BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 6, pp. 1243–1252, 1995

0032-3861/95/$10.00+0.00

Compatibilization effect of a block copolymer in two random copolymer blends

Jin Kon Kim
Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, Kyungbuk 790-784, Korea
(Received 28 June 1994; revised 4 October 1994)

The stability limit and spinodal points of a multicomponent polymer system have been studied with the structure factors, $\tilde{S}_{ij}(q)$, which were obtained using the random phase approximation and incompressibility constraint. Emphasis was placed on the effect of the volume fraction of component A, f_I, in a block copolymer, A-*block*-B, on the spinodal points for macrophase separation of an (A-*block*-B)/(B-*ran*-C)/(A-*ran*-D) mixture. The behaviour of the spinodal point for macrophase separation, and thus the compatibilization effect, depends very much on f_I for given weight fractions of the two homopolymers (or a homopolymer and a random copolymer). The spinodal points of microphase transitions in addition to those of macrophase separation are also discussed.

(Keywords: block copolymer; random copolymer mixtures; compatibility)

INTRODUCTION

Block and graft copolymers have been used to improve the compatibility of two immiscible homopolymers[1–5]. Since a block or graft copolymer can be located at the interface of two immiscible polymers due to thermodynamic driving forces, the interfacial tension of the blend decreases significantly, and thus polymer alloys with morphology having smaller sizes of dispersed phase can be obtained[6].

Compatibilization of two immiscible homopolymers by addition of a diblock copolymer (A-*block*-B) has recently been studied theoretically[6–10]. The chemical structure of two immiscible homopolymers can be the same as (or different from) that of the constituent component of the block copolymer. Using a functional integral formalism Noolandi and Hong[7] have developed a theory which predicts the interfacial tension of a blend and the concentration profile of an A-*block*-B near the interface between the two homopolymers A and B. Later Vilgis and Noolandi[8] extended the theory to an (A-*block*-B)/C/D system where two homopolymers C and D have chemical structures different from those of the constituent components of the block copolymer.

In preparing multicomponent polymer systems, the construction of a phase diagram is highly desirable. Here a '*m*-component' polymer system is referred to as a system consisting of '*m* different monomers'. The A-*block*-B copolymer can be regarded as a 'two-component' polymer system. Thus, the (A-*block*-B)/(B-*ran*-C)/(A-*ran*-D) system is referred to as a 'four-component' polymer system, since there are 'four' different monomers, A–D.

Although Banaszak and Whitmore[11] have developed a theory which will enable one to construct a phase diagram for an (A-*block*-B)/A/B mixture, at present there is no theory predicting the phase diagram for multicomponent polymer systems, such as the (A-*block*-B)/C/D blend system. Note that the block copolymers considered in the study of Banaszak and Whitmore[11] were assumed to have lamellar microstructure, which cannot show the effect of the volume fraction of each block in a block copolymer on the compatibilization of two immiscible polymer blends.

Recently, a new method was developed to calculate the spinodal points (or stability limits) for a multicomponent polymer system[12]. There are two types of spinodal points for a multicomponent system which consists of a block copolymer: (1) the spinodal point for macrophase separation $(\chi N)_{\mathrm{s,macro}}$ where the scattering intensity $I(q)$ becomes infinite at a wave vector of $q=q^*=0$; and (2) the spinodal point for microphase separation $(\chi N)_{\mathrm{s,micro}}$ where $I(q)$ becomes infinite at $q=q^*$, in which χ is Flory's interaction parameter between block components and N is the total number of statistical segments of the block copolymer. It can be stated that a block copolymer can play the role of effective compatibilizer in two immiscible polymer blends if $\partial(\chi N_\mathrm{I})_{\mathrm{s,macro}}/\partial\phi_\mathrm{I}>0$ where ϕ_I is the volume fraction of a block copolymer in the blend and is assumed to be $\ll 1$. Note that as $(\chi N_\mathrm{I})_{\mathrm{s,macro}}$ increases, the critical temperature (T_c) above which the mixture becomes homogeneous decreases since mixtures considered in this study are assumed to have an upper critical solution temperature (*UCST*) behaviour. Thus at a given temperature the increased value of $(\chi N_\mathrm{I})_{\mathrm{s,macro}}$ means better mixing between two incompatible homopolymers, and thus better compatibilization can be expected.

This paper focuses on the stability limit of a four-component system of an (A-*block*-B)/(B-*ran*-C)/(A-*ran*-D) mixture. Emphasis is placed on investigating how the volume fraction of block A, f_I in (A-*block*-B), and the relative magnitude of Flory's interaction parameters between all components in the blend can affect the compatibilization of two immiscible polymers.

THEORY

The structure factors $\tilde{S}_{ij}(q)$ for a multicomponent system is given by[12]:

$$\tilde{S}_{ij}(q)=\sum_{k=1}^{m-1} A_{ik}^{-1}(q)[S_{kj}(q)-v_k(q)S_{mj}(q)] \qquad (1)$$

$$(i=1,2\ldots,m-1;\ j=1,2\ldots,m-1)$$

where $S_{ij}(q)$ is the Fourier transform of the density–density correlations of monomers i and j for ideal Gaussian chains and q is the wave vector defined by $q=(4\pi/\lambda)\sin(\theta/2)$, in which λ and θ are the wavelength of the incident radiation and scattering angle in the medium, respectively. The matrix **A** and $v_i(q)$ in equation (1) are given by:

$$A_{ij}(q)=\sum_{p=1}^{m}[S_{ip}(q)-v_i(q)S_{mp}(q)](\chi_{pj}-\chi_{pm})+v_i(q)+\delta_{ij} \qquad (2)$$

$$v_i(q)=t_i(q)/t_m(q) \qquad (3)$$

where

$$t_j(q)=\sum_{r=1}^{m} S_{jr}(q) \qquad (4)$$

Note that in the derivation of equation (1), we used the incompressibility constraint and symmetry property of the structure factor [i.e. $\tilde{S}_{ij}(q)=\tilde{S}_{ji}(q)$].

The determinant $\|D\|$ of $A_{ij}(q)$ for a four-component polymer system is given by:

$$\|D\|=[S_4(q)/t_4(q)]/F(q) \qquad (5)$$

where $S_4(q)$ is the sum of $S_{ij}(q)$:

$$S_4(q)=\sum_{i=1}^{4} t_i(q)=\sum_{i,j=1}^{4} S_{ij}(q) \qquad (6)$$

and $F(q)$ is given by[12]:

$$F(q)=1+\sum_{i,j}^{4}\bar{S}_{ij}(q)\chi_{ij}+\sum_{\substack{i,j\\k,l}}^{4}D_{2,ijkl}(q)\chi_{ij}\chi_{kl}+2[W_4(q)/S_4(q)]\chi_D \qquad (7)$$

where $W_4(q)$ is the determinant of $S_{ij}(q)$:

$$W_4(q)=\|S_{ij}(q)\| \qquad (8a)$$

and

$$\bar{S}_{ij}(q)=S_{ij}(q)-t_i(q)t_j(q)/S_4(q) \qquad (8b)$$

$$\begin{aligned}D_{2,ijkl}(q)=(1/4)\{&2[S_{ij}(q)\bar{S}_{kl}(q)+S_{kl}(q)\bar{S}_{ij}(q)]\\&-[S_{ik}(q)\bar{S}_{jl}(q)+S_{jl}(q)\bar{S}_{ik}(q)\\&+S_{il}(q)\bar{S}_{jk}(q)+S_{jk}(q)\bar{S}_{il}(q)]\\&+S_{ik}(q)S_{jl}(q)+S_{il}(q)S_{jk}(q)-2S_{ij}(q)S_{kl}(q)\}\end{aligned} \qquad (8c)$$

$$\begin{aligned}\chi_D=\;&\chi_{12}\chi_{13}\chi_{23}+\chi_{12}\chi_{14}\chi_{24}+\chi_{23}\chi_{24}\chi_{34}+\chi_{13}\chi_{14}\chi_{34}\\&-[(\chi_{12}+\chi_{34})(\chi_{13}\chi_{24}+\chi_{14}\chi_{23}-\chi_{12}\chi_{34})\\&+(\chi_{13}+\chi_{24})(\chi_{12}\chi_{34}+\chi_{14}\chi_{23}-\chi_{13}\chi_{24})\\&+(\chi_{14}+\chi_{23})(\chi_{12}\chi_{34}+\chi_{13}\chi_{24}-\chi_{14}\chi_{23})]\end{aligned} \qquad (8d)$$

With the aid of equation (2) the structure factors $\tilde{S}_{\alpha\beta}(q)$ in equation (1) can be written as[12]:

$$\tilde{S}_{\alpha\beta}(q)=\left\{\bar{S}_{\alpha\beta}(q)+2\sum_{k,l}^{4}D_{2,\alpha\beta kl}(q)\chi_{kl}+[W_4(q)/S_4(q)]\chi_{\alpha\beta,2}\right\}\Big/F(q) \qquad (9)$$

$$(\alpha=1,2,3;\ \beta=1,2,3)$$

where

$$\chi_{\alpha\alpha,2}=2(\chi_{\gamma\delta}\chi_{\gamma\varepsilon}+\chi_{\delta\varepsilon}\chi_{\gamma\delta}+\chi_{\gamma\varepsilon}\chi_{\delta\varepsilon})-(\chi_{\gamma\delta}^2+\chi_{\delta\varepsilon}^2+\chi_{\gamma\varepsilon}^2) \qquad (10a)$$

$$(\gamma\neq\delta\neq\varepsilon\neq\alpha \text{ and } \gamma<\delta<\varepsilon)$$

$$\begin{aligned}\chi_{\alpha\beta,2}=\;&2(\chi_{\alpha\beta}\chi_{\gamma\delta}+\chi_{\alpha\gamma}\chi_{\beta\gamma}+\chi_{\alpha\delta}\chi_{\beta\delta})\\&-\chi_{\gamma\delta}(\chi_{\alpha\gamma}+\chi_{\alpha\delta}+\chi_{\beta\gamma}+\chi_{\beta\delta})-\chi_{\alpha\gamma}\chi_{\beta\delta}-\chi_{\alpha\delta}\chi_{\beta\gamma}+\chi_{\delta\gamma}^2\end{aligned}$$

$$(\gamma\neq\delta\neq\alpha\neq\beta \text{ and } \gamma<\delta) \qquad (10b)$$

The indices α, β, γ, δ and ε appearing in equations (9) and (10) are not dummy variables, so the summation of these indices must not be taken.

For four-component systems, the scattering intensity $I(q)$ is given by:

$$I(q)\sim\sum_{i,j=1}^{3}(a_i-a_4)(a_j-a_4)\tilde{S}_{ij}(q) \qquad (11)$$

where a_i is the scattering power of monomer i. It can be seen from equation (11) that $I(q)$ cannot easily be determined quantitatively even if all $\tilde{S}_{ij}(q)$ are known, in the situation where accurate information for all a_i is not available. Therefore, we consider only the stability limit, where $I(q)$ becomes infinite at $q=q^*$:

$$I(q^*)\rightarrow\infty \qquad (12)$$

From equation (11) the spinodal point of a four-component system can be obtained easily since every $\tilde{S}_{ij}(q)$ has the determinant of $A_{ij}(q)$ in the denominator. Note that if the determinant of $A_{ij}(q)$ is equal to zero [or $F(q)$ given in equation (7) becomes zero], all $\tilde{S}_{ij}(q)$ become infinite. In order to calculate $F(q)$ for four-component systems, we need six different Flory interaction parameters ($\chi_{12}, \chi_{13}, \chi_{14}, \chi_{23}, \chi_{24}$ and χ_{34}) and four different values of the degree of polymerization (N_1, N_2, N_3 and N_4). For given values of N_i ($i=1-4$), $\{(\chi_s)_{ij}\}$, which makes $F(q^*)$ equal to zero, can exist. Note that q^* can be obtained from the value of q_m where $F(q_m=q^*)$ becomes zero [or, $I(q_m=q^*)$ diverges to infinity] at $(\chi_s)_{ij}$. q_m is the value of q which makes $F(q)$ a minimum at given χ_{ij}, and q_m can change with χ_{ij} for four-component polymer systems. For $q^*=0$, $\{(\chi_s)_{ij}\}$ describes the spinodal or the limit of thermodynamic stability for the macrophase transition (or separation), whereas for $q^*\neq 0$, $\{(\chi_s)_{ij}\}$ describes the spinodal point for the microphase transition (or separation).

Let us now consider the four-component system of (A-*block*-B)/(B-*ran*-C)/(A-*ran*-D) mixtures, for which $S_{ij}(q)$ are given by:

$$S_{11}(q)=\phi_{\mathrm{I}}N_{\mathrm{I}}g(f_{\mathrm{I}},N_{\mathrm{I}})+\phi_{\mathrm{III}}N_{\mathrm{III}}\psi_{\mathrm{III}}^2g(1,N_{\mathrm{III}}) \qquad (13a)$$

$$S_{22}(q)=\phi_{\mathrm{I}}N_{\mathrm{I}}g(1-f_{\mathrm{I}},N_{\mathrm{I}})+\phi_{\mathrm{II}}N_{\mathrm{II}}\psi_{\mathrm{II}}^2g(1,N_{\mathrm{II}}) \qquad (13b)$$

$$S_{33}(q)=\phi_{\mathrm{II}}N_{\mathrm{II}}(1-\psi_{\mathrm{II}})^2g(1,N_{\mathrm{II}}) \qquad (13c)$$

$$S_{44}(q)=\phi_{\mathrm{III}}N_{\mathrm{III}}(1-\psi_{\mathrm{III}})^2g(1,N_{\mathrm{III}}) \qquad (13d)$$

$$S_{12}(q)=(1/2)\phi_{\mathrm{I}}N_{\mathrm{I}}[g(1,N_{\mathrm{I}})-g(f_{\mathrm{I}},N_{\mathrm{I}})-g(1-f_{\mathrm{I}},N_{\mathrm{I}})] \qquad (13e)$$

$$S_{23}(q)=\phi_{\mathrm{II}}N_{\mathrm{II}}\psi_{\mathrm{II}}(1-\psi_{\mathrm{II}})g(1,N_{\mathrm{II}}) \qquad (13f)$$

$$S_{14}(q)=\phi_{\mathrm{III}}N_{\mathrm{III}}\psi_{\mathrm{III}}(1-\psi_{\mathrm{III}})g(1,N_{\mathrm{III}}) \qquad (13g)$$

$$S_{13}(q)=S_{24}(q)=S_{34}(q)=0 \qquad (13h)$$

where ϕ_{I}, ϕ_{II} and ϕ_{III} are the volume fractions of A-*block*-B, B-*ran*-C and A-*ran*-D copolymers, respectively, in the mixture ($\phi_{\mathrm{I}}+\phi_{\mathrm{II}}+\phi_{\mathrm{III}}=1$); N_{I}, N_{II} and N_{III}

are the degrees of polymerization (or numbers of statistical segments) for A-*block*-B, B-*ran*-C and A-*ran*-D copolymers; and $f_{\rm I}$ is the volume fraction of component A in A-*block*-B copolymer; $\psi_{\rm II}$ is the volume fraction of B in B-*ran*-C copolymer and $\psi_{\rm III}$ the volume fraction of A in A-*ran*-D copolymer. Here, the subscripts 1–4 in $S_{ij}(q)$ represent monomers A–D in the mixture, thus, $S_{23}(q)$ means $S_{\rm BC}$, while the subscripts I–III in ϕ and N mean A-*block*-B, B-*ran*-C and A-*ran*-D copolymers, respectively. Note that $S_{ij}(q)$ of a random copolymer is different from that of a block copolymer[13]. Also, $g(f_i, N_i)$ is given by:

$$g(f_i, N_i) = 2[f_i x_i + \exp(-f_i x_i) - 1]/x_i^2 \tag{14a}$$

where

$$x_i = (qR_{gi})^2 \tag{14b}$$

in which R_{gi} is the radius of gyration of component i and is given by:

$$R_{gi} = b(N_i/6)^{1/2} \tag{14c}$$

Note that the statistical segment length b in equation (14c) is assumed to be the same for components A, B, C and D.

It should be noted that for a special four-component system where $\psi_{\rm II} = \psi_{\rm III} = 0$; $\chi_{12} = \chi_{14} = \chi_{23} = \chi_{34} = \chi$, $\chi_{13} = \chi_{24} = 0$; and $a_1 = a_3$, $a_2 = a_4$ equation (11) becomes (see Appendix):

$$I(q) \sim (a_1 - a_2)^2/[S_2(q)/W_2(q) - 2\chi] \tag{15}$$

where

$$S_2(q) = S_4(q) = S_{\rm AA}(q) + 2S_{\rm AB}(q) + S_{\rm BB}(q) \tag{16a}$$

$$W_2(q) = S_{\rm AA}(q)S_{\rm BB}(q) - [S_{\rm AB}(q)]^2 \tag{16b}$$

in which

$$S_{\rm AA}(q) = S_{11}(q) + S_{33}(q) \tag{16c}$$

$$S_{\rm BB}(q) = S_{22}(q) + S_{44}(q) \tag{16d}$$

$$S_{\rm AB}(q) = S_{12}(q) \tag{16e}$$

where S_{11}, S_{22}, S_{33}, S_{44} and S_{12} are given by equations (13a)–(13e) with $\psi_{\rm II} = \psi_{\rm III} = 0$. It should be mentioned that previously others[13–15] derived equations (15) and (16) to obtain the spinodal limits for the (A-*block*-B)/A/B mixture, by assuming implicitly that the concentration fluctuation of component A, $\delta n_{\rm A,C}$, in the block copolymer would be the same as that of component A in the homopolymer, $\delta n_{\rm A,H}$ and similarly $\delta n_{\rm B,C} = \delta n_{\rm B,H}$. It should be mentioned that $\delta n_i(q)$ is given by[16–18]:

$$\delta n_i(q) = -\beta \sum_{j=1}^{m} \tilde{S}_{ij}(q) U_j(q) \tag{17}$$

where $U_j(q)$ is the external potential exerted by adding the jth monomer, and $\beta = 1/(k_{\rm B}T)$ in which $k_{\rm B}$ is the Boltzmann constant and T is the absolute temperature. Applying the incompressibility constraint and symmetry properties of $\tilde{S}_{ij}(q)$ to equation (17), we obtain

$$\delta n_i(q) = -\beta \sum_{k=1}^{m-1} \tilde{S}_{ik}(q)[U_k(q) - U_m(q)] \tag{18}$$

From equation (18) we note that in general δn_1 (or $\delta n_{\rm A,C}$) is not the same as δn_3 (or $\delta n_{\rm A,H}$), and that δn_2 is not necessarily the same as δ_{n4}. In this study, equation (15) was obtained from (1) specific relationships of χ_{ij} (i.e. $\chi_{12} = \chi_{14} = \chi_{23} = \chi_{34} = \chi$, $\chi_{13} = \chi_{24} = 0$), (2) $a_1 = a_3$, $a_2 = a_4$, (3) incompressibility constraint and (4) symmetric properties of $S_{ij}(q)$. Of course, when any of these requirements is not satisfied, the scattering intensity $I(q)$ cannot be given by equation (15). Note further that if $S_{\rm AB}(q)$ in equation (16e) is replaced by $S_{12}(q) + S_{34}(q)$, equation (15) can be used to calculate $I(q)$ for binary mixtures of two block copolymers having the same constituent components, $(\text{A-}block\text{-B})_1/(\text{A-}block\text{-B})_2$.

Let us consider the spinodal curves for the macrophase separation in the (A-*block*-B)/(B-*ran*-C)/(A-*ran*-D) system. Using relationships of $F(q^* = 0) = 0$ and $W(q^* = 0) = 0$, the spinodal curves of the macrophase separation for this system can be obtained from equation (7):

$$\begin{aligned} &1/(N_{\rm I}N_{\rm II}\phi_{\rm I}\phi_{\rm II}) + 1/(N_{\rm I}N_{\rm III}\phi_{\rm I}\phi_{\rm III}) + 1/(N_{\rm II}N_{\rm III}\phi_{\rm II}\phi_{\rm III}) \\ &\quad - 2[\chi_{\rm I,II}/(N_{\rm III}\phi_{\rm III}) + \chi_{\rm I,III}/(N_{\rm II}\phi_{\rm II}) + \chi_{\rm II,III}/(N_{\rm I}\phi_{\rm I})] \\ &\quad + 2(\chi_{\rm I,II}\chi_{\rm I,III} + \chi_{\rm I,II}\chi_{\rm II,III} + \chi_{\rm I,III}\chi_{\rm II,III}) \\ &\quad - [(\chi_{\rm I,II})^2 + (\chi_{\rm I,III})^2 + (\chi_{\rm II,III})^2] = 0 \end{aligned} \tag{19}$$

where

$$\begin{aligned} \chi_{\rm I,II} = {}& f_{\rm I}(1-\psi_{\rm II})\chi_{13} + (1 - f_{\rm I} - \psi_{\rm II})(1-\psi_{\rm II})\chi_{23} \\ & - f_{\rm I}(1 - f_{\rm I} - \psi_{\rm II})\chi_{12} \end{aligned} \tag{20a}$$

$$\begin{aligned} \chi_{\rm I,III} = {}& (f_{\rm I} - \psi_{\rm III})(1-\psi_{\rm III})\chi_{14} + (1 - f_{\rm I})(1-\psi_{\rm III})\chi_{24} \\ & - (1 - f_{\rm I})(f_{\rm I} - \psi_{\rm III})\chi_{12} \end{aligned} \tag{20b}$$

$$\begin{aligned} \chi_{\rm II,III} = {}& \psi_{\rm II}\psi_{\rm III}\chi_{12} + (1-\psi_{\rm II})\psi_{\rm III}\chi_{13} + \psi_{\rm II}(1-\psi_{\rm III})\chi_{24} \\ & + (1-\psi_{\rm II})(1-\psi_{\rm III})\chi_{34} - \psi_{\rm II}(1-\psi_{\rm II})\chi_{23} \\ & - \psi_{\rm III}(1-\psi_{\rm III})\chi_{14} \end{aligned} \tag{20c}$$

Here, subscripts 1–4 in χ represent the monomers A–D, while the subscripts I–III in χ represent A-*block*-B, B-*ran*-C, and A-*ran*-D copolymers. Note that equations (19) and (20) can also be used to calculate the spinodal points of an (A-*ran*-B)/(B-*ran*-C)/(A-*ran*-D) blend since spinodal points for macrophase separation of an A-*block*-B copolymer are the same as those of an A-*ran*-B copolymer when the volume fraction of A in (A-*block*-B) is equal to that in (A-*ran*-B).

Let us first consider a special case for an (A-*block*-B)/(B-*ran*-C)/(A-*ran*-D) mixture where $\psi_{\rm II} = \psi_{\rm III} = 0$, $\chi_{13} = \chi_{24} = 0$, and $\chi_{12} = \chi_{14} = \chi_{23} = \chi_{34} = \chi$ which represents as (A-*block*-B)/A/B mixture. For this mixture, from equations (19) and (20) $(\chi N_{\rm I})_{\rm s,macro}$ is given by:

$$\begin{aligned} (\chi N_{\rm I})_{\rm s,macro} = {}& [1/(r_{\rm II}\phi_{\rm I}\phi_{\rm II}) + 1/(r_{\rm III}\phi_{\rm I}\phi_{\rm III}) + 1/(r_{\rm II}r_{\rm III}\phi_{\rm II}\phi_{\rm III})]/ \\ & \{2[1/\phi_{\rm I} + f_{\rm I}^2/(r_{\rm II}\phi_{\rm II}) + (1-f_{\rm I})^2/(r_{\rm III}\phi_{\rm III})]\} \end{aligned} \tag{21}$$

where

$$r_{\rm II} = N_{\rm II}/N_{\rm I} \quad \text{and} \quad r_{\rm III} = N_{\rm III}/N_{\rm I} \tag{22}$$

The optimum value of $f_{\rm I}$, $f_{\rm I,max}$, at which $(\chi N_{\rm I})_{\rm s,macro}$ becomes the maximum for given $r_{\rm II}$, $r_{\rm III}$, $\phi_{\rm II}$ and $\phi_{\rm III}$, can be obtained from:

$$\begin{aligned} [\partial(\chi N_{\rm I})_{\rm s,macro}/\partial f_{\rm I}] = {}& 2g(r,\phi)[-f_{\rm I}/(r_{\rm II}\phi_{\rm II}) \\ & + (1-f_{\rm I})/(r_{\rm III}\phi_{\rm III})] = 0 \end{aligned} \tag{23}$$

where

$$\begin{aligned} g(r,\phi) = {}& [1/(r_{\rm II}\phi_{\rm I}\phi_{\rm II}) + 1/(r_{\rm III}\phi_{\rm I}\phi_{\rm III}) + 1/(r_{\rm II}r_{\rm III}\phi_{\rm II}\phi_{\rm III})]/ \\ & \{2[1/\phi_{\rm I} + f_{\rm I}^2/(r_{\rm II}\phi_{\rm II}) + (1-f_{\rm I})^2/(r_{\rm III}\phi_{\rm III})]\}^2 \end{aligned} \tag{24}$$

From equations (23) and (24), $f_{\rm I,max}$ can easily be given by:

$$f_{\rm I,max} = 1/[1 + (r_{\rm III}\phi_{\rm III})/(r_{\rm II}\phi_{\rm II})] \tag{25}$$

It is of interest to see from equation (25) that a block copolymer with $f_I > 0.5$ becomes more efficient than a block copolymer with $f_I < 0.5$ in compatibilizing two immiscible polymer blends where homopolymer B becomes the disperse phase in the matrix of homopolymer A (or $\phi_{II} > \phi_{III}$) when the molecular weight of homopolymer A is similar to that of B. Conversely, when homopolymer A becomes the disperse phase, a block copolymer having a longer block of B is more efficient in compatibilization.

Recently Kim and co-workers[19] have studied the effect of the weight fraction of the polystyrene (PS) block, $w_{PS(b)}$, in a polystyrene-*block*-polyisoprene (SI) copolymer on the phase separation kinetics in a binary blend of PS and polyisoprene (PI). They found that for a blend where the weight fraction of PS is 0.81 (thus the PS phase becomes the matrix) a block copolymer having a greater value of $w_{PS(b)}$ is more efficient in retarding the macrophase separation of the mixture, indicating a better compatibilization in the PS/PI blend. Specifically, SI-112 copolymer having $w_{PS(b)} = 0.81$ is the most effective, SI-114 having $w_{PS(b)} = 0.6$ is intermediate, and SI-113 having $w_{PS(b)} = 0.35$ is the least effective in retarding the macrophase separation of the blend. Note that all three block copolymers have almost the same molecular weight (120000). Their experimental results are in agreement with the theoretical predictions of equation (25).

Also, the sign of $\partial(\chi N_I)_{s,macro}/\partial\phi_I$ becomes very important in judging the effectiveness of a compatibilizer of a block copolymer[20]. When $\partial(\chi N_I)_{s,macro}/\partial\phi_I > 0$, a block copolymer enhances compatibilization of two immiscible homopolymers, while a block copolymer does not play the role of compatibilizer if $\partial(\chi N_I)_{s,macro}/\partial\phi_I < 0$. It should be examined whether or not there exists a value of ϕ_I, ϕ_I^* above which $\partial(\chi N_I)_{s,macro}/\partial\phi_I < 0$ even if $\partial(\chi N_I)_{s,macro}/\partial\phi_I > 0$ at smaller values of ϕ_I. If there exists ϕ_I^*, the amount of block copolymer used must be smaller than ϕ_I^* in order to enhance compatibilization. The value of ϕ_I^* can be obtained from equation (21):

$$[\partial(\chi N_I)_{s,macro}/\partial\phi_I]_{\phi_I^*} = [(A - 1/r_{III})(\Phi - B/r_{II})(\phi_I^*)^2 - 2A(\Phi - B/r_{II})\phi_I^* + A(\Phi - B/r_{II}) + \Phi/r_{III}]/\{2r_{II}[h(\phi, r)]^2\} = 0 \qquad (26)$$

where

$$h(\phi, r) = (1 - \phi_I)[(1 - \phi_I)\Phi + B\phi_I/r_{II}] \qquad (27a)$$

$$A = 1 - [1 - (r_{II}/r_{III})]\phi_H \qquad (27b)$$

$$B = f_I^2(1 - \phi_H) + (1 - f_I)^2\phi_H r_{II}/r_{III} \qquad (27c)$$

$$\phi_H = \phi_{II}/(\phi_{II} + \phi_{III}) = \phi_{II}/(1 - \phi_I) \qquad (27d)$$

$$\Phi = \phi_H(1 - \phi_H) \qquad (27e)$$

From equation (26) ϕ_I^* is given by:

$$(\phi_I^*)_+ = [1 \pm (1 - DD)^{1/2}]/(1 - X^{-1}) \qquad (28)$$

where

$$DD = (1 - 1/X)(1 + 1/\{X[1 - B/(r_{II}\Phi)]\}) \qquad (29a)$$

$$X = r_{III}A \qquad (29b)$$

Note that DD in equation (29a) must be < 1 in order for ϕ_I^* appearing in equation (28) to become real. From the possible solutions given by equation (28), only $(\phi_I^*)_-$ is acceptable since $0 < \phi_I^* < 1$. For $X = 1$ (or $A = 1/r_{III}$), ϕ_I^* in equation (28) reduces to:

$$\phi_I^* = (1/2)\{1 + 1/[1 - B/(r_{II}\Phi)]\} \qquad (30)$$

From equations (28) and (29), one can obtain the following conditions for Φ defined by equation (27e) in order to satisfy the constraint $0 < (\phi_I^*)_- < 1$.

$$\Phi < \Phi^* = B/[r_{II}(1 + 1/X)] \qquad (31)$$

It can be seen from equation (26) that at $(\phi_I^*)_-$ $(\chi N_I)_{s,macro}$ has a minimum when $(A - 1/r_{III})(\Phi - B/r_{II})$ is positive, while this becomes the maximum when $(A - 1/r_{III})(\Phi - B/r_{II})$ becomes negative.

RESULTS AND DISCUSSION

(A-block-B)/A/B blend

For $f_I = 0.5$, and r_{II} $(= N_{II}/N_I) = r_{III}$ $(= N_{III}/N_I) = r$, plots of $(\chi N_I)_{s,macro}$ *versus* ϕ_H at various values of ϕ_I for different r are given in *Figure 1*. Here, N_I, N_{II} and N_{III} are the total degree of polymerization for A-*block*-B copolymer, homopolymer A and homopolymer B, respectively. In this situation from equations (27b) and (27c) we obtain $A = 1$

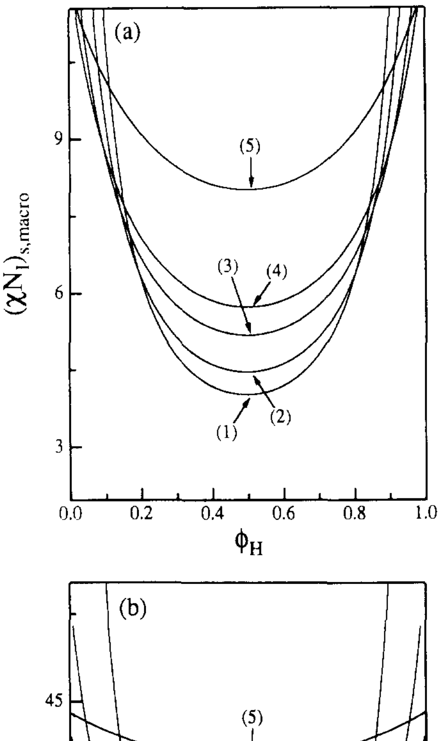

Figure 1 Plots of $(\chi N_I)_{s,macro}$ *versus* ϕ_H for the (A-*block*-B)/A/B blend where $f_I = 0.5$ and $r_{II} = r_{III} = r$ at various values of ϕ_I for two values of r: (a) $r = 0.5$, curve (1) for $\phi_I = 0$, curve (2) for $\phi_I = 0.1$, curve (3) for $\phi_I = 0.225$, curve (4) for $\phi_I = 0.3$, curve (5) for $\phi_I = 0.5$; (b) $r = 0.1$, curve (1) for $\phi_I = 0$, curve (2) for $\phi_I = 0.06$, curve (3) for $\phi_I = 0.1$, curve (4) for $\phi_I = 0.3$, curve (5) for $\phi_I = 0.5$

and $B=1/4$ regardless of r. It can be seen in *Figure 1a* (i.e. for $r=0.5$) that $(\chi N_I)_{s,macro}$ increases as ϕ_I increases for $\Phi>\Phi^*=1/6$ [or ϕ_H^* is either 0.211 or 0.788 obtained from equations (31) and (27e)]. When $\Phi<\Phi^*$, $(\chi N_I)_{s,macro}$ decreases until $\phi_I=(\phi_I^*)_-$, and increases again as ϕ_I increases. That is, $(\chi N_I)_{s,macro}$ exhibits a minimum at $(\phi_I^*)_-$ since $(A-1/r_{III})$ $(\Phi-B/r_{II})$ becomes positive due to the constraint of $\Phi\leqslant 1/4$ [see equation (27e)]. For instance, when $\Phi=0.1$ (i.e. $\phi_H=0.113$ and 0.887), $(\chi N_I)_{s,macro}$ decreases until ϕ_I reaches $(\phi_I^*)_-$ of 0.225 and then increases again as ϕ_I increases, which was previously demonstrated by Figure 3 in reference 20. When $\phi_H<0.211$ or >0.789, the added block copolymer to the mixture reduces $(\chi N_I)_{s,macro}$, which means that the block copolymer does not play the role of compatibilizer in the two homopolymers. Thus, if one wants to use a block copolymer having $f_I=0.5$ as an effective compatibilizer, the volume fraction of the homopolymer A in two immiscible homopolymers, ϕ_H, must be controlled between 0.211 and 0.789. Of course, a better compatibilization effect is expected when ϕ_H lies near 0.5.

When r is decreased from 0.5 to 0.1, plots of $(\chi N_I)_{s,macro}$ *versus* ϕ_H at various values of ϕ_I are given in *Figure 1b*, where Φ^* increases from 0.167 to 0.227. Note that the regions for ϕ_H where $(\chi N_I)_{s,macro}$ decreases initially with increasing ϕ_I, are expanded. For example, when ϕ_H is kept at 0.27, as ϕ_I increases $(\chi N_I)_{s,macro}$ decreases initially for $r=0.1$ while this increases for $r=0.5$. For smaller values of r, ϕ_H must be close to 0.5 in order to increase $(\chi N_I)_{s,macro}$ with increasing ϕ_I. Otherwise, a block copolymer will not become an effective compatibilizer in two immiscible homopolymer blends.

In order to study the effect of f_I on the compatibilization of this blend we consider an asymmetric value of f_I. For $f_I=0.8$ and $r_{II}=r_{III}=r$, plots of $(\chi N_I)_{s,macro}$ *versus* ϕ_H at various values of ϕ_I for different r are given in *Figure 2*. It can be seen in *Figure 2a* that for $r=0.5$, $(\chi N_I)_{s,macro}$ increases with ϕ_I for $0.448<\phi_H<0.952$. However, outside this region of ϕ_H, $(\chi N_I)_{s,macro}$ decreases initially, reaches a minimum, and then increases again with increasing ϕ_I. Note from *Figures 1a* and *2a* that the regions for ϕ_H, where $\partial(\chi N_I)_{s,macro}/\partial\phi_I<0$, move toward larger values of ϕ_H with increasing f_I. Thus, for larger values of f_I, ϕ_H must be >0.5 in order to have positive value of $\partial(\chi N_I)_{s,macro}/\partial\phi_I$. General trends of $(\chi N_I)_{s,macro}$ for $f_I=0.8$ at various values of r are similar to those for $f_I=0.5$ at the corresponding values of r. For instance, with decreasing r, the regions for ϕ_H, where $\partial(\chi N_I)_{s,macro}/\partial\phi_I<0$, are expanded. It should be pointed out that as ϕ_I increases, microphase separation rather than macrophase separation becomes a dominant mode. Therefore, the above analysis for $(\chi N_I)_{s,macro}$ might be applied to regions when $\phi_I<\phi_{I,C}$, above which $(\chi N_I)_{s,micro}<(\chi N_I)_{s,macro}$.

The plots of $(\chi N_I)_s$ *versus* ϕ_I at two different values of r, 0.5 and 0.1, are given in *Figure 3* where $\phi_{I,C}\approx 0.50$ when $r=0.5$ and $\phi_H=0.7$. It can be seen in *Figure 3* that $(\chi N_I)_{s,macro}$ for $\phi_H=0.7$ is always greater than that for $\phi_H=0.3$, indicating that a block copolymer having a longer block of A in the A-*block*-B copolymer will be more effective as a compatibilizer in the mixture of homopolymers A and B in which the homopolymer A becomes the matrix phase.

If r is further decreased from 0.5 to 0.1, plots of $(\chi N_I)_{s,macro}$ *versus* ϕ_H at various values of ϕ_I are given in *Figure 2b*. In this situation where $\phi_H<0.65$, $(\chi N_I)_{s,macro}$ decreases initially with increasing ϕ_I, which can also be seen in *Figure 3b*.

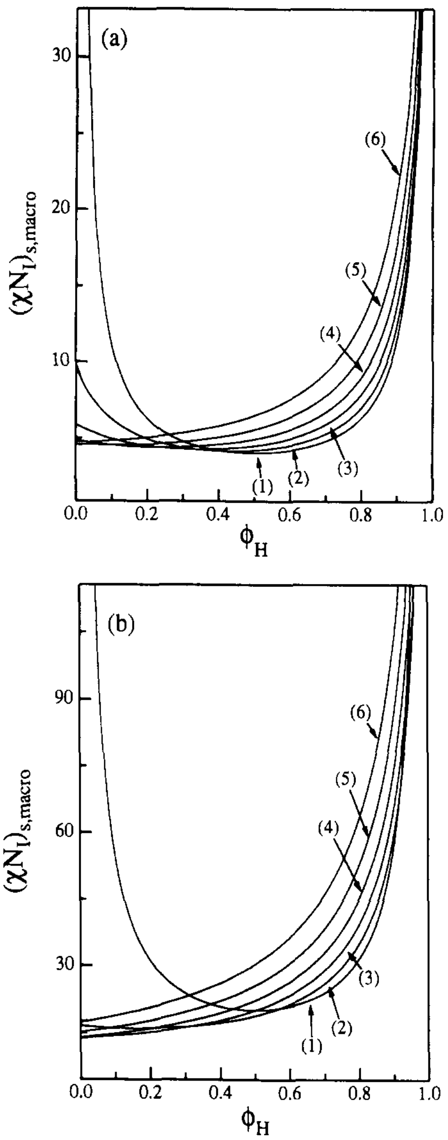

Figure 2 Plots of $(\chi N_I)_{s,macro}$ *versus* ϕ_H for the (A-*block*-B)/A/B blend where $f_I=0.8$ and $r_{II}=r_{III}=r$ at various values of ϕ_I for two values of r: (a) $r=0.5$, curve (1) for $\phi_I=0$, curve (2) for $\phi_I=0.1$, curve (3) for $\phi_I=0.2$, curve (4) for $\phi_I=0.3$, curve (5) for $\phi_I=0.4$, curve (6) for $\phi_I=0.5$; (b) $r=0.1$, curve (1) for $\phi_I=0$, curve (2) for $\phi_I=0.1$, curve (3) for $\phi_I=0.2$, curve (4) for $\phi_I=0.3$, curve (5) for $\phi_I=0.4$, curve (6) for $\phi_I=0.5$

(A-block-B)/C/D blend

Let us consider (A-*block*-B)/C/D mixtures where the chemical structures of C and D are different from those of A and B in the block copolymer, and six χ_{ij}s are assumed to be known. In this case, equation (19) becomes:

$$a[(\chi N_I)_{s,macro}]^2-b(\chi N_I)_{s,macro}+c=0 \quad (32)$$

where

$$a=2(R_{I,II}R_{I,III}+R_{I,II}R_{II,III}+R_{I,III}R_{II,III}) -[(R_{I,II})^2+(R_{I,III})^2+(R_{II,III})^2] \quad (33a)$$

$$b=2[R_{I,II}/(r_{III}\phi_{III})+R_{I,III}/(r_{II}\phi_{II})+R_{II,III}/\phi_I] \quad (33b)$$

$$c=1/(r_{II}\phi_I\phi_{II})+1/(r_{III}\phi_I\phi_{III})+1/(r_{II}r_{III}\phi_{II}\phi_{III}) \quad (33c)$$

in which

$$r_{II}=N_{II}/N_I;\quad r_{III}=N_{III}/N_I \quad (33d)$$

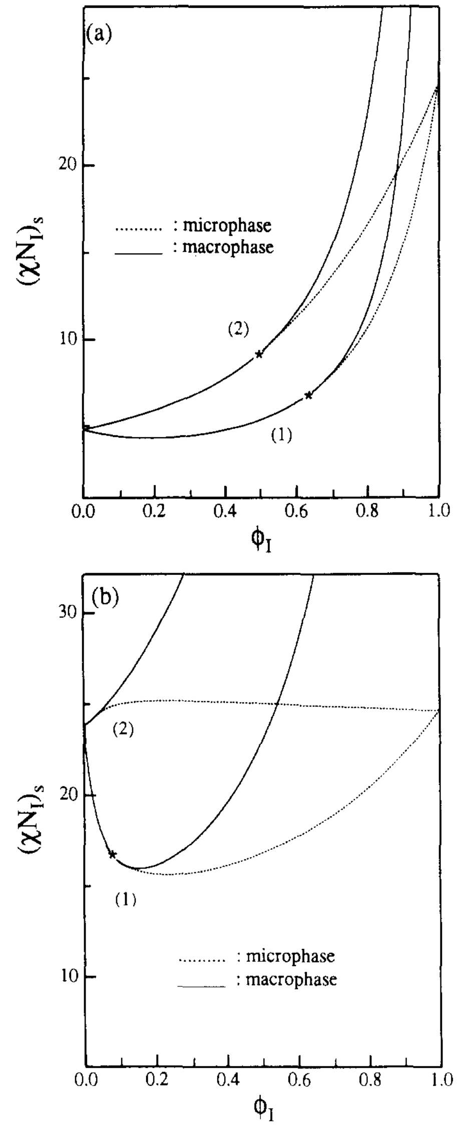

Figure 3 Plots of $(\chi N_I)_s$ *versus* ϕ_I for the (A-*block*-B)/A/B blend where $f_I = 0.8$ and $r_{II} = r_{III} = r$ at different values of ϕ_H for two values of r: (a) $r = 0.5$, curve (1) for $\phi_H = 0.3$, curve (2) for $\phi_H = 0.7$; (b) $r = 0.1$, curve (1) for $\phi_H = 0.3$, curve (2) for $\phi_H = 0.7$. The asterisks represent $\phi_{I,C}$ above which $(\chi N_I)_{s,\mathrm{micro}}$ is smaller than $(\chi N_I)_{s,\mathrm{macro}}$

$$R_{I,II} = \chi_{I,II}/\chi_{12}; \quad R_{I,III} = \chi_{I,III}/\chi_{12}; \quad R_{II,III} = \chi_{II,III}/\chi_{12} \qquad (33e)$$

and $\chi_{I,II}$, $\chi_{I,III}$ and $\chi_{II,III}$ are given by equations (20a), (20b) and (20c) with $\psi_{II} = \psi_{III} = 0$. Here, the subscripts I–III in equations (33) represent A-*block*-B copolymer, homopolymer C and homopolymer D, respectively.

It is of interest to see from equation (32) that unless a is not equal to zero, $(\chi N_I)_{s,\mathrm{macro}}$ has two values if $(b^2 - 4ac) > 0$. In order to test whether or not the two values of $(\chi N_I)_{s,\mathrm{macro}}$ represent the spinodal for macrophase separation, one must have plots of $F(q)$ *versus* q near $q = q^* = 0$ where $F(q)$ is given by equation (7). In order to have a physical significance of the spinodal point for macrophase separation, $F(q^* = 0)$ must be minimum at $q^* = 0$, in addition to $F(q^* = 0) = 0$.

Let us consider a special case where the interaction parameters are given by the following relationships:

$$\chi_{13} = \chi_{24} = \chi_{34} = \chi_{12} \qquad (34a)$$

$$\chi_{14} = \chi_{23} = \beta\chi_{12} \qquad (34b)$$

Although we are well aware of the fact that a blend system satisfying equation (34) may be very rare, we use this relation since this was considered by Vilgis and Noolandi[8].

For $f_I = 0.5$, $r_{II} = r_{III} = 0.5$, and $\beta = 2$, plots of $(\chi N_I)_{s,\mathrm{macro}}$ *versus* ϕ_H at various values of ϕ_I, and plots of $(\chi N_I)_s$ *versus* ϕ_I at two values of ϕ_H are given in *Figures 4a* and *b*, respectively. In this system there exist two values of $(\chi N_I)_{s,\mathrm{macro}}$, i.e. $(\chi N_I)^{(-)}_{s,\mathrm{macro}}$ and $(\chi N_I)^{(+)}_{s,\mathrm{macro}}$, where $(\chi N_I)^{(-)}_{s,\mathrm{macro}} < (\chi N_I)^{(+)}_{s,\mathrm{macro}}$, from equation (32). But, the value of $(\chi N_I)^{(-)}_{s,\mathrm{macro}}$ is taken as $(\chi N_I)_{s,\mathrm{macro}}$ in *Figures 4a* and *b* since at $(\chi N_I)^{(-)}_{s,\mathrm{macro}}$, $F(q^* = 0)$ becomes a minimum while $F(q = 0)$ at $(\chi N_I)^{(+)}_{s,\mathrm{macro}}$ becomes a maximum although $F(q = 0)$ becomes zero at both values of $(\chi N_I)_{s,\mathrm{macro}}$. This is demonstrated in *Figure 5*.

It is interesting to note in *Figure 4a* that $(\chi N_I)_{s,\mathrm{macro}}$ becomes a minimum at $\phi_H = 0.5$ for values of $\phi_I < 0.12$, while this becomes a maximum at $\phi_H = 0.5$ for larger values of ϕ_I. This indicates that the block copolymer becomes an effective compatibilizer for the mixtures of homopolymers C and D having ϕ_{II} equal to ϕ_{III} when

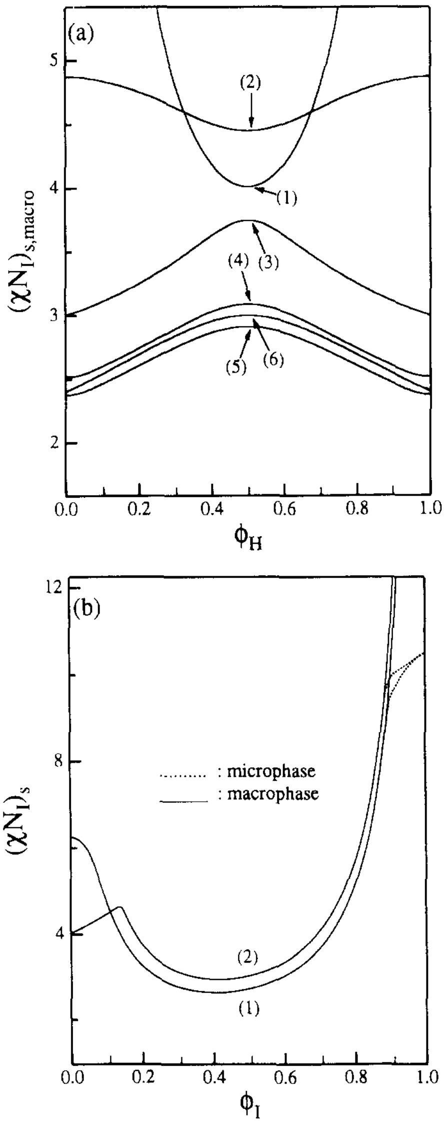

Figure 4 (a) Plots of $(\chi N_I)_{s,\mathrm{macro}}$ *versus* ϕ_H for the (A-*block*-B)/C/D blend where $f_I = 0.5$, $r_{II} = r_{III} = 0.5$ and $\beta = 2$ at various values of ϕ_I: curve (1) for $\phi_I = 0$; curve (2) for $\phi_I = 0.1$; curve (3) for $\phi_I = 0.2$; curve (4) for $\phi_I = 0.3$; curve (5) for $\phi_I = 0.4$; curve (6) for $\phi_I = 0.5$. (b) Plots of $(\chi N_I)_s$ *versus* ϕ_I at two values of ϕ_H: curve (1) for $\phi_H = 0.2$; curve (2) for $\phi_H = 0.5$

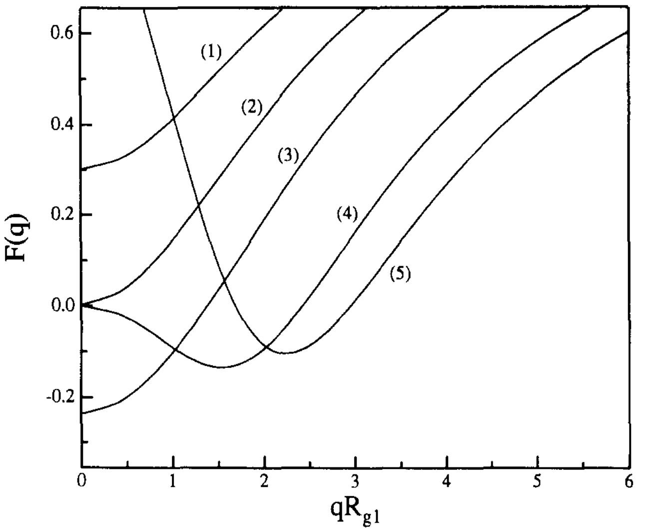

Figure 5 Plots of $F(q)$ *versus* qR_{g1} for the (A-*block*-B)/C/D blend where $f_I = 0.5$, $r_{II} = r_{III} = 0.5$, $\phi_I = 0.2$, $\phi_H = 0.2$ and $\beta = 2$ for various values of (χN_I): (1) 2.0; (2) 3.25; (3) 5.0; (4) 9.02; (5) 12. Here $(\chi N_I)^{(-)}_{s,\text{macro}} = 3.25$ and $(\chi N_I)^{(+)}_{s,\text{macro}} = 9.02$

the amount of block copolymer in the mixture is relatively large (say, $\phi_I > 0.13$). Also, it can be seen in *Figure 4b* that for $\phi_H = 0.2$, $(\chi N_I)_{s,\text{macro}}$ decreases until it reaches a minimum at $\phi_I = 0.4$, and increases again as ϕ_I increases. For larger values of ϕ_H with increasing ϕ_I, $(\chi N_I)_{s,\text{macro}}$ increases initially, reaches a maximum, then decreases until reaching a minimum point, and eventually increases. In the blend system considered above, macrophase separation dominates over microphase separation, since the latter only becomes significant for $\phi_I > \sim 0.9$.

When f_I is increased to 0.8, plots of $(\chi N_I)_s$ *versus* ϕ_I at various values of ϕ_H are given in *Figure 6*. Note that macrophase separation dominates microphase separation until ϕ_I reaches ~0.95 although this is not included due to lack of space. The general feature of $(\chi N_I)_s$ is very similar to that given in *Figure 4b*. For example, with increasing ϕ_I, $(\chi N_I)_{s,\text{macro}}$ increases initially at $\phi_H = 0.7$ and decreases at $\phi_H = 0.3$, very similar behaviour to that observed in the (A-*block*-B)/A/B mixtures (*Figure 3a*). However, if the behaviour of $(\chi N_I)_s$ for (A-*block*-B)/C/D mixtures is compared with that for (A-*block*-B)/A/B mixtures (*Figures 6* and *3a*), the copolymer in the former is not so good for compatibilization as that in the latter if the value of $(\chi N_I)_{s,\text{macro}}$ is only considered. When the value of β is decreased from 2.0 to 1.5, the plots of $(\chi N_I)_s$ *versus* ϕ_I at $\phi_H = 0.3$ and 0.7 are given in *Figure 6b*. When the value of β decreases, $(\chi N_I)_{s,\text{macro}}$ increases, and thus an enhanced compatibilization is expected.

It should be pointed out that, owing to the assumption of a mean field approximation, theoretical predictions made in this study are valid at weak segregation regimes where incompatibility between two homopolymers is not strong, but not at strong segregation regimes. Thus, in the strong segregation regime where a polymer blend becomes highly incompatible, the fact that the value of $(\chi N_I)_{s,\text{macro}}$ is increased does not necessarily mean an enhanced compatibilization. In such a situation one must consider the interfacial concentration of a block copolymer near the interface[6–8].

In other words, in the strong segregation regime the overall inhomogeneity increases at a given temperature as the value of $(\chi N_I)_{s,\text{macro}}$ decreases. However, a block copolymer can locate more easily at (or near) the interface of two immiscible polymers, resulting in a reduced interfacial tension of the mixtures. As can be seen in Figure 3 in reference 8, when the value of β is increased, the interfacial concentration of the block copolymer at (or near) the interface becomes greater. This means that as the value of β increases there is little chance that a block copolymer exists in the homopolymer phase, resulting in lower values of $(\chi N_I)_{s,\text{macro}}$ (*Figure 6*).

(*A*-block-*B*)/*C*/(*A*-ran-*D*) *blend*

Recently, many groups have studied the compatibilization effect of a block copolymer in a mixture of two homopolymers where at least one homopolymer is a random copolymer. For example, Stadler and coworkers[21,22] reported that poly(styrene-*block*-methyl methacrylate) (SM) can be used as a compatibilizer in a mixture of poly(1,4-dimethyl-2,6-phenylene ether) (PPE) and poly(styrene-*ran*-acrylonitrile) (PSAN). In this situation, the spinodal points for macrophase separation can

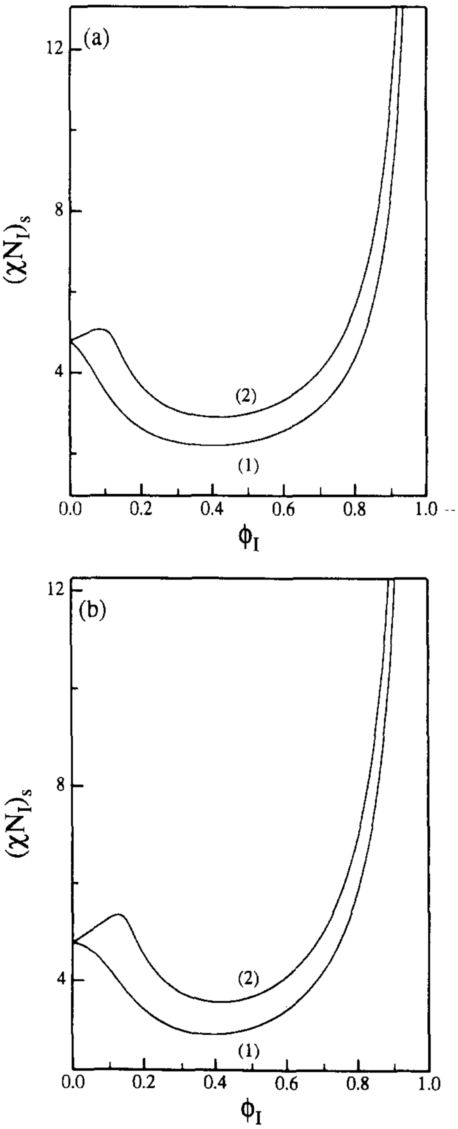

Figure 6 Plots of $(\chi N_I)_s$ *versus* ϕ_I for the (A-*block*-B)/C/D blend where $f_I = 0.8$, and $r_{II} = r_{III} = 0.5$ at two values of ϕ_H for different β: (a) $\beta = 2.0$, curve (1) for $\phi_H = 0.3$, curve (2) for $\phi_H = 0.7$; (b) $\beta = 1.5$, curve (1) for $\phi_H = 0.3$, curve (2) for $\phi_H = 0.7$

be obtained from equations (19) and (20) with $\psi_{\text{II}}=0$. The crucial step to obtain $(\chi N_{\text{I}})_{\text{s,macro}}$ from equations (19) and (20) is to have values of six interaction parameters, χ_{ij}s. Note that experimental data of χ_{ij} vary considerably when different experimental methods, for instance, turbidity measurement, small-angle neutron scattering (SANS) and the ellipsoidal method are employed[23]. In the present study the values of six χ_{ij}s were taken from various experimental studies (*Table 1*). Also, in order to change the weight fraction of each component in the mixtures to volume fraction, the density of each component in the blend was chosen from reference 28, i.e. $\rho_{\text{PS}}=1.05$, $\rho_{\text{PMMA}}=1.17$, $\rho_{\text{PPE}}=1.07$ and $\rho_{\text{PSAN}}=1.18\,\text{g}\,\text{cm}^{-3}$.

Plots of $(\chi N_{\text{I}})_{\text{s,macro}}$ *versus* ϕ_{H} $[=\phi_{\text{PPE}}/(\phi_{\text{PPE}}+\phi_{\text{PSAN}})]$ for $r_{\text{II}}(=N_{\text{II}}/N_{\text{I}})=0.25$, $r_{\text{III}}(=N_{\text{III}}/N_{\text{I}})=0.5$ and $\psi_{\text{III}}=0.77$ (i.e. 75 wt% PS in PSAN) are given in *Figure 7a* for $f_{\text{I}}=0.53$ (i.e. 50 wt% PS in SM), and in *Figure 7b* for $f_{\text{I}}=0.72$ (i.e. 70 wt% PS in SM). Here, the subscripts I, II, and III in N represent A-*block*-B, homopolymer C and A-*ran*-D copolymer, respectively. It can be seen from *Figure 7a* that with increasing ϕ_{I}, $(\chi N_{\text{I}})_{\text{s,macro}}$ decreases gradually until ϕ_{I} reaches ~0.3 and increases again. The values of $(\chi N_{\text{I}})_{\text{s,macro}}$ at any ϕ_{I} are less than those for mixtures without a block copolymer. As can be seen in *Figure 7b*, for $f_{\text{I}}=0.72$ $(\chi N_{\text{I}})_{\text{s,macro}}$ increases steadily with increasing ϕ_{I} in the regions of $0.38<\phi_{\text{H}}<0.7$. Thus, it can be concluded that at a given N_{I}, the block copolymers having larger PS block or larger f_{I} would be effective in compatibilization of the PPE and PSAN blend system

Table 1 Values of χ_{ij} used in the numerical computation

	S/AN	S/MMA	AN/MMA	S/PE	PE/MMA	PE/AN
χ_{ij}	1.14[a]	0.03[a]	0.69[a]	−0.1	0.48	1.49[b]
Ref.	24	24	24	25	26	27

[a] χ_{ij} were obtained from the reported values of B_{ij} ($B_{\text{S/AN}}=6.74$; $B_{\text{S/MMA}}=0.18$; $B_{\text{AN/MMA}}=4.11\,\text{cal}\,\text{cm}^{-3}$) in Table 4 of reference 24 using the relationship, $\chi_{ij}=B_{ij}V_{\text{ref}}/(RT)$. Here, $V_{\text{ref}}=100\,\text{cm}^3\,\text{mol}^{-1}$ and $T=298\,\text{K}$ were used

[b] $\chi_{\text{PE/AN}}$ is different from the value in reference 27 since it is obtained from equation (3) in reference 27 using $\chi_{\text{S/AN}}=1.15$ instead of $\chi_{\text{S/AN}}=0.17$ reported in reference 27

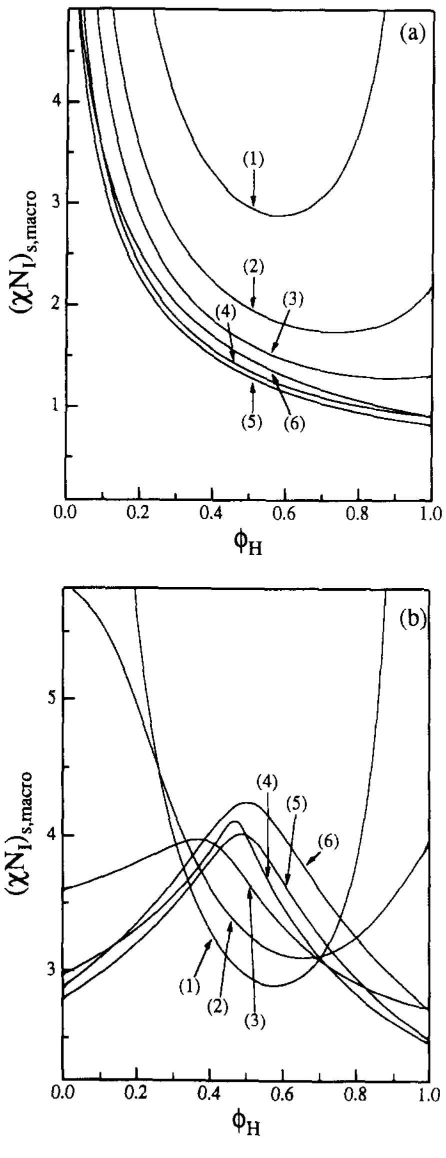

Figure 7 Plots of $(\chi N_{\text{I}})_{\text{s,macro}}$ *versus* ϕ_{H} for the (A-*block*-B)/C/(A-*ran*-D) blend, where $\psi_{\text{III}}=0.77$, $r_{\text{II}}=0.25$, $r_{\text{III}}=0.5$ and χ_{ij}s are given in *Table 1*, at various values of ϕ_{I} for two values of f_{I}: (a) $f_{\text{I}}=0.53$; curve (1) for $\phi_{\text{I}}=0$, curve (2) for $\phi_{\text{I}}=0.05$, curve (3) for $\phi_{\text{I}}=0.1$, curve (4) for $\phi_{\text{I}}=0.2$, curve (5) for $\phi_{\text{I}}=0.3$, curve (6) for $\phi_{\text{I}}=0.5$; (b) $f_{\text{I}}=0.72$, curve (1) for $\phi_{\text{I}}=0$, curve (2) for $\phi_{\text{I}}=0.1$, curve (3) for $\phi_{\text{I}}=0.2$, curve (4) for $\phi_{\text{I}}=0.3$, curve (5) for $\phi_{\text{I}}=0.4$, curve (6) for $\phi_{\text{I}}=0.5$

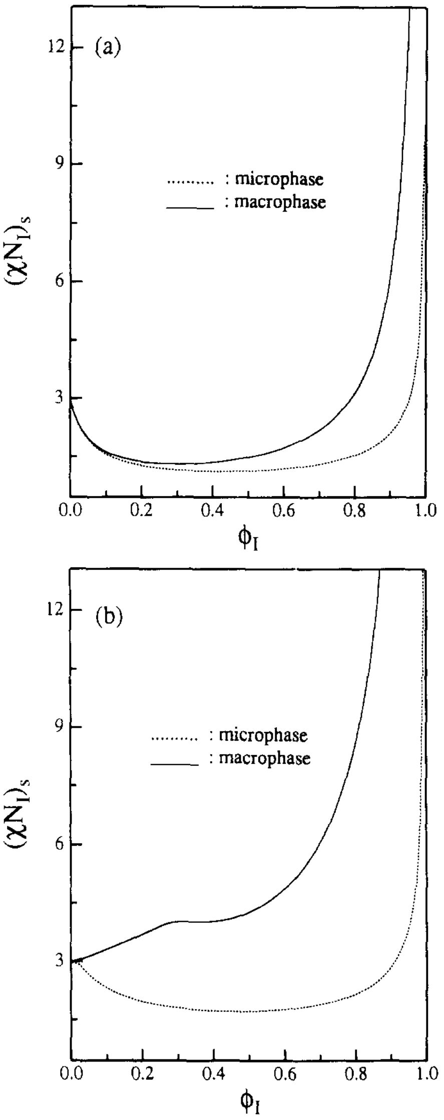

Figure 8 Plots of $(\chi N_{\text{I}})_{\text{s}}$ *versus* ϕ_{I} for the (A-*block*-B)/C/(A-*ran*-D) blend, where $\psi_{\text{III}}=0.77$, $\phi_{\text{H}}=0.5$, $r_{\text{II}}=0.25$, $r_{\text{III}}=0.5$ and χ_{ij}s are given in *Table 1*, at two values of f_{I}: (a) $f_{\text{I}}=0.53$; (b) $f_{\text{I}}=0.72$

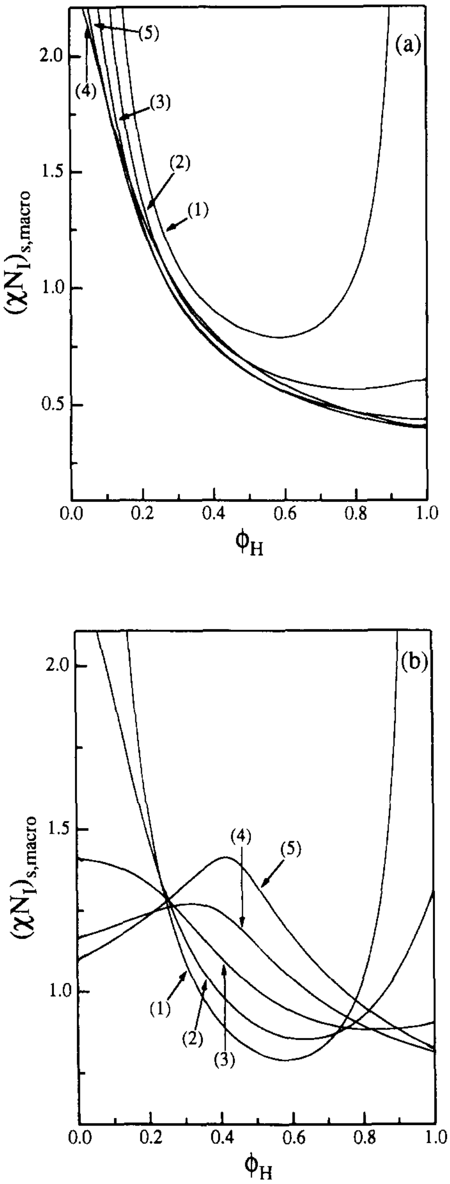

Figure 9 Plots of $(\chi N_I)_{s,macro}$ *versus* ϕ_H for the (A-*block*-B)/C/(A-*ran*-D) blend, where $\psi_{III}=0.63$, $r_{II}=0.25$, $r_{III}=0.5$ and χ_{ij}s are given in *Table 1*, at various values of ϕ_I for two values of f_I: (a) $f_I=0.22$, curve (1) for $\phi_I=0$, curve (2) for $\phi_I=0.1$, curve (3) for $\phi_I=0.2$, curve (4) for $\phi_I=0.3$, curve (5) for $\phi_I=0.4$; (b) $f_I=0.53$, curve (1) for $\phi_I=0$, curve (2) for $\phi_I=0.1$, curve (3) for $\phi_I=0.2$, curve (4) for $\phi_I=0.3$, curve (5) for $\phi_I=0.4$

if $(\chi N_I)_{s,macro}$ is only considered. It should be mentioned that in this blend microphase separation becomes dominant over macrophase separation, as can be seen in *Figure 8*.

In order to study the effect of weight per cent of PAN in PSAN on compatibilization of the PAN and PSAN blend, we consider the PSAN homopolymer with 40 wt% PAN. *Figures 9a* and *b* show $(\chi N_I)_{s,macro}$ varies with ϕ_H for two values of f_I. It can be seen in *Figure 9a* that for $f_I=0.22$, $(\chi N_I)_{s,macro}$ decreases initially then increases again with increasing ϕ_I. However, for $f_I=0.53$ $(\chi N_I)_{s,macro}$ increases with ϕ_I as can be seen in *Figure 9b*, although this value is less than that for PSAN with 20 wt% PAN (*Figure 7a*). This suggests that a blend of PSAN with a smaller amount of PAN and PPE is more miscible than a blend of PSAN with a larger amount of PAN and PPE, which is consistent with the experimental results of Stadler and co-workers[21,22]. However, their studies do not consider the effect of volume fraction (or block length) of PS in SM on compatibilization of PPE and PSAN when the total number of segments (or roughly, the total molecular weights) of SM is kept the same. Thus, the above prediction that a block copolymer with a larger amount of PS is more effective in compatibilization in the PPE and PSAN blend than one with a smaller amount of PS can be tested by a careful experiment.

CONCLUSIONS

In this paper, we have considered the stability limit of a four-component polymer system, an (A-*block*-B)/(B-*ran*-C)/(A-*ran*-D) mixture, using the structure factors, $\tilde{S}_{ij}(q)$, which were obtained from the random phase approximation and incompressibility constraint. We then discussed the effect of the volume fraction of A, f_I, of the A-*block*-B copolymer on compatibilization of two immiscible random copolymers, by investigating the values of spinodal points of macrophase separation, $(\chi N_I)_{s,macro}$, for three four-component polymer systems, namely, (1) mixtures of an A-*block*-B copolymer and two homopolymers A and B, (2) mixtures of an A-*block*-B copolymer, and two homopolymers C and D, and (3) mixtures of an A-*block*-B copolymer, a homopolymer C and A-*ran*-D copolymer. We have found that for the (A-*block*-B)/A/B system, the optimum value of f_I at which $(\chi N_I)_{s,macro}$ becomes a maximum at a given N_I can change with the weight fraction of the homopolymer A in the mixture of two homopolymers. A block copolymer having $f_I>0.5$ is more efficient than one having $f_I<0.5$ in increasing $(\chi N_I)_{s,macro}$, and thus in increasing compatibilization, for a mixture where homopolymer B becomes a disperse phase in the matrix of homopolymer A. This theoretical prediction is in agreement with the experimental results of the PS/PI blend system having SI copolymer as a compatibilizer[19].

The effect of f_I on $(\chi N_I)_{s,macro}$ for the (A-*block*-B)/C/(A-*ran*-D) system has also been studied. Again, depending on the value of f_I, $(\chi N_I)_{s,macro}$ increases with increasing weight fraction of the block copolymer.

It should be pointed out that owing to the assumption of a mean field approximation theoretical predictions made in this study would be more valid near the weak segregation regime of a blend than near the strong segregation regime. Thus, in the strong segregation regime (or highly incompatible polymer blend) one must include the interfacial concentration of a block copolymer near the interface in addition to the above approach.

Finally, it is suggested that since the analysis here predicts only spinodal points (or stability limits) of a multicomponent system, (A-*block*-B)/C/D mixtures, it should be expanded to predict the phase diagram for this system which is very important in the preparation of a polymer blend.

ACKNOWLEDGEMENTS

I wish to acknowledge that Mr Hee-Hyun Lee prepared the drawings of all the figures in this paper. This work was supported in part by the Research Institute of Science and Technology (No. R94048), Pohang, Korea.

REFERENCES

1 Utracki, L. A. 'Polymer Alloys and Blends', Oxford University Press, New York, 1989

2 Fayt, R. and Teyssie, Ph. *Polym. Eng. Sci.* 1990, **30**, 937

3 Sakellariou, P., Eastmond, G. C. and Miles, I. S. *Polymer* 1991, **32**, 2351

4 Thomas, S. and Prud'homme, R. E. *Polymer* 1992, **33**, 4260

5 Adedeji, A. and Jamieson, A. M. *Polymer* 1993, **34**, 5038

6 Noolandi, J. *Polym. Eng. Sci.* 1984, **24**, 70

7 Noolandi, J. and Hong, K. M. *Macromolecules* 1982, **15**, 382; 1984, **17**, 1531

8 Vilgis, T. A. and Noolandi, J. *Macromolecules* 1990, **23**, 2341

9 Leibler, L. *Macromol. Chem. Macromol. Symp.* 1988, **16**, 1

10 Shull, K. K. and Kramer, E. J. *Macromolecules* 1990, **23**, 4769

11 Banaszak, M. and Whitmore, M. D. *Macromolecules* 1992, **25**, 249, 2351

12 Kim, J. K., Kimishima, K. and Hashimoto, T. *Macromolecules* 1993, **26**, 125

13 Mori, K., Tanaka, H. and Hashimoto, T. *Macromolecules* 1987, **20**, 381

14 Hashimoto, T., Koizumi, S. and Hasegawa, H. *Macromolecules* 1994, **27**, 1562

15 Leibler, L. and Benoit, H. *Polymer* 1981, **22**, 195

16 de Gennes, P. G. *J. Phys. (Paris)* 1970, **31**, 235

17 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, New York, 1979

18 Leibler, L. *Macromolecules* 1980, **13**, 1602

19 Kim, J., Lee, S. W., Ahn, J. B., Park, D. W. and Lee, D. S. 'Proceedings of 35th IUPAC Symposium', Akron, July 1994, p. 1013

20 Tanaka, H. and Hashimoto, T. *Polym. Commun.* 1988, **29**, 212

21 Auschra, C., Stadler, R. and Voigt-Martin, I. G. *Polymer* 1993, **34**, 2081, 2094

22 Auschra, C. and Stadler, R. *Macromolecules* 1993, **26**, 6364

23 Kressler, J., Higashida, N., Shimomai, K., Inoue, T. and Ougizawa, T. *Macromolecules* 1994, **27**, 2448

24 Gan, P. P., Paul, D. R. and Padwa, A. R. *Polymer* 1994, **35**, 1487

25 Kambour, R. P., Bendler, J. T. and Bopp, R. C. *Macromolecules* 1983, **16**, 753

26 Kressler, J., Kammer, H. W., Morgenstern, U., Litauszki, B., Berger, W. and Karasz, F. E. *Makromol. Chem.* 1990, **191**, 243

27 Kressler, J. and Kammer, H. W. *Makromol. Chem. Macromol. Symp.* 1988, **18**, 63

28 Van Krevelen, S. W. 'Properties of Polymer', 3rd edn, Elsevier, New York, 1990, pp. 790–800

APPENDIX

Derivation of equation (15)

Consider an (A-*block*-B)/(B-*ran*-C)/(A-*ran*-D) mixture with $\psi_{\mathrm{II}} = \psi_{\mathrm{III}} = 0$, which reduces to an (A-*block*-B)/C/D mixture, for which the following two equations are satisfied.

$$\chi_{12} = \chi_{14} = \chi_{23} = \chi_{34} = \chi; \; \chi_{13} = \chi_{24} = 0 \qquad \text{(A1)}$$

$$a_1 = a_3; \; a_2 = a_4 \qquad \text{(A2)}$$

In this case $F(q)$ in equation (7) and $\tilde{S}_{ij}(q)$ in equation (9) become:

$$F(q) = 1 + [\bar{S}_{12}(q) + \bar{S}_{14}(q) + \bar{S}_{23}(q) + \bar{S}_{34}(q)]\chi \qquad \text{(A3)}$$

$$\tilde{S}_{\alpha\beta}(q) = [\bar{S}_{\alpha\beta}(q) + 2D^*_{\alpha\beta}(q)]/F(q) \qquad \text{(A4)}$$

where

$$D^*_{\alpha\beta}(q) = 2\sum_{k,l}^{4} D_{2,\alpha\beta kl}(q)\chi_{kl} \qquad \text{(A5)}$$

In the derivation of equations (A3) and (A4), the following relationships were used:

$$\sum_{\substack{i,j\\k,l}}^{4} D_{2,ijkl}(q)\chi_{ij}\chi_{kl} = 0 \qquad \text{(A6)}$$

$$\chi_{\alpha\beta,2} = 0\,(\alpha = 1,2,3,4; \; \beta = 1,2,3,4); \; \chi_D = 0 \qquad \text{(A7)}$$

From equations (A1), (A5) and (8c) we have the following relationships:

$$D^*_{11}(q) = D^*_{33}(q) = -D^*_{13}(q) \qquad \text{(A8a)}$$

$$D^*_{22}(q) = D^*_{44}(q) = -D^*_{24}(q) \qquad \text{(A8b)}$$

$$D^*_{12}(q) = D^*_{34}(q) = -D^*_{14}(q) = -D^*_{23}(q) \qquad \text{(A8c)}$$

Substitution of equations (A3), (A4), (A8), and (9) into equation (11) gives:

$$\begin{aligned} I(q) \sim (a_1 - a_2)^2[\bar{S}_{11}(q) + 2\bar{S}_{13}(q) + \bar{S}_{33}(q)]/ \\ \{1 + 2[\bar{S}_{12}(q) + \bar{S}_{14}(q) + \bar{S}_{23}(q) + \bar{S}_{34}(q)]\chi\} \end{aligned} \qquad \text{(A9)}$$

Also, from equations (6) and (8b), we have:

$$\begin{aligned} &\bar{S}_{11}(q) + 2\bar{S}_{13}(q) + \bar{S}_{33}(q) \\ &\quad = \{[S_{11}(q) + S_{33}(q)][S_{22}(q) + S_{44}(q)] \\ &\qquad - [S_{12}(q)]^2\}/S_4(q) \end{aligned} \qquad \text{(A10)}$$

and

$$\begin{aligned} &1 + 2[\bar{S}_{12}(q) + \bar{S}_{14}(q) + \bar{S}_{23}(q) + \bar{S}_{34}(q)]\chi \\ &\quad = \{S_4(q) - 2[(S_{11}(q) + S_{33}(q))(S_{22}(q) \\ &\qquad + S_{44}(q)) - S_{12}^2(q)]\chi\}/S_4(q) \end{aligned} \qquad \text{(A11)}$$

Finally, substitution of equations (A10) and (A11) into equation (A9) gives equation (15).