

Miscibility of associated polymer blend solutions: 1. One-end-aminated polystyrene/one-end-carboxylated poly(ethylene glycol) blends in toluene

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The effects of polymer associations on miscibility are investigated for polymer blend solutions of one-end-aminated polystyrene (APS) and one-end-carboxylated poly(ethylene glycol) (CPEG), which are able to associate with each other by means of the functional groups at the end of the respective polymer chains. Cloud points are measured for their toluene solutions, where the strength of association and the segment interaction vary with the total polymer concentration. The following conclusions are deduced from the experimental results and a Flory–Huggins type theory for associated polymer blend solutions developed here. (1) The introduction of an amino group onto the polystyrene (PS) chain end gives substantially no effect on miscibility with poly(ethylene glycol) (PEG), whereas the carboxyl group introduced onto PEG reduces the miscibility of PS and PEG. Blend solutions of APS/CPEG exhibit higher miscibility than those of PS/CPEG. (2) The theory can interpret these experimental results well, showing that the strength of association between carboxyl groups is stronger than that between carboxyl and amino groups. (3) The strength of association between amino and carboxyl groups is not so strong as to show two peaks in the phase diagram of solvent fraction against polymer composition, which is theoretically expected for a strongly associated system.

(Keywords: functional polymer; blend miscibility; association)

INTRODUCTION

Associated polymer blends with functional groups can exhibit a wide variety of compatibility and microstructure^{1–10}. Polymer blends with functional groups at the chain ends tend to take on a more regular microstructure than that with functional groups randomly attached onto the polymer chains. Blends of both-end-aminated and both-end-carboxylated polymers have been revealed to form mesophases that are similar to those observed in block copolymers, owing to the association of chain ends^{7–10}. The association behaviour of one-end-functional polymers must be simpler to treat theoretically than that when both ends are functionalized.

A blend system consisting of two polymers that are able to associate with each other by means of functional groups at one end of the respective polymer chains may exhibit a wide variety of phase behaviour according to the strength of association of the end-groups and the segmental segregation strength. At the limit of strong association, the blend behaves like a mixture of block copolymer and homopolymer; while at the limit of weak association, it behaves like an ordinary polymer blend.

Tanaka and coworkers have extensively studied

theoretically the phase behaviour of such associated blends as a function of the association and segregation strengths^{11,12}.

It is not so easy, however, to find such blend systems for experimental studies, because most polymer pairs are too immiscible to see the phase behaviour at experimentally accessible temperatures. An idea adopted here for overcoming this difficulty was to investigate the miscibility in solution on changing the association strength and the segment interaction by varying the total polymer concentration, instead of changing the temperature.

In this study, we take a blend of one-end-aminated polystyrene (APS) and one-end-carboxylated poly(ethylene glycol) (CPEG), and use toluene as the solvent, as it is thermodynamically good for both polymers. Miscibility has been investigated by measuring the solvent content of the cloud point at fixed temperature as a function of polymer composition for various combinations of polymers with and without functional groups. The results are discussed on the basis of a theory developed here for associated polymer blend solutions.

EXPERIMENTAL

Samples

Polystyrenes (PS) were products of Pressure Chemical

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Co. and Toso Co. with narrow molecular-weight distributions. Poly(ethylene glycol) (PEG) was a product of Aldrich Co. PS with an amino group at one end (APS) was synthesized by anionic polymerization, followed by amination of the living end¹³. Functionality of amino groups was more than 0.94. PEG with a carboxyl group at one end (CPEG) was made by carboxylation of a hydroxyl group at the end of the PEG¹³. Functionality of carboxyl groups was 0.96. Weight-average molecular weight M_w and polydispersity index M_w/M_n for the samples with code names are listed in Table 1.

Toluene, used as the solvent, was purified by fractional distillation.

Cloud-point measurements

The intensity of light scattered from the samples under cooling was measured at an apparent scattering angle of about 30° to determine the cloud point. Blend solutions were prepared by mixing two polymers and the solvent in a glass tube for light scattering, followed by flame-sealing under mild vacuum. The blend solution was homogenized by vibrating the glass tube with a mixing machine at about 110°C in the one-phase region.

The cloud point, T_{cl} , was defined as the temperature at which the scattered light intensity began to increase during cooling at the rate of 0.76°C min⁻¹. Only a subtle dependence of T_{cl} on cooling rate was observed. T_{cl} was obtained as a function of solvent concentration C_s for a fixed polymer-polymer composition. T_{cl} had an extremely strong dependence on C_s ; in other words, the solvent concentration $C_{s,cl}$ at the cloud point, which is here referred to as cloud solvent concentration, was very weakly dependent on temperature. $C_{s,cl}$ at 90°C was determined from plots of T_{cl} against C_s as a function of polymer composition. Solvent concentration and polymer-polymer composition in weight fraction were transformed to those of volume fraction with reported density data, i.e. 1.0327 g ml⁻¹ for PS¹⁴, 1.0758 g ml⁻¹ for PEG^{15,16} and 0.7981 g ml⁻¹ for toluene at 90°C.

Experimental results of cloud points will be illustrated as a quasibinary presentation. Namely, cloud solvent concentrations $\phi_{s,cl}$ in volume fraction were plotted against volume fraction Φ_{PEG} (or Φ_{CPEG}) of PEG (or CPEG) in total polymers. Denoting volume of component X as $v[X]$, they were defined as $\phi_{s,cl} = v[\text{toluene}]/v[\text{total}$

blend solution] and $\Phi_{PEG} = v[\text{PEG}]/v[\text{total polymers}]$ (or $\Phi_{CPEG} = v[\text{CPEG}]/v[\text{total polymers}]$.)

RESULTS

Effect of amino (NH_2) groups

Experimental results of cloud points for APS15/PEG6 with those of PS13/PEG6 are shown in Figure 1. The cloud-point curve $\phi_{s,cl}$ vs. Φ_{PEG} was almost identical for both blend solutions. This means that the NH_2 end has substantially no effect on miscibility.

Effects of carboxyl ($COOH$) groups

Results for PS13/CPEG6 are also plotted in Figure 1. In contrast to the case of NH_2 groups, the cloud-point curve of $\phi_{s,cl}$ vs. Φ_{CPEG} shifts towards higher solvent concentration with introduction of $COOH$ ends onto PEG. That is, the $COOH$ end-groups make PEG less miscible with PS, which suggests that associations between $COOH$ groups take place and increase the effective molecular weight of PEG.

Effects of $NH_2/COOH$ association

Figure 2 represents the effects of $NH_2/COOH$ association, where cloud points are shown for APS15/CPEG6 and APS6/CPEG6 blend solutions, with those of the corresponding PS/CPEG blends without amino ends. Introduction of amino ends onto PS increases compatibility with CPEG. Association between APS and CPEG must be responsible for this.

In the following section, a more quantitative interpretation will be presented to confirm the above-mentioned effects of associations between end-groups on miscibility.

DISCUSSION

To describe the present associated polymer blend solution, the free energy of mixing was evaluated in the framework of a Flory-Huggins type mean-field theory. Since polymers can be associated with other chains at one end, the solution can be regarded as a mixture of free and associated polymer chains in a thermodynamically good solvent, as illustrated in Figure 3. Under the quasibinary approximation, the effective part ΔF_{eff} of the free energy for determining the phase equilibrium can be

Table 1 Characteristics of sample polymers

Samples	Codes	M_w^a	M_w/M_n^b	Funct. ^c	P^d
Polystyrene	PS6	6200	1.04		52
	PS13	13000	1.06		109
One-end-aminated	PS6	5600	1.06	1.00	47
	PS15	15500	1.12	0.94	130
Poly(ethylene glycol)	PEG6	5700	1.05		46
One-end-carboxylated	CPEG6	5700	1.05	0.96	46

^a Determined by M_n with M_w/M_n , where M_n was measured by vapour-pressure osmometry

^b Determined by size exclusion chromatography

^c Functionalities of amino groups and carboxyl groups

^d Degree of polymerization, corresponding to fN or $(1-f)N$ in the theoretical treatment, defined by [molar volume of polymer]/[molar volume of toluene]

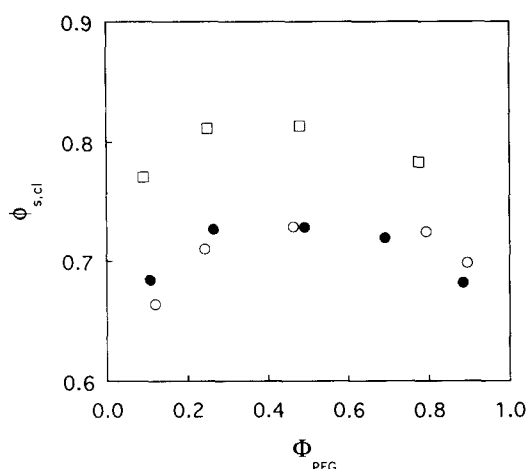


Figure 1 Quasibinary presentation of cloud points for PS13/PEG6 (○), APS15/PEG6 (●) and PS13/CPEG6 (□) at 90°C

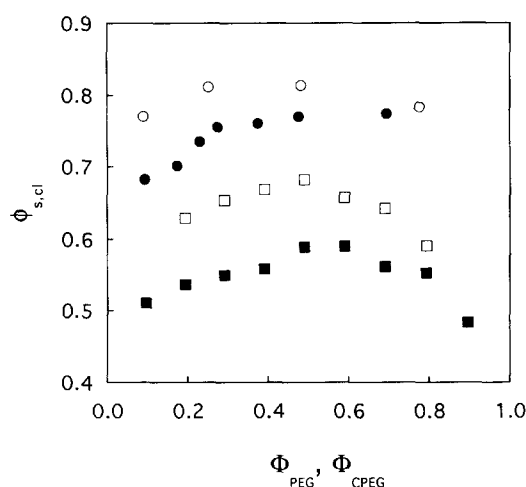


Figure 2 Quasibinary presentation of cloud points for PS13/CPEG6 (○), APS15/CPEG6 (●), PS6/CPEG6 (□) and APS6/CPEG6 (■) at 90°C

written as:

$$\begin{aligned}
 [\Delta F] &= \frac{N\Delta F_{\text{eff}}}{\phi M k T} \\
 &= \frac{\theta_a \ln \theta_a}{f} + \frac{\theta_b \ln \theta_b}{1-f} \\
 &\quad + \frac{\phi}{2} \left(\frac{K_{aa} \theta_a^2 (1 + 2 \ln \theta_a)}{f} + \frac{K_{bb} \theta_b^2 (1 + 2 \ln \theta_b)}{1-f} \right. \\
 &\quad \left. + 2K_{ab} \theta_a \theta_b [1 + \ln(\theta_a \theta_b)] \right) \\
 &\quad + \phi N \chi \Phi_a \Phi_b
 \end{aligned} \quad (1)$$

with

$$\theta_a + \phi K_{aa} \theta_a^2 + f \phi K_{ab} \theta_a \theta_b = \Phi_a \quad (2)$$

and

$$\theta_b + \phi K_{bb} \theta_b^2 + (1-f) \phi K_{ab} \theta_a \theta_b = \Phi_b = 1 - \Phi_a \quad (3)$$

Here N is the sum of the polymeric indices of polymers a and b , and the polymeric index of polymer a is given by

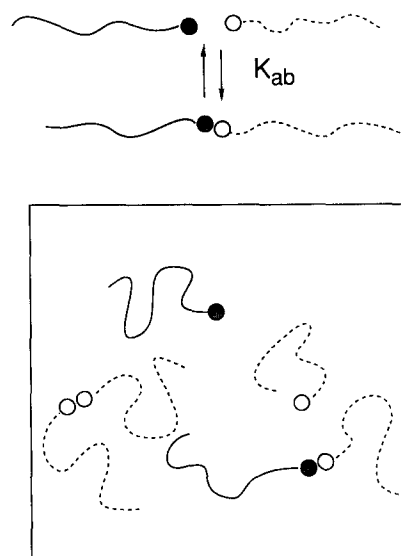


Figure 3 Schematic illustration of associated polymer blend solutions with one functional end-group per molecule

fN . The volume fraction of total polymer a and b in the solution is $\phi (= 1 - \phi_s)$, and the fraction of polymer a in the total polymers is Φ_a . The fractions θ_x and θ_{xy} of polymer x are that dissolved in solution as free chains and that associated with a polymer y chain, respectively ($x, y = a, b$); χ is the segment-segment interaction parameter χ_{ab} between polymers a and b ; and K_{xy} is the association constant for x - y pairs. Details of the derivations are described in the Appendix.

For a system with a set of given N , f , χ and K_{xy} , the free energy of mixing is given as a function of Φ_a and ϕ_s , so that Φ_a of coexisting phases for a fixed ϕ_s can be determined by a conventional method of thermodynamics. Calculations with changing ϕ_s yield the coexistence curve, ϕ_s vs. Φ_a . The fractions of free chains and associated chains are also calculated by equations (2) and (3) for a given solution. Hereafter, the polymer a is assigned to CPEG (or PEG), and the polymer b to APS (or PS).

Polymeric indices were given as the ratio of molar volume of polymers to molar volume of toluene, shown in Table 1, so that the χ -parameter was per site, the size of which was the volume of a toluene molecule.

First, the value of χ between PS and PEG was determined such that the theoretical coexistence curve reproduced the cloud-point curve of PS13/PEG6, where there were no associations, i.e. $K_{aa} = K_{bb} = K_{ab} = 0$. The χ value determined was 0.112. The calculated and experimental curves are compared in Figure 4. Then, the association constant K_{aa} between COOH and COOH was evaluated by fitting to the cloud points of PS13/CPEG6 with $K_{bb} = K_{ab} = 0$ and the χ value obtained above (see Figure 4). The estimated value of K_{aa} was 480.* The association between carboxyl groups was so strong that most of the CPEG chains formed associations, and the apparent molecular weight of PEG was almost

* The association between carboxyl groups was so strong that the accuracy of K_{aa} obtained by fitting was not good, because the location of the coexistence curve has a limit with increasing K_{aa} , and becomes insensitive to K_{aa} .

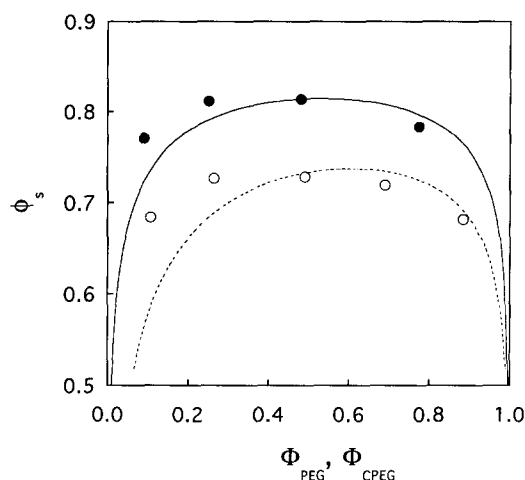


Figure 4 Comparison of calculated and experimental phase boundaries for evaluation of χ and K_{aa} : (○) PS13/PEG6; (●) PS13/CPEG6; (---) calculated with $\chi = 0.112$; (—) calculated with $\chi = 0.112$ and $K_{aa} = 480$ ($fN = 46$; $(1-f)N = 109$)

doubled. This resulted in a decrease of the miscibility. The calculated fractions of free and associated CPEG chains at $\phi_s = 0.7$ are represented in Figure 5.

Since introduction of amino groups has almost no effect on the miscibility as seen in the blend solution of APS15/PEG6, one can put $K_{bb} = 0$. Hence, using the cloud-point curve of APS15/CPEG6, the association constant K_{ab} between amino and carboxyl groups could be evaluated by fitting with the parameters obtained above: $K_{aa} = 480$, $K_{bb} = 0$ and $\chi = 0.112$. The fitting curve with experimental results and calculated fractions of associated chains are shown in Figures 6 and 7, respectively. The value of K_{ab} was 53, which was smaller than K_{aa} . The fraction of NH_2/COOH associates is not so large, some of the CPEG chains are associated with themselves (CPEG chains), and there even exist NH_2 free chains. Increase of miscibility by NH_2/COOH association is cancelled out with decrease in miscibility by COOH/COOH association.

To confirm the validity of the model and explanation of the experimental results, it was examined whether the theory consistently reproduced other experimental results using the same parameters as obtained above.

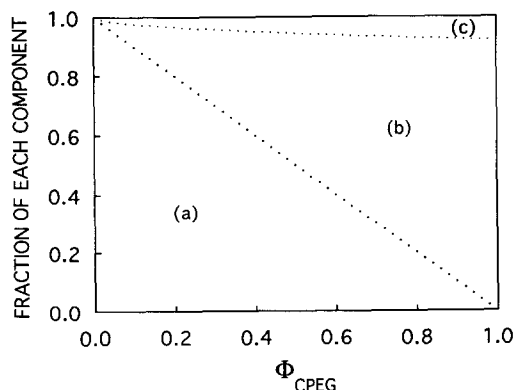


Figure 5 Fractions of free and associated polymer chains for PS13/CPEG6 at $\phi_s = 0.7$, with $\chi = 0.112$ and $K_{aa} = 480$ ($fN = 46$; $(1-f)N = 109$): (a) free PS θ_b ; (b) CPEG-CPEG associates θ_{aa} ; (c) free CPEG θ_a

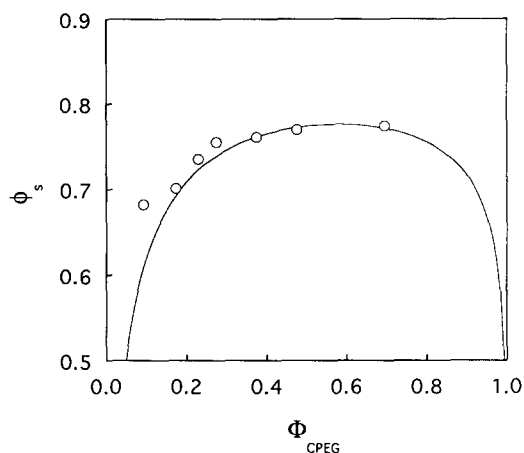


Figure 6 Comparison of calculated and experimental phase boundaries for evaluation of K_{ab} : (○) APS15/CPEG6; (—) calculated with $\chi = 0.112$, $K_{aa} = 480$ and $K_{ab} = 53$ ($fN = 46$; $(1-f)N = 130$)

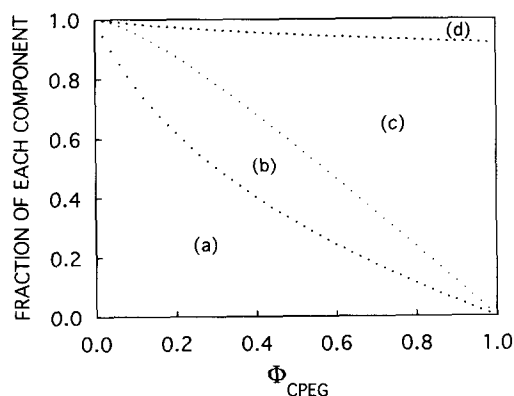


Figure 7 Fractions of free and associated polymer chains for APS15/CPEG6 at $\phi_s = 0.7$ with $\chi = 0.112$, $K_{aa} = 480$ and $K_{ab} = 53$ ($fN = 46$; $(1-f)N = 130$): (a) free APS θ_b ; (b) APS-CPEG associates θ_{ab} ; (c) CPEG-CPEG associate θ_{aa} ; (d) free CPEG θ_a

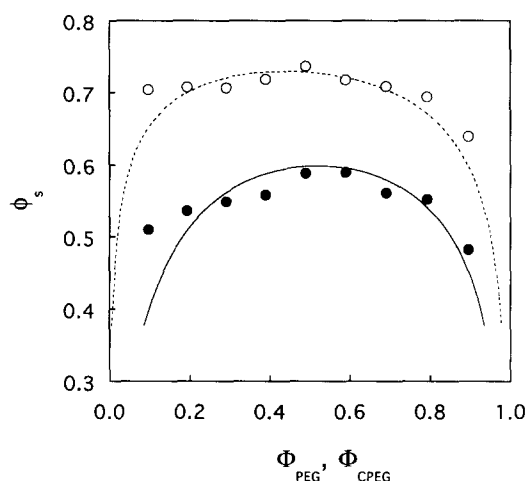


Figure 8 Comparison of calculated and experimental phase boundaries for testing validity of the theory: (○) PS6/CPEG6; (●) APS6/CPEG6; (---) calculated with $\chi = 0.112$, $K_{aa} = 480$ and $K_{ab} = 0$ ($fN = 46$; $(1-f)N = 52$); (—) calculated with $\chi = 0.112$, $K_{aa} = 480$ and $K_{ab} = 53$ ($fN = 46$; $(1-f)N = 47$)

Figure 8 represents the comparison for PS6/CPEG6 and APS6/CPEG6. Good agreement between theoretical and experimental results was obtained for blend solutions with PS molecular weight being different

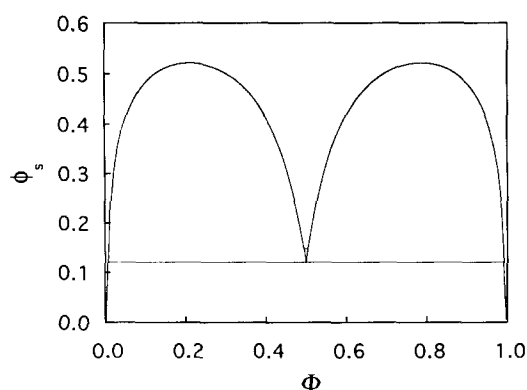


Figure 9 Calculated coexistence curve for $K_{ab} = 500$, $K_{aa} = K_{bb} = 0$, $N = 100$, $f = 0.5$ and $\chi = 0.24$

from that of the previous blends used for evaluating the parameters. The agreement suggests that the theoretical interpretation presented here works reasonably well.

In the case of strong a–b association, it is theoretically expected that the coexistence curve can have two peaks. An example of such a case is shown in *Figure 9*, where $K_{ab} = 500$, $K_{aa} = K_{bb} = 0$, $N = 100$ with $f = 0.5$ and $\chi = 0.24$. The two-peak phase behaviour has already been predicted theoretically for associated polymer bulk blends by Tanaka^{11,12}. In the present experimental cases, the cloud-point curves did not show this type of phase behaviour primarily because of the weak association between amino and carboxyl groups.

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APPENDIX

Phase diagrams of associated polymer blend solutions

Polymers a and b are able to associate with each other at one end of the polymer chains. The polymeric indices of polymers a and b are $N_a = fN$ and $N_b = (1 - f)N$, respectively, with N being the sum $N_a + N_b$, and the asymmetry factor f being defined by N_a/N . Consider a polymer blend solution with the compositions in volume fraction of polymer a, polymer b and the solvent being $\Phi_a\phi$, $\Phi_b\phi$ and ϕ_s , respectively, where the volume fraction of total polymers in the solution is given by $\phi = 1 - \phi_s$, and Φ_a and Φ_b are the fractions of polymers a and b in the total polymers. Some of the polymer chains form a–a, b–b and a–b associates, and others are free. Hence, denoting the volume fraction of free polymer x as ϕ_x and that of associates of polymer x /polymer y as ϕ_{xy} , mass conservation for total polymers is written as:

$$\phi = \phi_a + \phi_b + \phi_{aa} + \phi_{bb} + \phi_{ab}$$

The mass-conservation relations for total polymers, polymer a and polymer b are respectively expressed, in terms of volume fractions in the total polymers θ_a , θ_b , θ_{aa} , θ_{bb} and θ_{ab} , as:

$$\Phi_a + \Phi_b = \theta_a + \theta_b + \theta_{aa} + \theta_{bb} + \theta_{ab} = 1 \quad (\text{A1})$$

$$\Phi_a = \theta_a + \theta_{aa} + f\theta_{ab} \quad (\text{A2})$$

$$\Phi_b = \theta_b + \theta_{bb} + (1 - f)\theta_{ab} \quad (\text{A3})$$

In the framework of a Flory–Huggins type theory, the free energy ΔF of mixing of the solution can be expressed as the sum of combinatorial entropy $\Delta F(\text{comb})$, segment–segment interaction energy $\Delta F(\text{seg})$ and association energy $\Delta F(\text{ass})$:

$$\Delta F = \Delta F(\text{comb}) + \Delta F(\text{seg}) + \Delta F(\text{ass})$$

(i) $\Delta F(\text{comb})$ is given by:

$$\frac{\Delta F(\text{comb})}{MkT} = \frac{\phi_a \ln \phi_a}{fN} + \frac{\phi_b \ln \phi_b}{(1-f)N} + \frac{\phi_{aa} \ln \phi_{aa}}{2fN} + \frac{\phi_{bb} \ln \phi_{bb}}{2(1-f)N} + \frac{\phi_{ab} \ln \phi_{ab}}{N} + \phi_s \ln \phi_s$$

where M is the total number of lattice sites of the system, k is the Boltzmann constant and T is the absolute temperature.

(ii) $\Delta F(\text{seg})$ is expressed by the Flory–Huggins χ parameter χ_{xy} for segmental interaction between components x and y ($x, y = a, b$) as:

$$\frac{\Delta F(\text{seg})}{MkT} = \phi_a \phi_b \chi_{ab} + \phi_a \phi_s \chi_{as} + \phi_b \phi_s \chi_{bs}$$

(iii) $\Delta F(\text{ass})$ is expressed as:

$$\frac{\Delta F(\text{ass})}{MkT} = \frac{\phi_{aa} \Delta_{aa}}{2fN} + \frac{\phi_{bb} \Delta_{bb}}{2(1-f)N} + \frac{\phi_{ab} \Delta_{ab}}{N}$$

where $kT\Delta_{xy}$ is the association energy per chain-end pair between polymers x and y .

The free energy of mixing ΔF is given as the sum of the above three free energies, and can be rewritten in terms of ϕ and fractions (θ_x, θ_{xy}) of various components in the total polymers as:

$$\begin{aligned} \frac{\Delta F}{MkT} = & (1 - \phi) \ln(1 - \phi) \\ & + \left(\frac{\phi \ln \phi}{N} \right) \left(\frac{\Phi_a}{f} + \frac{\Phi_b}{1-f} - \frac{\theta_{aa}}{2f} - \frac{\theta_{bb}}{2(1-f)} \right) \\ & + \frac{\phi}{N} \left[\frac{\theta_a \ln \theta_a}{f} + \frac{\theta_b \ln \theta_b}{1-f} + \theta_{ab} \ln \left(\frac{\theta_{ab}}{\phi} \right) \right. \\ & \left. + \frac{\theta_{aa} \ln \theta_{aa}}{2f} + \frac{\theta_{bb} \ln \theta_{bb}}{2(1-f)} \right] \\ & + \phi(1 - \phi)(\chi_{as}\Phi_a + \chi_{bs}\Phi_b) + \phi^2\chi_{ab}\Phi_a\Phi_b \\ & + \frac{\phi\Delta_{ab}\theta_{ab}}{N} + \frac{\phi\Delta_{as}\theta_{aa}}{2fN} + \frac{\phi\Delta_{bb}\theta_{bb}}{2(1-f)N} \end{aligned} \quad (A4)$$

In the association equilibrium:

$$\partial F / \partial X_i = 0 \quad (A5)$$

for $X_i = \theta_{aa}, \theta_{bb}$ and θ_{ab} . Equation (A5) with equation (A4) yields:

$$\theta_{aa} = \phi K_{aa} \theta_a \theta_a \quad (A6)$$

$$\theta_{bb} = \phi K_{bb} \theta_b \theta_b \quad (A7)$$

$$\theta_{ab} = \phi K_{ab} \theta_a \theta_b \quad (A8)$$

where K_{xy} is the association constant between polymers x and y , defined by:

$$K_{aa} = \exp(1 - \Delta_{aa}) \quad (A9)$$

$$K_{bb} = \exp(1 - \Delta_{bb}) \quad (A10)$$

$$K_{ab} = \exp(1 - \Delta_{ab}) \quad (A11)$$

Therefore, θ_a and θ_b are given as a function of Φ_a (Φ_b) and ϕ by the following simultaneous equations for a system specified with f and K_{xy} :

$$\theta_a + \phi K_{aa} \theta_a^2 + f \phi K_{ab} \theta_a \theta_b = \Phi_a \quad (A12)$$

$$\theta_b + \phi K_{bb} \theta_b^2 + (1 - f) \phi K_{ab} \theta_a \theta_b = \Phi_b = 1 - \Phi_a \quad (A13)$$

These were derived from equations (A6)–(A8) with equations (A2) and (A3). Then, θ_{xy} are also given by equations (A6)–(A8) with these θ_a and θ_b .

Substituting these fractions θ into the free-energy expression (equation (A4)), one obtains:

$$\begin{aligned} \frac{\Delta F}{\phi MkT} = & \frac{(1 - \phi)}{\phi} \ln(1 - \phi) + \left(\frac{\ln \phi}{N} \right) \left(\frac{\Phi_a}{f} + \frac{\Phi_b}{1-f} \right) \\ & + (1 - \phi)(\chi_{as}\Phi_a + \chi_{bs}\Phi_b) \\ & + \frac{1}{N} \left(\frac{\theta_a \ln \theta_a}{f} + \frac{\theta_b \ln \theta_b}{1-f} \right) \\ & + \frac{\phi}{2N} \left(\frac{K_{aa}\theta_a^2(1 + 2 \ln \theta_a)}{f} \right. \\ & \left. + \frac{K_{bb}\theta_b^2(1 + 2 \ln \theta_b)}{1-f} \right. \\ & \left. + 2K_{ab}\theta_a\theta_b[1 + \ln(\theta_a\theta_b)] \right) \end{aligned} \quad (A14)$$

If the solvent is thermodynamically good enough for both polymers, the quasibinary approximation may be valid, where the solvent concentration ϕ_s (accordingly ϕ) is approximately equal in both of the coexisting phases. In the quasibinary approximation, the effective part ΔF_{eff} of the free energy for determining the phase equilibrium consists of the fourth, fifth and sixth terms in equation (A14), and is written as:

$$\begin{aligned} [\Delta F] = & \frac{N\Delta F_{\text{eff}}}{\phi MkT} \\ = & \frac{\theta_a \ln \theta_a}{f} + \frac{\theta_b \ln \theta_b}{1-f} \\ & + \frac{\phi}{2} \left(\frac{K_{aa}\theta_a^2(1 + 2 \ln \theta_a)}{f} + \frac{K_{bb}\theta_b^2(1 + 2 \ln \theta_b)}{1-f} \right. \\ & \left. + 2K_{ab}\theta_a\theta_b[1 + \ln(\theta_a\theta_b)] \right) + \phi N \chi_{ab} \Phi_a \Phi_b \end{aligned} \quad (A15)$$

Equation (A15) with equations (A12) and (A13) gives the free energy of mixing as a function of Φ_a , so that one can determine the coexistence curve by the conventional method of thermodynamics.

It should be noted here that the present treatment supposes a disordered state only, excluding the possibility of mesophase formation. In reality, a mesophase could be formed around the stoichiometric composition $\Phi_a = f$ if the association is strong enough.