–Huggins-type mean-field theory. The calculations are primarily restricted to systems that polymerize upon cooling, but examples are also given for systems that polymerize upon heating. In the former case, we find that an increase in the magnitude of enthalpy of propagation $|\Delta h|$ (“sticking energy”) leads to an elevation of the critical temperature T_c and to a decrease of the critical composition ϕ_c when $|\Delta h|$ exceeds a critical value $|\Delta h_c|$. The shifts in the critical temperature and composition, $\Delta T_c \equiv T_c(\Delta h) - T_c(\Delta h = 0)$ and $\Delta \phi_c \equiv \phi_c(\Delta h) - \phi_c(\Delta h = 0)$, vary linearly with Δh for $|\Delta h| > |\Delta h_c|$ over a large range of sticking energies $|\Delta h|$, so that ΔT_c is proportional to $\Delta \phi_c$ for a sufficiently large sticking energy. Variations in the phase boundaries with Δh are also evaluated for systems that polymerize upon heating, but the presence of *multiple* critical points in this case renders a general description of these changes difficult. The polymerization line is found to be *independent* of solvent quality (χ interaction parameter) within the simple Flory–Huggins model, but the phase stability is strongly influenced by the magnitude of both χ and Δh . Similarities between living polymers and other types of associating polymers (thermally reversible gels, micelles) suggest that some of the thermodynamic consequences of particle association in these self-assembling systems are insensitive to the detailed nature of the clustering process. Thus, our results may have a much broader range of applicability than living polymer solutions (e.g., gelation in clay and other colloidal suspensions, polyelectrolyte solutions, cell aggregation, and self-organization of biologically significant structures that exist at equilibrium). © 2000 American Institute of Physics. [S0021-9606(00)50102-0]

I. INTRODUCTION

The tendency for particles to aggregate (“self-assemble”) into clusters under equilibrium conditions has many implications for understanding the phase stability, scattering, and transport properties of self-associating liquids. Attractive interactions that are large relative to thermal energies and that lead to particle association can be expected to strongly influence the phase stability of these particle dispersions. In particular, the shape of the resulting phase diagrams should be affected by the relative positions of two characteristic temperatures, the temperature T_p at which clustering initiates (the temperature of thermally reversible gelation, polymerization, micellization, etc.) and the “bare” critical temperature for phase separation $T_{c,o}$ of the same system in the absence of associative interactions. (We specialize our discussion mainly to the case where phase separation and polymerization occur upon cooling.) If T_p significantly exceeds $T_{c,o}$ and leads to the formation of diffuse “polymerlike” clusters, then the phase diagram is anticipated to be distorted into the highly asymmetric form normally found for high molecular weight polymer solutions. On the other hand, the phase diagram should be more like that for the monomer/solvent system if T_p lies well below $T_{c,o}$ since in this case little association exists near the critical

temperature T_c of the associating fluid. These simple considerations indicate that associative interactions can cause, depending on their strength, large changes in miscibility (T_c) and can grossly influence the shape of the phase diagram for living polymers and other systems where equilibrium particle association occurs. We anticipate that certain aspects of the thermodynamics of associating polymers should be *insensitive* to the mode of association, and this invites comparison between the different types of self-assembling systems (thermoreversible gels, equilibrium living polymers, micelles).

The present paper considers, perhaps, the simplest example of a self-associating fluid, the equilibrium association of difunctional monomers into polymer chains. Chain growth is facilitated by an *initiator* that reacts with the monomer to form “living” polymer chains with a distribution of lengths governed by the condition of equilibrium.^{1,2} The present discussion primarily restricts attention to living polymers for which the enthalpy and entropy of chain propagation are both negative, so that polymerization occurs below a “ceiling temperature” (see Refs. 2 and 3 for review). Many systems [e.g., poly(α -methylstyrene) in methylcyclohexane or tetrahydrofuran] exhibit living polymerization of this kind.^{2,3} The polymerization temperature depends on the initial monomer concentration, and the monomers associate into poly-

mers as the temperature is lowered below a line representing the monomer concentration dependence of the polymerization temperature.^{2,3} Under equilibrium conditions the polymers revert to their monomeric form when the temperature is returned above the polymerization temperature line (albeit slowly, so that the observed transition temperature depends on the rate of temperature change as in glass forming liquids) and the system displays physical aging as it approaches equilibrium.

The polymerization transition clearly bears some resemblance to a critical phenomenon,⁴ and this connection can be established formally in the limit of a vanishing initiator concentration. The existence of a nonzero initiator concentration r plays the role of an external field in spin models of equilibrium polymerization.^{4,5} This fieldlike variable “rounds” (strictly speaking, eliminates) the second order phase transition. Nevertheless, the polymerization “transition” for $r > 0$ can bear some resemblance to a second-order phase transition when the initiator concentration is “very small” (see Paper I). One beneficial aspect of the presence of initiator is that its presence diminishes fluctuations and thereby implies that the application of mean-field theory to the description of polymerization should be especially accurate, regardless of the temperature range. Excluded volume interactions are not treated correctly by a mean-field lattice model, however, and deviations due to excluded volume interactions become important in good solvents when the chains are long and the total polymer concentration is low.

Our microscopic model of living polymerization also incorporates nearest-neighbor monomer–monomer (as well as monomer–solvent and solvent–solvent) interactions which allow us to study the interplay between the polymerization and phase separation. Notably, phase separation in our reversible equilibrium polymer/monomer/solvent system is likewise described by a mean-field lattice approximation. Hence, additional clustering processes associated with the phase separation are neglected.⁶ This leads to some inaccuracy in the estimation of the critical temperature and of other thermodynamic properties in the vicinity of the critical point. Despite the mean-field approximation, our model of phase separation in living polymer solutions provides many interesting insights into the coupling between particle association and phase separation.

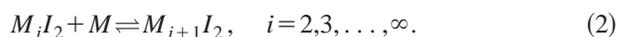
Apart from the theoretical motivations for studying living polymerization summarized in our previous paper (Paper I), we emphasize that “associating polymers” have a wide range of practical applications in material science^{7–10} (foods and food processing, fluid “thickeners,” cosmetics, enhanced oil recovery, floor coverings and other coatings, drug reducing agents, etc.) and in the formation and function of numerous biological systems^{11–18} (cellular movement, the action of muscles, transport processes within cells, mechanical properties of the cell as a whole, self-organization of numerous types of biological structures, disease and biotechnology processing applications associated with protein aggregation,¹⁹ etc.). Given the practical importance of associating polymers, it seems surprising to us that quantitative scientific investigations of living polymers and other associating polymer systems have been so limited. There exist

many studies involving associating polymers, of course, but they are usually phenomenological, or are oriented towards engineering applications or towards the chemistry of these systems. The work of Greer *et al.*^{2,3} is notable for its attempt to fill this gap in the case of living polymerization. On the theoretical side, we mention the recent simulations by Kumar and Panagiotopoulos²⁰ and the theoretical contributions of Coniglio *et al.*^{21,22} and Tanaka and Stockmayer²³ in modeling thermally reversible gelation. There has also been notable progress in modeling and simulating micelle formation.^{24–27} An appreciation of the similarities between different kinds of associating polymer systems has developed only rather recently.^{1,20}

The present paper avoids the simple adjustment of the χ parameter solely to “fit the data,” but rather focuses on *qualitative trends* in the miscibility of living polymer solutions that are associated with the variation of the sticking energy and the mean-field theory interparticle interaction χ . These general trends are derived from the Flory-type lattice model and should be robust in comparison with experiment, at least at a qualitative level. Quantitative comparison of our lattice model calculations to measurements on living polymer solution phase separation²⁸ is deferred until the development of an improved lattice model of living polymerization, incorporating fluid compressibility, monomer and solvent structures, and correlations associated with chain connectivity. The simple Flory-type model of the phase separation of living polymer solutions is considered in some detail in the next section, while the subsequent section describes the intricate interplay between self-association and phase separation.

II. MODEL AND GENERAL THEORY

Initially, the unreacted system is composed of n_s solvent molecules, n_m^0 monomers of species M , and n_I molecules of the initiator which activates the monomers and thereby enables them to propagate into polymers. We assume that polymerization occurs under conditions of chemical equilibrium and that the smallest propagating species is a bifunctional dimer M_2I_2 involving two molecules of the initiator I (see Paper I and references therein),



The equilibrium system contains no free initiator, but only unreacted monomers M , polymers M_iI_2 , ($i = 2, 3, \dots, \infty$), and solvent molecules, with numbers n_m , $\{n_i\}$, and n_s , respectively. This equilibrium system is described by a minimal incompressible Flory–Huggins lattice model with N_l total lattice sites and with a single site occupancy constraint for the individual monomers of all polymers and for both solvent and initiator molecules. As shown¹ in Paper I, after imposition of the equilibrium constraint, the Helmholtz free energy F for the equilibrium system reduces to the form,

$$\begin{aligned} \frac{F}{N_1 k_B T} = & (1 - \phi_m^0 - \phi_I) \ln(1 - \phi_m^0 - \phi_I) + \phi_m \ln \phi_m \\ & + \phi_m(1 - \phi_m^0 - \phi_I)\chi + \frac{\phi_I}{2(1-A)} \\ & \times \left[(1-A) \ln \frac{\phi_I(1-A)}{z} + A \ln A - (2-A) \right. \\ & \times \ln J + \chi(1 - \phi_m^0 - \phi_I)(4 - 3A) + \frac{\Delta f}{k_B T} \\ & \left. + 3 - 2A \right], \end{aligned} \quad (3)$$

where the concentration $\phi_m = n_m/N_1$ of unreacted monomers is evaluated as

$$\phi_m = \frac{B - \sqrt{B^2 - 4(\phi_m^0 - \phi_I)G}}{2G}, \quad (4)$$

with the parameters,

$$\begin{aligned} B & \equiv 1 + (\phi_m^0 - \phi_I/2)G, \quad G \equiv \exp(-\Delta f/k_B T)J, \\ J & \equiv [1 + (z-2)\exp(-\epsilon/k_B T)], \end{aligned} \quad (5)$$

explicit functions of the temperature T , initial monomer concentration $\phi_m^0 = n_m^0/N_1$, initiator concentration $\phi_I = n_I/N_1 \equiv r\phi_m^0$, and the free energy Δf of the polymerization reaction in Eq. (2). The parameter $r = \phi_I/\phi_m^0$ plays the role of the dimensionless initiator composition, and k_B designates Boltzmann's constant. As explained in Paper I,¹ the dependence of ϕ_m and F on the "bending" energy ϵ (i.e., the energy difference between *gauche* and *trans* polymer conformations) is contained in the factor $\ln J$ which varies almost linearly with inverse temperature (over the temperature ranges of interest), leading simply to a renormalization of the free energy Δf . (Thus, the factor J is dropped, and the value of $\Delta f \approx \Delta g$ is taken from the earlier works that ignore polymer chain semiflexibility.) The quantity $A(T, \phi_m^0, \phi_I, \Delta f)$ of Eq. (3) is given by

$$A \equiv \phi_m \exp(-\Delta f/k_B T)J, \quad (6)$$

while the monomer-solvent interaction parameter χ ,

$$\chi = \frac{z}{2k_B T} (\epsilon_{mm} + \epsilon_{ss} - 2\epsilon_{sm}) \quad (7)$$

is defined in terms of nearest neighbor van der Waals attractive monomer-monomer, solvent-solvent, and solvent-monomer interaction energies $\{\epsilon_{ij}\}$. The lattice coordination number z in Eq. (7) plays the role of a proportionality factor between χ and $\{\epsilon_{ij}\}$.

Equations (3)–(6) indicate that the living polymerization solution formally has the same number of independent composition variables (ϕ_m^0, ϕ_I) as a compressible binary polymer blend with two independent volume fractions (ϕ_1, ϕ_2). This formal analogy implies that the existence of a stable (or metastable) homogeneous phase, therefore, requires the stability conditions,

$$\left. \frac{\partial^2 F}{\partial \phi_m^0{}^2} \right|_{N_1, T, \phi_I} > 0, \quad \left. \frac{\partial^2 F}{\partial \phi_I^2} \right|_{N_1, T, \phi_m^0} > 0, \quad (8)$$

and

$$\left. \frac{\partial^2 F}{\partial \phi_m^0{}^2} \right|_{N_1, T, \phi_I} \left. \frac{\partial^2 F}{\partial \phi_I^2} \right|_{N_1, T, \phi_m^0} - \left[\left. \frac{\partial^2 F}{\partial \phi_m^0 \partial \phi_I} \right|_{N_1, T} \right]^2 > 0, \quad (9)$$

where the Helmholtz free energy F is specified by Eq. (3). Equating the left-hand side of the inequality (9) to zero produces the constant volume spinodal curves $T = T(\phi_m^0)$ for given r and Δf . The second derivatives of the free energy F with respect of ϕ_I and ϕ_m^0 can be calculated analytically, but these expressions are lengthy and are therefore not presented here. The critical point is characterized²⁹ by the following equations:

$$\left. \frac{\partial^2 F}{\partial \phi_m^0{}^2} \right|_{N_1, T, \phi_I} \left. \frac{\partial^2 F}{\partial \phi_I^2} \right|_{N_1, T, \phi_m^0} - \left[\left. \frac{\partial^2 F}{\partial \phi_m^0 \partial \phi_I} \right|_{N_1, T} \right]^2 = 0, \quad (10)$$

and

$$\begin{aligned} \left. \frac{\partial^3 F}{\partial \phi_m^0{}^3} \right|_{N_1, T, \phi_I} + \left. \frac{\partial^3 F}{\partial \phi_m^0 \partial \phi_I^2} \right|_{N_1, T} \left(\frac{\mu_{12}}{\mu_{22}} \right)^2 - 2 \left. \frac{\partial^3 F}{\partial \phi_m^0{}^2 \partial \phi_I} \right|_{N_1, T} \left(\frac{\mu_{12}}{\mu_{22}} \right) \\ = 0, \end{aligned} \quad (11)$$

with

$$\mu_{12} \equiv \left. \frac{\partial^2 F}{\partial \phi_m^0 \partial \phi_I} \right|_{N_1, T}, \quad \mu_{22} \equiv \left. \frac{\partial^2 F}{\partial \phi_I^2} \right|_{N_1, T, \phi_m^0}, \quad (12)$$

and again all quantities may be obtained analytically. Equations (10)–(12) correspond to Eqs. (16.70) in Ref. 29, derived by Gibbs for constant pressure systems. The slight differences between Eqs. (10)–(12) and (16.70) of Ref. 29 arise from the fact that our system is an incompressible, constant volume mixture.

Another important transition curve characterizing the stability of living polymer solutions is the polymerization line $T_p = T_p(\phi_m^0)$. As described in Paper I, we define the polymerization temperature as the temperature at which the specific heat C_p ,

$$C_p \approx C_v = -k_B T^2 \left. \frac{\partial^2 [F/k_B T]}{\partial T^2} \right|_{N_1, \phi_m^0, \phi_I}, \quad (13)$$

has a maximum. When $r=0$, the above definition coincides with the usual Dainton and Ivin expression,³⁰

$$T_p^{(o)} = \frac{\Delta h}{\Delta s + k_B \ln \phi_m^0}, \quad (14)$$

where Δh and Δs denote, respectively, the enthalpy and the entropy of the polymerization reaction in Eq. (2). The super-

script (*o*) emphasizes that this result applies to the idealized limit of $r \rightarrow 0$, and more generally we find that T_p (maximum in specific heat) depends on r (see Paper I). We refer to $T_p^{(o)}$ as the “ideal polymerization temperature.” For systems that polymerize upon cooling, the monomers remain largely unpolymerized above T_p , and significant polymerization occurs for $T \leq T_p$. The reverse situation exists for systems that polymerize upon heating. It is convenient also to define the “absolute polymerization temperature” T_p^* by the limiting value of T_p for $\phi_m^0 \rightarrow 1$. For systems that polymerize upon cooling, T_p^* is an upper bound on the polymerization temperature T_p .

III. PHASE STABILITY OF LIVING POLYMER SOLUTIONS

We begin the analysis by probing the influence of variations in the enthalpy Δh of chain propagation on the phase separation (spinodal curve) of a living polymer solution when the entropy of polymerization Δs and the monomer-solvent interaction parameter $\chi = c/T$ are fixed as $\Delta s = -105 \text{ J/(mol K)}$ and $c = 301.93 \text{ K}$, respectively. The enthalpy Δh is chosen to be negative unless otherwise specified, so that polymerization occurs upon cooling. The lattice coordination number z is taken as $z = 6$, appropriate to a cubic lattice in three dimensions, and the stiffness factor J is set to unity since the contributions from stiffness are subsumed into Δs and Δh . The dimensionless initiator concentration $r = \phi_1/\phi_m^0$ is assumed to be 0.0044 as in the experiments of Greer *et al.* for the living poly(α -methylstyrene) system in methylcyclohexane (or tetrahydrofuran) with sodium naphthalide as the initiator.^{3,31} The living polymerization parameters correspond to those measured for poly(α -methylstyrene) except that the Δh is treated as a variable. The experimental value of Δh for poly(α -methylstyrene) is $\Delta h = -35 \text{ kJ/mol}$.³²

Figure 1 displays the spinodal curves (solid lines) and polymerization lines (dotted lines) for various values of Δh , and the critical points are indicated by \times 's. (The calculation of the critical point is described in the previous section.) We observe that an increase in the magnitude of the “sticking energy” $|\Delta h|$ causes a substantial shift of the critical temperature T_c and critical composition ϕ_c , relative to the critical temperature $T_{c,o}$ and critical composition $\phi_{c,o}$ of the mixture in the absence of a sticking interaction [$T_c(\Delta h = 0) \equiv T_{c,o}$, and $\phi_c(\Delta h = 0) \equiv \phi_{c,o}$]. Interestingly, there is no shift of the critical temperature unless Δh exceeds a critical value $\Delta h_c \approx -16 \text{ kJ/mol}$. The shift of the critical point with Δh is quantified in Figs. 2(a) and 2(b). The changes ΔT_c and $\Delta \phi_c$ in T_c and ϕ_c , respectively, are defined as,

$$\Delta T_c = T_c(\Delta h) - T_c(\Delta h = 0), \quad (15)$$

$$\Delta \phi_c = \phi_c(\Delta h) - \phi_c(\Delta h = 0). \quad (16)$$

These shifts are nearly linear in Δh for $|\Delta h| > |\Delta h_c| = 16 \text{ kJ/mol}$. The critical point for $|\Delta h| < |\Delta h_c|$ occurs for $\phi_c \approx 1/2$, appropriate to a symmetric fluid binary mixture when the sticking energy is sufficiently weak, i.e., when $|\Delta h| < |\Delta h_c| = 16 \text{ kJ/mol}$. We observe that the critical composition ϕ_c appears to jump to a value larger than 1/2 for $|\Delta h|$

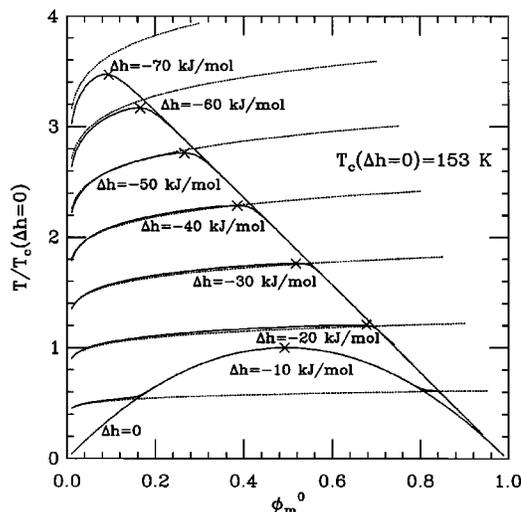


FIG. 1. Influence of sticking energy Δh on the phase boundary of living polymer solutions. Dotted lines denote polymerization (“ceiling”) temperature lines, and solid lines indicate spinodal curves. The \times 's mark the positions of the critical points. The monomer-solvent interaction parameter is $\chi = 302/T$, while all the other model parameters have been fixed as the values determined for poly(α -methylstyrene) except for the sticking energy Δh which is varied from 0 to -70 kJ/mol . The phase diagram is symmetric and unchanged by variation of Δh for small sticking energies, whereas a strong sticking energy makes the polymerization line rise to higher temperatures and causes the phase diagram to become increasingly asymmetric. The temperature scale is normalized by the critical temperature $T_c(\Delta h = 0)$ of the system in the absence of particle sticking. The line of polymerization temperatures intersects the critical point for phase separation when $\Delta h \approx -30 \text{ kJ/mol}$.

$>16 \text{ kJ/mol}$ and then decreases back towards zero as the magnitude of Δh increases. The critical sticking energy $|\Delta h_c| \approx 16 \text{ kJ/mol}$ is the sticking energy for which the “absolute polymerization temperature” $T_p(\phi_m^0 \rightarrow 1) = T_p^*$ becomes equal to the critical temperature $T_{c,o}$ in the absence of polymerization. If polymerization occurs above $T_{c,o}$, then the critical temperature is shifted upward. On the other hand, if it occurs below $T_{c,o}$, then the critical point is unaffected by the polymerization. The relative positions of $T_{c,o}$ and T_p^* can be adjusted experimentally through the choice of solvents, since T_p should be rather insensitive to solvent quality, while $T_{c,o}$ is evidently highly dependent on χ . Further physical interpretation of Δh_c emerges in the $r \rightarrow 0$ limit, where $T_p^*(r \rightarrow 0) = \Delta h/\Delta s$ and $T_{c,o}(r \rightarrow 0) = c/2$ with c denoting the coefficient in the temperature dependence of $\chi = c/T$. Equality of these two temperatures leads to the interesting result,

$$\Delta h_c(r \rightarrow 0) = (1/2)c \Delta s, \quad (17)$$

which demonstrates that the critical enthalpy of polymerization in the limit of a vanishing initiator concentration is completely determined by two quantities: the entropy of polymerization and the interaction parameter $\chi = c/T$. Taking the values $\Delta s = -105 \text{ J/(mol K)}$ and $c = 301.93 \text{ K}$ employed in Fig. 1 produces $\Delta h_c(r \rightarrow 0) = -15.9 \text{ kJ/mol}$ which agrees extremely well with our estimation of $\Delta h_c \approx -16 \text{ kJ/mol}$ for $r = 0.0044$ as deduced from Figs. 2(a) and 2(b).

Previous studies of fluid mixtures indicate that both T_c and ϕ_c change in a response to a variety of applied

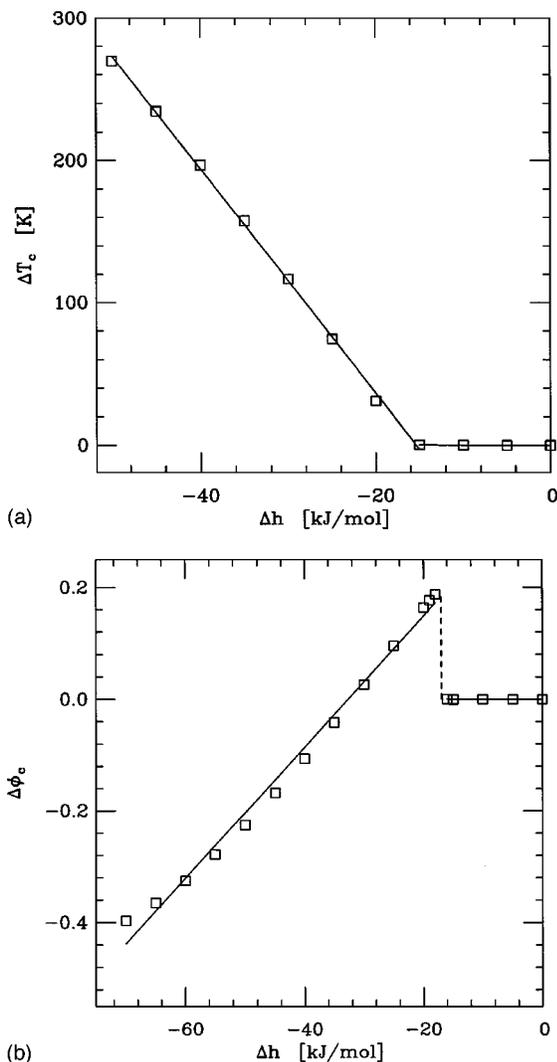


FIG. 2. (a) The shift of the critical temperature $\Delta T_c \equiv T_c - T_c(\Delta h = 0)$ as a function of sticking energy Δh . The critical point data correspond to the \times 's shown in Fig. 1. No change in the critical temperature occurs for $|\Delta h| < 16$ kJ/mol. A shift in the critical temperature appears when the "absolute polymerization temperature" $T_p^* \equiv T_p(\phi_m^0 \rightarrow 1)$ exceeds the "bare" critical temperature $T_{c,o}$ (i.e., the T_c in the absence of the sticking interaction). (b) The shift of the critical composition $\Delta \phi_c \equiv \phi_c - \phi_c(\Delta h = 0)$ as a function of sticking energy Δh . The critical point data correspond to the \times 's shown in Fig. 1. The shift $\Delta \phi_c$ also changes sharply for $|\Delta h| = |\Delta h_c| \approx 16$ kJ/mol. When $|\Delta h|$ exceeds 100 kJ/mol, both T_c and $\Delta \phi_c$ saturate to constant values.

perturbations.^{33,34} For example, Voronel and Giterman³⁴ have calculated the shifts ΔT_c and $\Delta \phi_c$ for fluid mixtures in an applied electric field and have found that both ΔT_c and $\Delta \phi_c$ are linear functions of the electric field energy and that ΔT_c is proportional to $\Delta \phi_c$. Jacobs³³ has suggested that a proportionality between ΔT_c and $\Delta \phi_c$ should hold for fluid mixtures subject to a variety of "perturbations." Our LCT calculations³⁵ for polymer blends diluted by a diblock copolymer demonstrate, however, that this type of relation between ΔT_c and $\Delta \phi_c$ is limited to symmetric diblock copolymer additives (Jacobs treats additives as a particular type of "perturbation"), so that the proportionality between ΔT_c and $\Delta \phi_c$ is not universal. However, the linear relation between ΔT_c and $\Delta \phi_c$ seems to hold commonly and we exam-

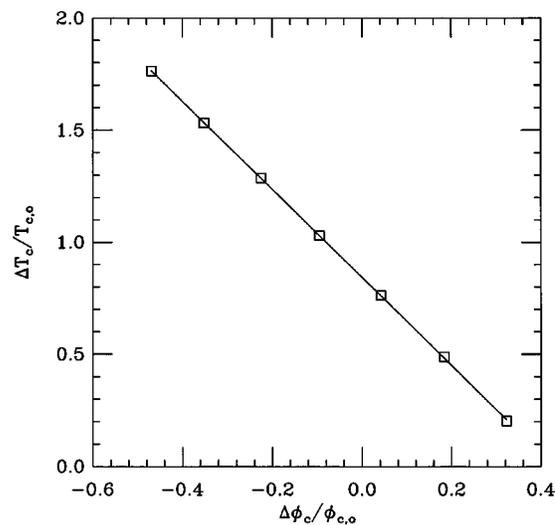


FIG. 3. The shift of the reduced critical temperature $\Delta T_c/T_c(\Delta h = 0)$ from Fig. 2(a) vs the shift of the reduced critical composition $\Delta \phi_c/\phi_c(\Delta h = 0)$ from Fig. 2(b). The shifts in the critical temperature and composition are normalized by dividing ΔT_c and $\Delta \phi_c$ by the corresponding critical parameter of the system without the "sticking" interactions (i.e., with $\Delta h = 0$). The slope is expected to be dependent on the strength c of the monomer-solvent interaction ($\chi = c/T$).

ine this possibility here. Figure 3 displays the variation of ΔT_c with $\Delta \phi_c$ for the living polymerization data in Figs. 2(a) and 2(b). A simple linear scaling,

$$\Delta T_c/T_{c,o} \approx (-2)\Delta \phi_c/\phi_{c,o} \quad (18)$$

describes the living polymerization data surprisingly well. (The constant of proportionality should more generally depend on the enthalpy and entropy of polymerization.) We conclude that sticking energy appears to exert a similar influence on the phase boundary as an applied field of some kind. This finding deserves further theoretical and experimental investigation.

The influence of monomer-solvent interactions on the phase diagram of living polymer solutions is illustrated in Fig. 4. The simple Flory approximation to the lattice model makes no allowance for the details of chain connectivity and monomer structures and predicts that the interaction parameter χ is a purely enthalpic quantity, i.e., $\chi = c/T$. The parameter $c = (z/2k_B)(\epsilon_{mm} + \epsilon_{ss} - 2\epsilon_{ms})$ represents the "strength" of the effective van der Waals interaction [see Eq. (7)]. (More generally, it is possible to derive an explicit "entropic" contribution to χ within a more general lattice cluster theory,^{36,37} see discussion.) The remaining parameters are chosen as $\Delta h = -35$ kJ/mol, $\Delta s = -105$ J/(mol K), and $r = 0.0044$ based on the experimental estimates by Greer *et al.*^{3,31} for poly(α -methylstyrene). A higher value of c implies that the effective interaction parameter has a stronger temperature dependence. Figure 4 demonstrates that a larger c , of course, leads to an increase of the critical temperature T_c and to a more symmetric phase diagram. The dotted line in Fig. 4 depicts the "ideal polymerization line" $T_p^{(o)}(\phi_m^0)$ [see Eq. (14)], and the dashed line denotes the polymerization line $T_p(\phi_m^0)$ (for $r = 0.0044$) corresponding to the occurrence of a maximum in the specific heat. Notably, the

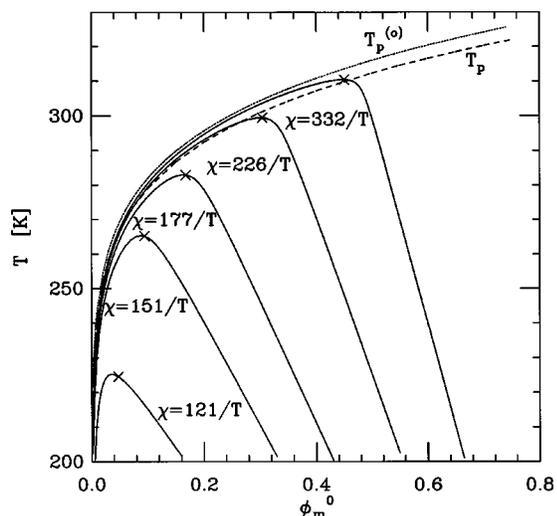


FIG. 4. Influence of the effective monomer-solvent interaction $\chi = c/T$ on the phase boundary of living polymer solutions (solid lines). The critical points are denoted by \times 's. The dashed and dotted lines indicate the true and ideal polymerization lines $T_p = T_p(\phi_m^0)$ and $T_p^{(o)} = T_p^{(o)}(\phi_m^0)$, respectively. The living polymerization model parameters are taken as $\Delta h = -35$ kJ/mol, $\Delta s = -105$ kJ/(mol K), and $r = 0.0044$. Phase separation is apparently suppressed if the monomer-monomer interaction is made too weak ($c < 60$ K). Recent simulations indicate that living polymer type structures form in dipolar particle gases (Ref. 57) and that condensation into a liquid is suppressed in these systems when the dispersive energy (i.e., c in the present paper) is below a threshold value (Ref. 58).

polymerization lines $T_p^{(o)}(\phi_m^0)$ and $T_p(\phi_m^0)$ are independent of χ , so the polymerization transition temperature remains unchanged for all five systems presented in Fig. 4. For small c , the difference $\delta T = T_p - T_c$ is positive, but quickly diminishes with growing c , and finally changes its sign at the point where T_c exceeds T_p . (This defines a critical value of the interparticle interaction χ .) The ideal polymerization line $T_p^{(o)}(\phi_m^0)$ represents an envelope curve which the spinodal curves increasingly approach with growing c . The deviation between the spinodal curve and the polymerization line becomes increasingly large as the monomer-solvent interaction weakens (i.e., c decreases). It is not possible for us to determine a critical point for phase separation when c becomes less than a critical value $c_{\text{crit}} \approx 60$ K because numerical instabilities appear for low temperatures and render the exact determination of c_{crit} difficult. (The particular critical value $c_{\text{crit}} \approx 60$ K depends on the enthalpy and entropy of polymerization.) However, it appears that the interparticle sticking eventually *overwhelms* phase separation if the effective monomer-solvent interaction is sufficiently weak. The strong modification of miscibility by interparticle interactions (see Fig. 4) is contrasted by the *insensitivity* of the polymerization line to the interaction parameter χ . Thus, the coupling of the polymerization and phase separation processes is then quite asymmetric between the relatively large value of the “sticking energy” Δh driving polymerization and the rather small monomer-solvent interaction parameter χ inducing phase separation. A similar asymmetry has recently been found by Guerin and Szeifer³⁸ for micelle forming systems.

The above discussion is restricted to living polymer so-

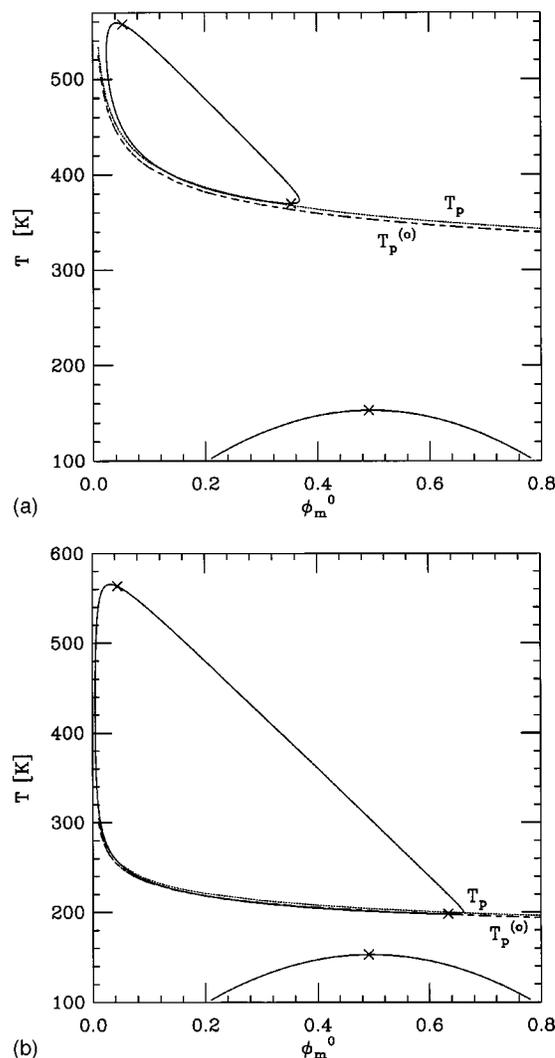


FIG. 5. (a) Illustrative example for phase boundaries of living polymer solutions that polymerize upon heating. The critical points are denoted by \times 's. The dotted and dashed lines indicate the true and ideal polymerization lines $T_p = T_p(\phi_m^0)$ and $T_p^{(o)} = T_p^{(o)}(\phi_m^0)$, respectively. The living polymerization model parameters are taken as $\Delta h = 35$ kJ/mol, $\Delta s = 105$ kJ/(mol K), $\chi = 302/T$, and $r = 0.0044$. The above values are identical to those employed in Fig. 1, except that both the enthalpy and entropy of polymerization are positive. (b) Another example of phase boundaries for living polymer solutions that polymerize upon heating. All parameters are the same as in (a) except that the sticking energy Δh is now smaller ($\Delta h = 20$ kJ/mol). This reduction in Δh leads to a substantial decrease in miscibility.

lutions that polymerize upon cooling. We expect rather different behavior when polymerization proceeds upon heating since the extent of particle clustering due to polymerization diminishes as the temperature is lowered, while particle clustering due to interparticle interaction tends to increase upon cooling if χ is still treated as a purely enthalpic quantity and is positive. Figure 5(a) displays a representative phase diagram for this complex situation where the phase separation and polymerization transition are competing with each other. The example of Fig. 5(a) is generated for $\chi = 302/T$, $r = 0.0044$, $|\Delta h| = 35$ kJ/mol, and $|\Delta s| = 105$ kJ/(mol K) as in Fig. 1, but both Δh and Δs are taken now as positive. The ideal polymerization line $T_p^{(o)}(\phi_m^0)$ and the polymerization line $T_p(\phi_m^0)$ are very close as in Fig. 4, but the polymeriza-

tion temperature now *decreases* with the monomer concentration ϕ_m^0 . (Compare with the observed polymerization line of rabbit muscle G-actin in a salt solution.)³⁹ The upper critical solution temperature point [denoted by \times at the bottom of Fig. 5(a)] is apparently unchanged from the case of $\Delta h = 0$ where no polymerization occurs, but a new “moon-shaped” window of immiscibility, which “hugs” the polymerization line $T_p(\phi_m^0)$ over a wide range of ϕ_m^0 , opens up in this *incompressible* fluid. The immiscibility window has two critical points that are indicated by the \times 's in the figure. Decreasing Δh leads to a lowering of the polymerization line, and Fig. 5(b) presents the phase diagram corresponding to $\Delta h = 20$ kJ/mol. The size of the moon-shaped region increases as Δh is diminished, and its lower critical temperature decreases significantly as well. The moon shaped region disappears entirely when Δh is sufficiently large. The critical value of Δh for the vanishing of this close loop phase diagram is on the order of 40 kJ/mol for the polymerization parameters specified above. Thus, an increase of the magnitude of the sticking energy Δh leads to *enhanced* miscibility of the living polymer solution (and finally to the disappearance of this immiscibility window). We then find that the intuitive view that particle sticking induces a diminished phase stability is not generally correct. Moreover, the competition between particle sticking (polymerization) and phase separation can produce a variety of other types of phase diagrams,^{40,41} and we presently find no organizing principle for characterizing the different types of phase diagrams which can occur when clustering upon heating competes with phase separation upon cooling. Scott⁴⁰ and Wheeler and co-workers^{41,42} present further discussion of the phase diagrams arising for systems that polymerize upon heating.

The equivalence of the living polymerization (for $r \rightarrow 0^+$) to the $m \rightarrow 0$ limit of the $O(m)$ spin model of phase transitions^{5,43} further implies that the mean-field model discussed here is relevant to describing a wide range of other phase transitions within mean-field theory. This situation arises because the order parameter dimension is largely unimportant in mean-field theory. Thus, we can understand why the phase diagram of living polymers in solution is similar to that of diluted Ising or Heisenberg magnets (order parameter dimensions $m = 1$ and 3 , respectively) and of mixtures of ^3He – ^4He ($m = 2$).⁴¹

IV. DISCUSSION

Our calculations exhibit a strong coupling between polymerization and phase separation in living polymer solutions. Very large shifts occur in the upper critical solution temperature as the enthalpy of polymerization Δh (“sticking energy”) varies over a substantial range. The Flory–Huggins χ parameter is taken as a purely enthalpic quantity, consistent with the simple Flory model. When polymerization proceeds upon cooling, the shift $\Delta T_c \equiv T_c(\Delta h) - T_c(\Delta h = 0)$ of the critical temperature $T_c(\Delta h)$, relative to the critical temperature $T_c(\Delta h = 0)$ in the absence of polymerization, is nearly linear in Δh for $|\Delta h| > |\Delta h_c|$ over a large range, but ΔT_c becomes *insensitive* to the sticking energy when $|\Delta h|$ is smaller than a critical value $|\Delta h_c| \approx 16$ kJ/mol for poly

(α -methylstyrene). The critical initial monomer composition $(\phi_m^0)_c$ approaches zero with increasing $|\Delta h|$, but drops abruptly to $1/2$ for $|\Delta h|$ below $|\Delta h_c|$. Thus, the shift ΔT_c in the critical temperature is directly correlated with the shift $\Delta \phi_c$ of the critical composition. Similar shifts have been predicted for fluid mixtures in applied electric fields and under other conditions (e.g., dilution of mixtures by solvents).^{34,35} The polymerization temperature T_p [at which the specific heat $C_p(T)$ exhibits a maximum] saturates to a constant temperature at large initial monomer concentration ϕ_m^0 , and the intersection point between the polymerization line and the spinodal curve switches from the monomer rich to the polymer rich branches of the spinodal curve when $|\Delta h|$ is somewhat larger than the $|\Delta h_c|$ value mentioned above. An increase of the interaction parameter χ (with Δh and r fixed) induces the monomer rich branch of the spinodal curve to approach the polymerization line over a large ϕ_m^0 concentration range. (We take $\chi = c/T$ where the parameter c defines the effective “strength” of the monomer-monomer interaction.) Phase separation apparently *ceases to exist* in the living polymer solution if c becomes too small.

The coupling between phase separation and particle clustering found both experimentally and theoretically for living polymer solutions appears to be quite similar to observations⁴⁴ and previous mean-field calculations^{21,38,45} for other types of associating polymers. For example, gelation measurements for atactic polystyrene in various solvents have been interpreted in terms of a “critical gelation concentration”^{44,46} below which gelation does not occur. This “gelation line” has a similar dependence on polymer concentration (the analog of the initial monomer concentration) as the dependence of the critical polymer concentration of living polymer solutions on ϕ_m^0 . The gelation line is often found to intersect the phase separation binodal near the critical point for liquid–liquid phase separation.⁴⁴ Notably, the gelation curves exhibit a sensitivity to solvent *type*, and some sensitivity of the polymerization temperature to solvent has also been observed.^{47,48} We likewise expect the solvent type to exert a small influence on the polymerization line of living polymers⁴⁰ through, for example, an “entropic” contribution to the interaction parameter $\chi = b + c/T$ (i.e., through the parameter b). The emergence of the “entropic” contribution to χ can be understood within the lattice model by incorporating short range correlations, arising from monomer and solvent structures and chain connectivity, into the lattice model of living polymers.³⁶ Models of this kind will be developed in subsequent work.

Similarities also exist between the thermodynamics of living polymerization and other self-organizing processes in which aggregates arise from particle association. The formation of spherical micelles in solution provides a good example of this type of “organized aggregation” in which relatively ordered structures form through particle association. Comparison of the phase stability of micelle forming liquids to living polymerization and thermally reversible gelation also displays many common features. The phase diagrams of micelle forming liquids tend to be highly asymmetric because of particle association into aggregates,^{25,49} and thermally reversible gelation in associating polymers leads to

increasingly asymmetric phase diagrams at elevated sticking energies.²⁰ Moreover, nonionic surfactants (monomers) in water tend to exhibit closed loop immiscibility gaps²⁵ similar to systems that form living polymers upon heating. The similarities between these associating particle systems are especially clear in Flory-type lattice model descriptions since the geometrical form of the aggregates is entirely neglected in calculating the entropy of mixing of the aggregates within this simple model. It is encouraging that the phase separation phenomenology of *real* associating polymer systems (living linear polymers, thermally reversible gels, micelle solutions) exhibits such common features, suggesting that the Flory-type lattice model correctly captures the zeroth order physics of these associating polymer systems. We may then anticipate that many generic phase separation properties of living polymer solutions, illustrated in the present paper, also have relevance for other types of associating systems—associating colloid particles in solution,^{50–53} biologically relevant structures formed through aggregation, protein aggregation, etc., although specific details may differ. Apparently associating polymers and systems aggregating at equilibrium, in general, share many thermodynamic features in common and exhibit similar patterns of phase stability.

Finally, we mention that the phase separation of charged particles in solution provides another context in which competition between phase separation and “clustering” should be important. Bjerrum *et al.*⁵⁴ long ago suggested that ions of opposite charge tend to cluster into “dipolar” pairs in order to rationalize shortcomings of the Debye–Hückel model for describing the phase separation of interacting charged, equal-sized hard spheres (“the restricted primitive model”).^{55,56} (Chain clustering similar to living polymerization has been observed in simulations of dipolar liquids^{57–60} and similar phenomena can be anticipated in polarizable charged particle suspensions.) Since Bjerrum’s work⁵⁴ there have been many suggestions in the physical chemistry literature of ion-clustering in charged particle solutions that are presumably at equilibrium. This implies that the combination of living polymerization and phase separation might have great relevance in understanding phase separations and aggregation in ionic fluids, protein solutions,⁶¹ charged colloidal solutions,⁶² and polyelectrolyte solutions,⁶³ and similarities between phase separation in living polymers and ionic fluids are expected if the equilibrium clustering hypothesis is correct. Fisher⁶⁴ notes the similarity in the shape of phase diagrams of ionic species in low dielectric constant solvents (“Coulombic solutions”) to the phase diagrams of high molecular polymer solutions. It would be interesting to change the electrolyte concentration, pressure, or some other solution parameter of ionic solutions to modify the tendency towards clustering (i.e., to change Δh in the polymerization model) to determine if the phase diagrams can be “tuned” through the range of shapes indicated in Fig. 1. This physics would also imply that these “perturbations” of the solution should induce large changes in the critical temperature since this property depends strongly on Δh under conditions where highly asymmetric phase diagrams are obtained.

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