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Thermodynamics of solubilization of functional copolymers in the grafted shell of core–shell impact modifiers: 1. Theory

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A thermodynamic model is developed to investigate the extent to which a free polymer, B, can be solubilized into a thin shell layer of grafted A chains of core–shell impact modifier particles. When there is a favourable enthalpy of mixing, free chains of A and B are fully miscible. However, when the A chains are grafted to a surface, only limited amounts of B can be solubilized into this grafted shell due to the conformational constraints. The model assumes a planar shell that only swells in one dimension and ignores any interfacial effects. While enthalpic and entropic terms in the free energy expression favour solubilization, conformational changes for both the free B chains and grafted A chains oppose solubilization. The extent of equilibrium solubilization of B in the shell of A, $(\phi_B)_s$, results from balancing these competing effects. Significant levels of solubilization can occur if the interaction energy between A and B is sufficiently favourable. How favourable the interaction must be depends on the molecular weights of A and B and the initial shell thickness. In general, the model predicts that solubilization is favoured when the B chains are small and the A chains are large and initially exist in a thin shell layer.

(Keywords: thermodynamics; styrene/maleic anhydride copolymers; core–shell impact modifiers)

INTRODUCTION

Recent work[1] has shown that styrene/maleic anhydride copolymers (SMA) aid the dispersion of emulsion-made core–shell impact modifiers into a nylon 6 matrix, thereby leading to toughened blends. The impact modifiers of interest have a rubber core to which a hard shell of poly(methyl methacrylate) (PMMA) is grafted, and particle diameters generally range from 0.1 to 0.6 μm. The proposed rationale for this approach to dispersal is that the styrene/maleic anhydride copolymers used, typically containing 8 or 14% by weight maleic anhydride (SMA8 or SMA14), are miscible with PMMA[2] and can be solubilized into the shell of the impact modifier particles and that these SMA chains can react with the amine end-groups of the polyamides via the anhydride units at the particle–matrix interface. The *in situ* graft copolymers formed during melt extrusion thus have a physical interaction with the impact modifier particles and a chemical interaction with the nylon 6 matrix. This 'compatibilization' effect leads to improved dispersion of the core–shell particles in the nylon 6 matrix and provides a mechanism for strengthening this interface. Rheological changes that accompany the grafting reaction also play a role in the morphology generated in such blends[3].

The PMMA shell on these particles is very thin; perhaps smaller than the unperturbed dimension of the grafted chains. The thinness of this layer and the fact that the PMMA chains are not free influence the extent to which SMA chains can be solubilized. In general, the conditions for miscibility of two polymers A and B become more stringent when one of the component chains exists in a constrained environment relative to the usual case where both chains are in the free or unconstrained state. For example, even though poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polystyrene (PS) homopolymers are completely miscible for all molecular weights[4–6], the constraints that exist in styrene block copolymers may prevent PPO from forming a single phase with the PS segments of the copolymer[7–15]. Recently, Tucker and Paul[14] developed a model for estimating the extent to which a homopolymer, like PPO, can form a mixed phase or be solubilized into the microdomains of styrene segments in block copolymers. This situation is very different from the classical problem of solubilizing PS homopolymer into such microdomains because of the favourable heat of mixing of PPO with PS. Tucker and Paul considered both the favourable enthalpic and entropic terms for mixing, as well as the unfavourable entropy terms due to conformational changes of the homopolymer and the copolymer segments during mixing. While the model is simple, it does agree with the experimental trends for solubilization of PPO into styrene-based block copolymers at least in a semiquantitative manner.

For the core–shell impact modifiers of interest here, the rubber core can be regarded as an impenetrable wall

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and the PMMA chains are like a layer of polymer brush where one end of each chain is grafted to this wall. Since about 1977, there has been an extensive discussion in the literature on polymer brushes showing their quite different conformational properties and mixing behaviour compared with 'free' polymer chains[16–22]. Even though SMA copolymers may be completely miscible with PMMA in the free state, the geometrical constraints of the shell layer limit the amount of SMA that can be solubilized into the grafted PMMA. In this paper, we theoretically examine the extent to which the conformational issues limit the solubilization of free polymer chains into the grafted chains forming the shell of core–shell impact modifiers. For this, we will use the approach employed by Tucker and Paul to develop a thermodynamic model for the solubilization of SMA copolymers in the PMMA grafted chains of core–shell impact modifiers, or any similar system. To apply this model requires information about the polymer–polymer (i.e. SMA–PMMA) interaction energy which, in principle, can be evaluated from separate experiments on blends where all chains are free. Other factors that can influence the solubilization limit like the grafted (PMMA) chain length, the molecular size of the added chains (SMA) and the shell thickness are included in the model. In the companion paper[23], we experimentally explore the extent to which SMA is solubilized into the shell of some particular core–shell impact modifiers. This is done by examining the glass transition behaviour of blends prepared by melt mixing and by transmission electron microscopy techniques.

THEORY

Figure 1 shows an idealization of a core–shell impact modifier particle. The thickness of the shell, $L_0 = R_s - R_c$, can be related to the relative mass of the shell W_s, to that of the core W_c, and the radii of the particle and core as follows

$$\frac{W_s}{W_c} = \frac{\rho_s}{\rho_c}\frac{(R_s^3 - R_c^3)}{R_c^3} \tag{1}$$

where ρ_s and ρ_c are the densities of core and shell materials. Rearrangement gives

$$\frac{R_s}{R_c} = \left(1 + \frac{\rho_c}{\rho_s}\frac{W_s}{W_c}\right)^{1/3} \tag{2}$$

$$L_0 = R_s\left[1 - \left(1 + \frac{\rho_c}{\rho_s}\frac{W_s}{W_c}\right)^{-1/3}\right] = R_c\left[\left(1 + \frac{\rho_c}{\rho_s}\frac{W_s}{W_c}\right)^{1/3} - 1\right] \tag{3}$$

Table 1 shows the shell thickness calculated from equation (3) for a wide range of R_s and typical W_s/W_c values[24]; the thickness varies from 60 to >300 Å. For one of the core–shell particles employed in the companion paper[23], $R_s = 1650$ Å, $W_s/W_c = 20/80$ and the calculated shell thickness is 110 Å. Most of the subsequent calculations are based on this value of L_0; however, the effect of varying shell thickness is also considered. Because the thickness is typically small relative to the radius of the particle, a planar approximation of the shell is a justifiable assumption that simplifies the following development.

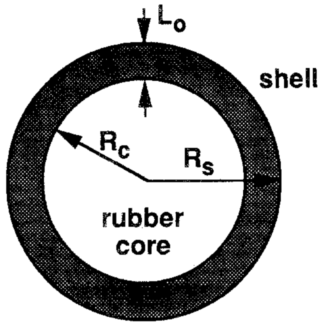

Figure 1 Schematic illustration of an emulsion-made core–shell impact modifier particle

Table 1 Shell thickness (L_0) of some typical core–shell impact modifiers[a]

	R_s (Å)			
W_s/W_c	900	1650	2000	3000
20/80	60	110	133	199
30/70	94	172	209	314

[a] Assumes $\rho_s = 1.19$ and $\rho_c = 1.09\,\mathrm{g\,cm^{-3}}$ for all calculations based on a PMMA shell and an n-butyl acrylate rubber core

The dimension of free Gaussian chains in the melt or unperturbed state can be expressed by the end-to-end distance, in terms of the characteristic ratio C_∞ for a coiled chain, the number of bonds n and the bond length l

$$\langle r^2\rangle_0 = C_\infty n l^2 = C_\infty\left(2\frac{M}{M_0}\right)l^2 = k_0 M \tag{4}$$

where M_0 is the monomer molecular weight [equation (4) assumes two bonds per monomer unit] and M is the chain molecular weight. The conformation of chains grafted to a planar surface may be considerably different from that of the unperturbed free chains for several reasons (see *Figure 2*). First, attaching one end to a planar surface forbids some conformations that a free chain is able to assume. According to DiMarzio[25], the mean square end-to-end distance perpendicular to the graft surface, $\langle z^2\rangle_B$, is twice the value in the absence of the boundary, $\langle z^2\rangle_0$. Since $\langle z^2\rangle_0 = \langle x^2\rangle_0 = \langle y^2\rangle_0 = 1/3\langle r^2\rangle_0$, the relationship of $\langle z^2\rangle_B$ to M follows

$$\langle z^2\rangle_B = 2\langle z^2\rangle_0 = 2/3 k_0 M \tag{5}$$

Here, we define the characteristic dimension of the grafted chain R_0 as the perpendicular end-to-end distance of a single grafted chain, unperturbed by thermodynamic effects or other constraints, i.e. $R_0^2 = \langle z^2\rangle_B$. *Table 2* shows how R_0 of grafted PMMA chains varies for typical molecular weights employed in the materials of interest.

The thickness of a grafted layer, in the absence of any diluent, must conform to the density considerations embodied in equation (3). Thus, the calculated thickness of a uniform shell layer may be greater or less than the natural dimension R_0 determined by conformational considerations of a single grafted chain, as suggested in *Figure 2*. When the shell consists of many short grafts, the A chains will be stretched ($L_0 > R_0$) while for a shell

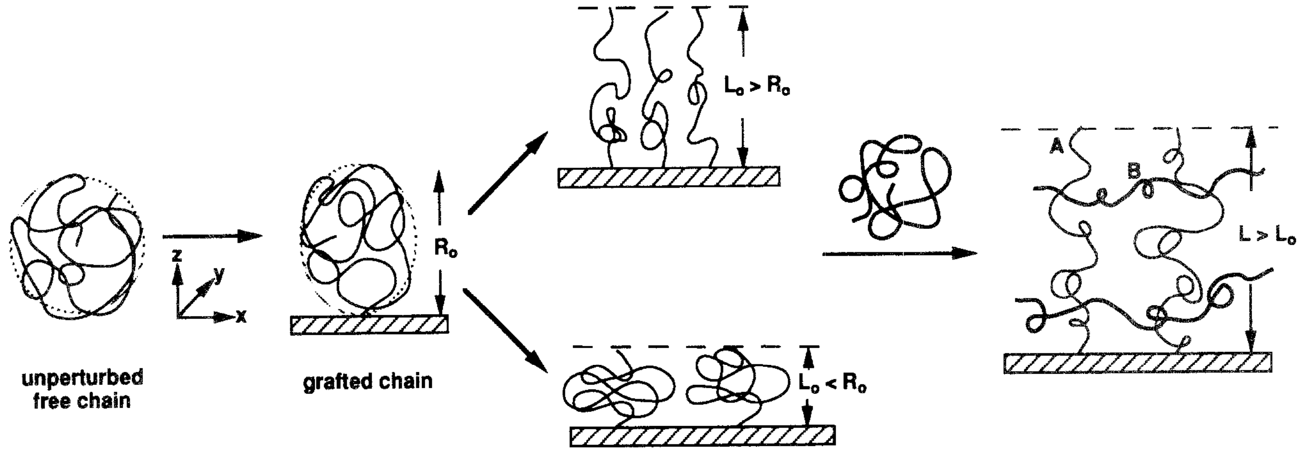

Figure 2 Schematic illustration of the conformational change of a polymer chain (A) due to grafting, change in grafting density, and swelling by another polymer (B)

Table 2 Perpendicular end-to-end distance of grafted PMMA chains of different molecular weights[a]

M_{PMMA}	10 000	30 000	80 000	200 000	300 000	600 000
R_0 (Å)	47	81	132	209	256	362

[a] Calculated from equation (5) with $k_0 = 0.327$ for PMMA, see ref. 26

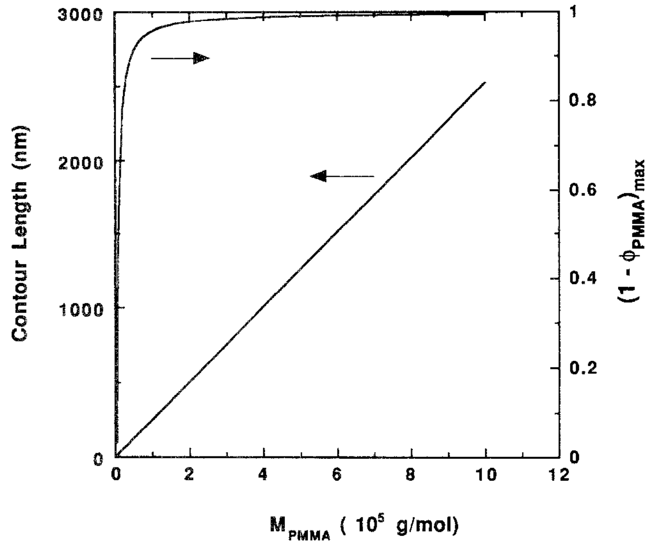

Figure 3 The maximum possible extent of swelling calculated from the contour length for PMMA chains as a function of molecular weight

comprising a smaller number of long grafts, the A chains will be compressed ($L_0 < R_0$) in the direction normal to the shell surface.

To simplify the following development, we assume that the free end of each grafted chain is located on a 'phantom surface' which initially is at a distance L_0 from the surface of the core. As the graft layer comprising chains of polymer A is equilibrated with free chains of polymer B, solubilization may occur as suggested in *Figure 2*. Assuming the interaction between polymer A and B is favourable enough, a high level of imbibition of B into the shell can occur. However, as B enters the shell its molecules may have to become compressed in the z-direction to fit into this thin layer while the chains of A must be stretched to accommodate the swelling that occurs ($L > L_0$). This can be expressed thermodynamically as entropy penalties associated with the conformational changes of the grafted polymer A and the free polymer B. The free energy associated with this solubilization process can be approximated as follows

$$\Delta G_{\mathrm{total}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} - T\Delta S_{\mathrm{A}}^{(\mathrm{e})} - T\Delta S_{\mathrm{B}}^{(\mathrm{e})} \qquad (6)$$

where ΔH_{mix} = heat of mixing; T = temperature; ΔS_{mix} = combinatorial entropy of mixing; $\Delta S_{\mathrm{A}}^{(\mathrm{e})}$ = entropy of conformational changes for A chains; and $\Delta S_{\mathrm{B}}^{(\mathrm{e})}$ = conformational changes for B chains.

As the free B chains are solubilized into the layer of graft chains A, the shell or brush layer swells from thickness L_0 to L; the dimensions in the lateral direction do not change and the area S is constant. Based on this picture, the volume fraction of A in the swollen shell is given by

$$\phi_{\mathrm{A}} = \frac{L_0}{L} \qquad (7)$$

The number of moles of A in this layer is given by

$$n_{\mathrm{A}} = \frac{L_0 S \rho_{\mathrm{A}}}{M_{\mathrm{A}}} \qquad (8)$$

where ρ_{A} = the bulk density and M_{A} = the molecular weight of polymer A.

Clearly, the grafted chains cannot be stretched without limit; chemical bonds would have to be broken if these chains were stretched beyond their contour length. *Figure 3* shows the relation between the contour length and molecular weight for PMMA chains calculated from bond angle and length data and the extent of swelling that would stretch PMMA chains to this limit. Clearly, the model that is developed subsequently must break down prior to reaching such a degree of swelling.

The contributions to the free energy change associated with imbibing B into the graft layer from each of the four terms in equation (6) are described below.

Heat of mixing

A van Laar type expression is assumed to give the total heat of mixing between grafted polymer A and added polymer B

$$\Delta H_{\mathrm{mix}} = (n_{\mathrm{A}}\tilde{V}_{\mathrm{A}} + n_{\mathrm{B}}\tilde{V}_{\mathrm{B}})B\phi_{\mathrm{A}}\phi_{\mathrm{B}} \qquad (9)$$

Table 3 Estimates of interaction energy density (B) between SMA copolymers and PMMA homopolymer[a]

Source	B_{12} (cal cm^{-3})	B_{13} (cal cm^{-3})	B_{23} (cal cm^{-3})	$B_{\mathrm{SMA8/PMMA}}$[b] (cal cm^{-3})	$B_{\mathrm{SMA14/PMMA}}$[b] (cal cm^{-3})
Brannock *et al.*[2]	14.9	0.181	9.30	−0.186	−0.336
Gan and Paul[29]	10.7	0.220	7.18	−0.011	−0.094

[a] 1 = styrene, 2 = maleic anhydride and 3 = methyl methacrylate

[b] Calculated from B_{ij} using equation (12); the ϕ_i' value is calculated from weight fraction

where $\tilde{V}_i$ is the molar volume of component i ($= M_i/\rho_i$) and B is the interaction energy density for mixing A and B, which is related to the customary χ interaction parameter.

The volume of the mixture can also be related to the thickness of the mixed layer by the following

$$n_{\mathrm{A}}\tilde{V}_{\mathrm{A}} + n_{\mathrm{B}}\tilde{V}_{\mathrm{B}} = LS = \frac{L_0 S}{\phi_{\mathrm{A}}} \qquad (10)$$

Consequently, we can write

$$\Delta H_{\mathrm{mix}} = L_0 S B \phi_{\mathrm{B}} \qquad (11)$$

For simplicity we will assume that the concentrations of A and B are uniform throughout the graft layer which, of course, is only a first approximation to what one can anticipate[14,27].

For the SMA/PMMA case, i.e. a homopolymer and a copolymer, B can be calculated from the binary interaction model[28]

$$B = B_{13}\phi_1' + B_{23}\phi_2' - B_{12}\phi_1'\phi_2' \qquad (12)$$

where 1 = styrene, 2 = maleic anhydride and 3 = methyl methacrylate; ϕ_i' = volume fraction of i units in the copolymer provided the B_{ij} values are known. The literature contains several estimates of the B_{ij} of interest here with some variations in the values reported depending on the source and method used for determination; see *Table 3*. Small variations in each B_{ij} can cause large variations in B. For example, B for the SMA8/PMMA pair is calculated to be $-0.186\,\mathrm{cal\,cm^{-3}}$ based on the work of Brannock *et al.*[2]; and $-0.011\,\mathrm{cal\,cm^{-3}}$ based on the work of Gan and Paul[29]. Corresponding estimates for the SMA14/PMMA pair are -0.336 and $-0.094\,\mathrm{cal\,cm^{-3}}$, respectively. At this time, it is not possible to know very precisely what the correct value of B is for PMMA/SMA, so in what follows we explore how solubilization is affected by the value of this parameter.

Combinatorial entropy of mixing

The combinatorial entropy of mixing mobile chains of polymer B into the grafted layer of polymer A is given by

$$\Delta S_{\mathrm{mix}} = -n_{\mathrm{B}} R \ln \phi_{\mathrm{B}} \qquad (13)$$

A term for grafted A chains is not included because they have no spatial freedom[30]. The number of moles of B in the graft layer is given by

$$n_{\mathrm{B}} = \frac{LS\phi_{\mathrm{B}}\rho_{\mathrm{B}}}{M_{\mathrm{B}}} \qquad (14)$$

Combining equations (13) and (14) gives

$$\begin{aligned} S_{\mathrm{mix}} &= -\frac{LS\phi_{\mathrm{B}}\rho_{\mathrm{B}}}{M_{\mathrm{B}}} R \ln \phi_{\mathrm{B}} \\ &= -\frac{L_0 S\phi_{\mathrm{B}}\rho_{\mathrm{B}}}{\phi_{\mathrm{A}} M_{\mathrm{B}}} R \ln \phi_{\mathrm{B}} \end{aligned} \qquad (15)$$

Conformational entropy changes for grafted A chains

Adding polymer B to the layer of grafted polymer A causes swelling that leads to a change in conformational entropy, which can be estimated by using the statistical theory of rubber elasticity[31–33], e.g.

$$\Delta S_{\mathrm{A}}^{(\mathrm{e})} = -\frac{n_{\mathrm{A}} R}{2} \frac{\langle r^2 \rangle_{\mathrm{i}}}{\langle r^2 \rangle_0} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \qquad (16)$$

where α_i = Cartesian molecular deformation ratio, $\langle r^2 \rangle_{\mathrm{i}}$ = initial end-to-end distance, and $\langle r^2 \rangle_0$ = unperturbed value. In the present case, we have

$$\langle r^2 \rangle_{\mathrm{i}} = L_0^2$$

$$\langle r^2 \rangle_0 = R_0^2 = \langle z^2 \rangle_{\mathrm{B}} = 2/3k_0\mathrm{M}$$

where L_0 is the initial shell thickness determined by equation (3) and R_0 is the perpendicular end-to-end distance of a grafted chain, see equation (5). Choosing x and y as the lateral directions and z as the direction perpendicular to the surface, the deformation ratios can be written as

$$\begin{aligned} \alpha_x &= \alpha_y = 1 \\ \alpha_2 &= \frac{L}{L_0} = \frac{1}{\phi_{\mathrm{A}}} \end{aligned} \qquad (17)$$

Combining the above gives

$$\Delta S_{\mathrm{A}}^{(\mathrm{e})} = -\frac{L_0 S \rho_{\mathrm{A}} R}{2M_{\mathrm{A}}} \frac{L_0^2}{R_0^2} (\phi_{\mathrm{A}}^{-2} - 1) \qquad (18)$$

Conformational entropy changes for B chains

In the free state, polymer B exists as random coils with a radius of gyration R_{g} that is related to its molecular weight M_{B} by

$$R_{\mathrm{g}} = \sqrt{\frac{1}{6}}\langle r^2 \rangle_0^{1/2} = \sqrt{\frac{k_0 M}{6}} \qquad (19)$$

Table 4 shows estimates of R_{g} for SMA copolymers as a function of molecular weight. Since the thickness dimension of the grafted layer may be comparable to or smaller than R_{g} (see *Tables 1* and *4*), the B chains may have to undergo a conformational rearrangement, i.e. compression in the z-direction, to enter this layer. The entropy or free energy change associated with this conformational change is analogous to that for partitioning of polymer B coils between slit-type pores and a dilute solution of B. The latter problem has been well studied in gel permeation chromatography[35–37], and the following expression for the partition coefficient K has been developed in terms of the ratio of the radius of gyration R_g and the pore dimension a (where $a = 1/2L$ for slit-like pores)

$$K = \frac{8}{\pi^2}\sum_{m=0}^{\infty}(2m+1)^{-2} \exp\left[-(2m+1)^2\left(\frac{\pi^2}{4}\right)\left(\frac{2\phi_A R_g}{L_0}\right)^2\right] \tag{20}$$

The entropy change associated with this conformational rearrangement is given by

$$\Delta S_B^{(e)} = n_B R \ln K = \frac{L_0 S \rho_B \phi_B}{M_B \phi_A} R \ln K \tag{21}$$

Table 4 Effect of molecular weight on the radius of gyration of SMA copolymers[a]

M_{SMA}	10 000	30 000	80 000	100 000	300 000	600 000
R_g (Å)	29	49	81	90	157	221

[a] Calculated from equation (19) using $k_0 = 0.49$ for SMA copolymers. This value is for polystyrene[26]; however, experimental studies[34] indicate that SMA copolymers of the composition of interest here will have very similar values

Total free energy

The total free energy associated with solubilizing B into the grafted layer is the appropriate sum of the four terms described above

$$\begin{aligned}\Delta G_{total} &= \Delta H_{mix} - T\Delta S_{mix} - T\Delta S_A^{(e)} - T\Delta S_B^{(e)} \\ &= L_0 S B \phi_B - \frac{L_0 S \phi_B \rho_B}{\phi_A M_B} RT \ln \phi_B \\ &\quad + \frac{L_0 S \rho_A RT}{2M_A}\frac{L_0^2}{R_0^2}(\phi_A^{-2} - 1) \\ &\quad - \frac{L_0 S \rho_B \phi_B}{M_B \phi_A} RT \ln K\end{aligned} \tag{22}$$

Figure 4 shows the contribution of each of the four terms in equation (22) to the total free energy change when polymer B is incorporated into the grafted layer of polymer A. The mixing terms, ΔH_{mix} (only exothermic cases are considered) and ΔS_{mix}, are always negative and favour imbibition of polymer B while the terms stemming from conformational changes, $\Delta S_A^{(e)}$ and $\Delta S_B^{(e)}$, are always positive and oppose solubilization. Both ΔS_{mix}

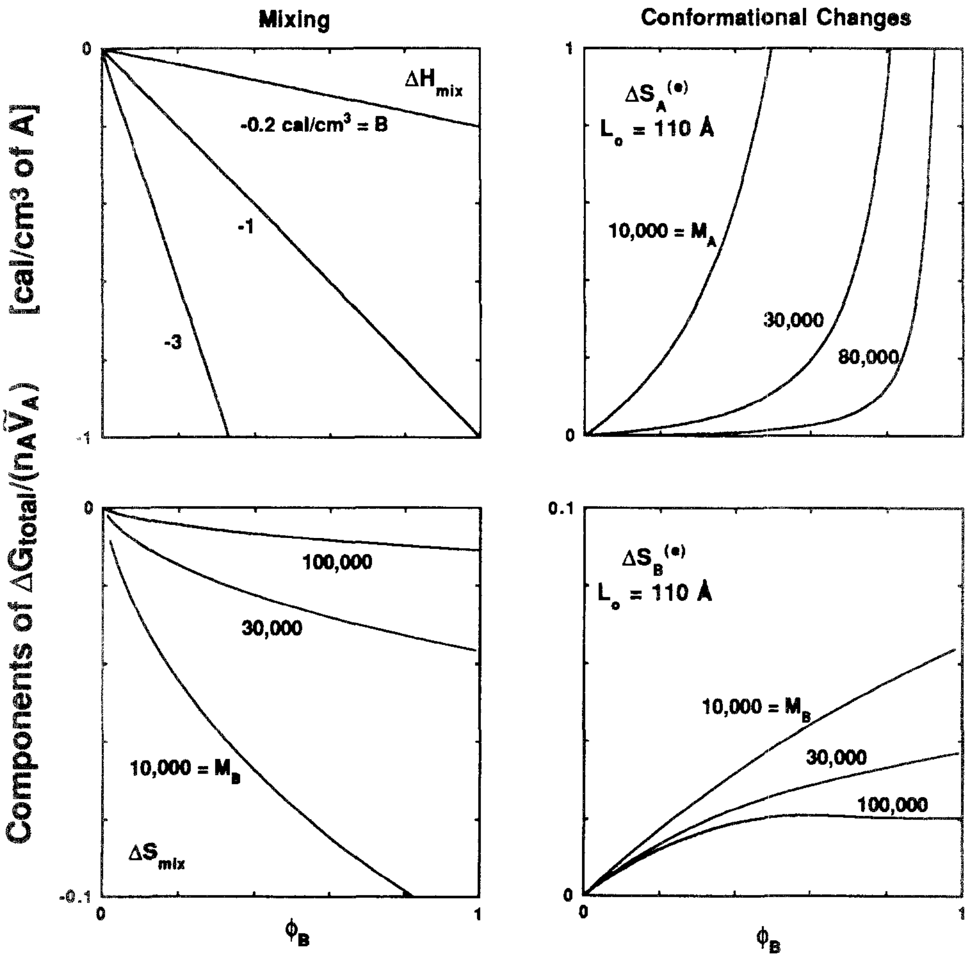

Figure 4 Contribution of each of the four terms in equation (22) for the total free energy change when the free polymer B is solubilized to a volume fraction ϕ_B into the shell layer of the grafted A chains. Mixing terms are on the left while terms due to conformational changes are on the right

and $\Delta S_B^{(e)}$ become smaller as M_B increases since this decreases the moles of B per unit volume. The term $\Delta S_A^{(e)}$ also becomes smaller as M_A increases. The conformational contributions depend on the initial shell thickness, L_0. As L_0 increases, $\Delta S_A^{(e)}$ becomes larger as indicated by equation (18) while $\Delta S_B^{(e)}$ becomes smaller because the conformational penalty is less for a thicker shell when the molecular weight of the B chains is fixed. Of course, the ΔH_{mix} term can be quite significant in comparison to the other terms, as seen in *Figure 4*.

Predicted equilibrium phase behaviour

The chemical potential of B in the swollen shell relative to a phase of pure B is given by

$$\mu_B - \mu_B^{\circ} = \left(\frac{\partial \Delta G_{total}}{\partial n_B}\right)_{T,P,n_A} \quad (23)$$

For convenience, we define

$$\Delta\mu_B = \frac{\mu_B - \mu_B^{\circ}}{\tilde{V}_B} \quad (24)$$

and perform the indicated operations on ΔG_{total} to obtain

$$\begin{aligned}\frac{\Delta\mu_B}{RT} &= \frac{B}{RT}(1-\phi_B)^2 + \frac{\rho_B}{M_B}(1-\phi_B+\ln\phi_B)\\ &+ \frac{\rho_A}{M_A}\left(\frac{L_0}{R_0}\right)^2\frac{1}{(1-\phi_B)}\\ &- \frac{\rho_B}{M_B}\left(\ln K - \phi_B\frac{\partial \ln K}{\partial \ln x}\right)\end{aligned} \quad (25)$$

where

$$x = \frac{R_g}{a} = \frac{R_g}{(L/2)} = \frac{2\phi_A R_g}{L_0} \quad (26)$$

We set $T = 240°C$ in the following calculations since this is the processing temperature used in the companion paper[23].

In general, the equilibrium solubilization limit of polymer B in the shell layer of polymer A, $(\phi_B)_s$, corresponds to a minimum in ΔG_{total} [equation (22)], which coincides with $\Delta\mu_B = 0$ [the root of equation (25)] as shown in *Figure 5* for the case $L_0 = 110$ Å, $M_B = 100\,000$ and $M_A = 30\,000$. The minimum in ΔG_{total} reflects the competition in equation (22) of the favourable enthalpic and entropic terms *versus* the unfavourable conformational terms. In the cases shown, the minimum represents a lower free energy state than that of the pure components; thus $\Delta\mu_B = 0$ corresponds to an equilibrium between a pure B phase and the mixed shell layer saturated with B. In all cases, $\Delta\mu_B$ goes to positive infinity as $\phi_B \rightarrow 1$, as a result of stretching the grafted A chains at high swelling; however, because of the finite contour length of A chains, the model may break down well before this point. The extent of solubilization of B in the shell, $(\phi_B)_s$, is very small when the interaction energy is small, i.e. in this example when $B = -0.05\,\text{cal cm}^{-3}$ or less, as shown in *Figure 5*. However, the extent of solubilization can be substantial when the interaction between polymer A and B is more favourable.

Under certain circumstances, the minimum of ΔG_{total} does not represent a lower free energy state than that of the pure components as shown in *Figure 6* for the case when $L_0 = 110$ Å and $M_B = 100\,000$ but M_A is set at 10 times the value used in *Figure 5*, i.e. 300 000. As B becomes less negative, the value of ΔG_{total} at the minimum shifts to higher values and eventually goes positive. Prior to this minimum, ΔG_{total} may show negative curvature which, in usual thermodynamic analyses, signals an instability of the mixture and separation into two phases of different compositions. However, such an interpretation is not appropriate here. This is a one-dimensional model (no fluctuations in composition are considered lateral to the graft surface) and the assumption that the free end of the grafted chain extends to $z = L$ precludes phase separation in this direction. Thus, in the context of this highly simplified model, the extent of equilibrium solubilization, or $(\phi_B)_s$, is defined only by roots of $\Delta\mu_B = 0$ that correspond to negative minima in ΔG_{total}, i.e. a state of lower free

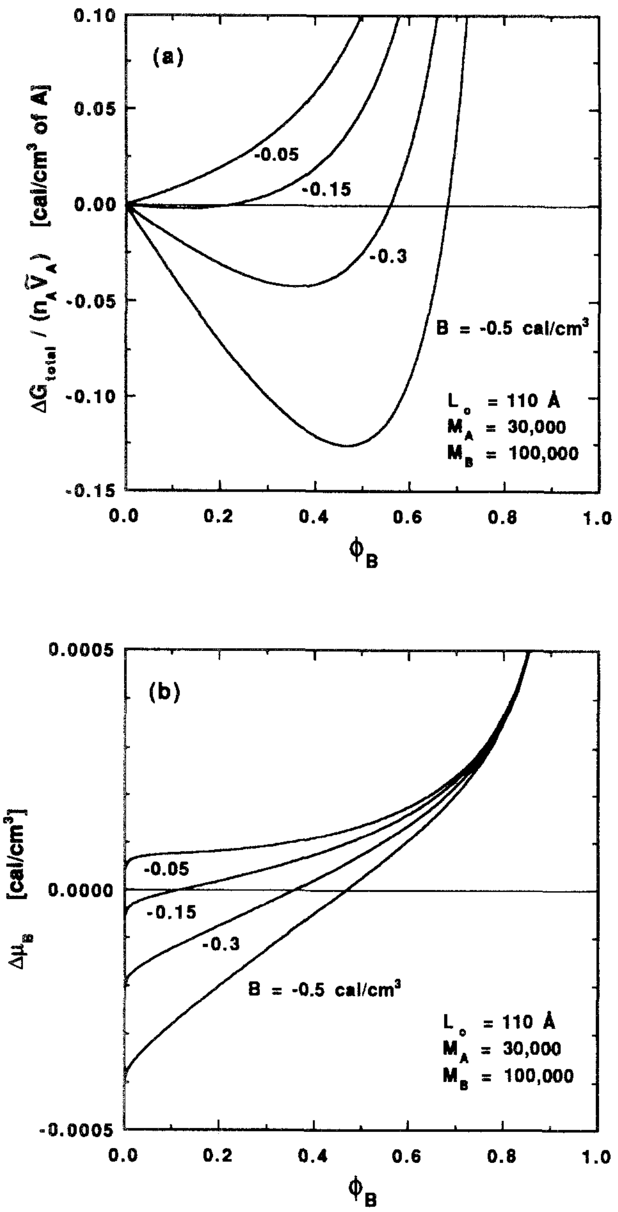

Figure 5 Total free energy change (a) and corresponding chemical potential of polymer B solubilized into the shell of grafted polymer A relative to pure state (b) for different values of the interaction energy density B when $L_0 = 110$ Å, $M_A = 30\,000$ and $M_B = 100\,000$

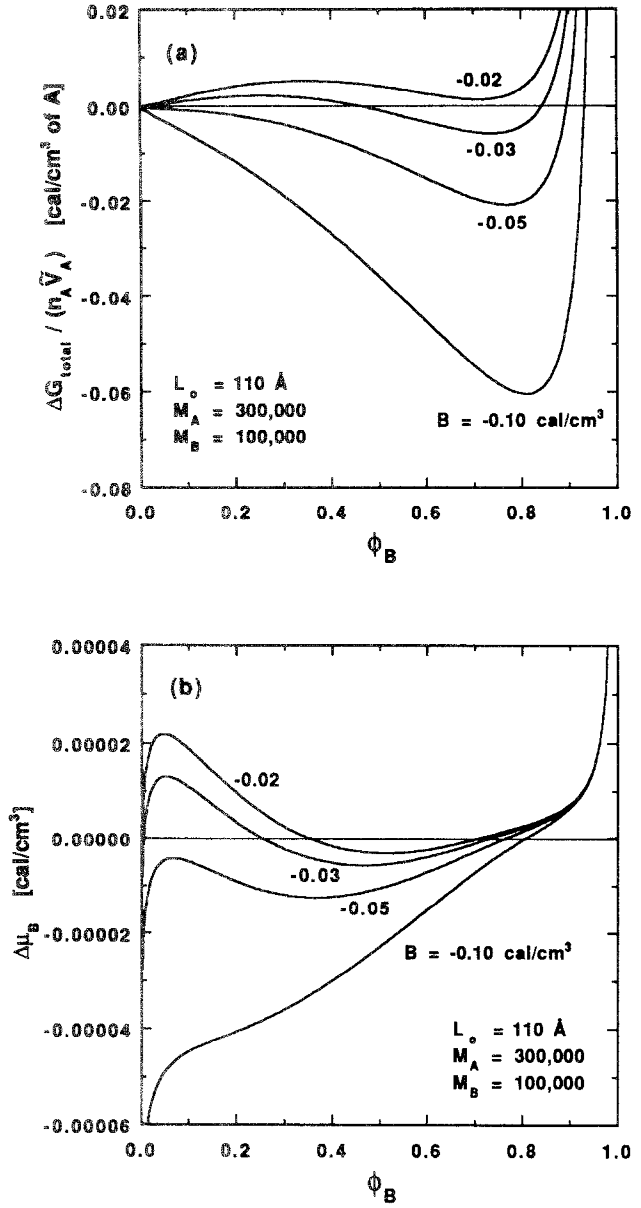

Figure 6 Total free energy change (a) and corresponding chemical potential of polymer B solubilized into the shell of grafted polymer A relative to pure state (b) for different values of the interaction energy density B when $L_0 = 110$ Å, $M_A = 300\,000$ and $M_B = 100\,000$

energy than that of the pure components. Positive minima in ΔG_{total} may occur when the interaction is weak and when the contribution from the conformational change of B chains becomes significant in comparison with that of the grafted A chains. For example, when the molecular weight of A chains increases, $\Delta S_A^{(e)}$ becomes smaller as shown in *Figure 4*. As discussed later, changing the molecular weight of B chains or the original shell thickness can also lead to a similar situation.

From equation (25), it is clear that at least four factors affect the degree of solubilization of polymer B in the grafted layer: the interaction energy density, B; the molecular weight of grafted polymer A; the molecular weight of added polymer B; and the shell thickness, L_0. The influence of each of these four factors on $(\phi_B)_s$ is discussed below.

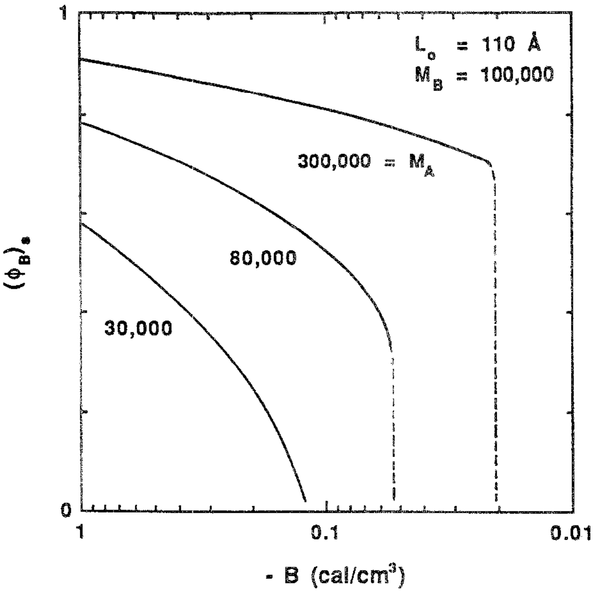

Figure 7 Effect of interaction energy on the extent of solubilization for three values of M_A when $L_0 = 110$ Å and $M_B = 100\,000$. The solid lines are regions where the minima in ΔG_{total} are negative while the dashed lines correspond to regions where the minima in ΔG_{total} are positive

Interaction energy density, B. The extent of equilibrium solubilization of B chains into a shell layer with original thickness $L_0 = 110$ Å, as predicted by this model, is plotted *versus* the interaction energy density, B, in *Figure 7* for three molecular weights of the grafted A chains. In general, the more favourable the interaction, the greater is the degree of solubilization. For each value of M_A, there is a critical interaction energy needed for significant levels of solubilization. When M_A is relatively large, the extent of solubilization decreases abruptly when the interaction energy becomes less favourable than this critical value as the minimum in ΔG_{total} becomes positive. In *Figure 7*, the solid lines are regions where the minima in ΔG_{total} are negative while the broken lines correspond to regions where the minima in ΔG_{total} are positive.

Grafted polymer molecular weight, M_A. It can be seen in *Figure 7*, for a fixed interaction energy, M_B and L_0, that more polymer B can be solubilized into the grafted layer as the molecular weight of polymer A is increased. This trend is shown more explicitly in *Figure 8*. In fact, very little of polymer B is imbibed by the grafted layer until M_A is above a critical value for each interaction energy. For example, when $B = -0.05\,\text{cal cm}^{-3}$ for the case shown, the molecular weight of polymer A needs to be above 89 000 to allow substantial solubilization; in fact, when $M_A < 89\,000$, the minimum in ΔG_{total} becomes positive, corresponding to the dashed line shown in *Figure 8*. However, when the interaction is more favourable, a lower molecular weight of polymer A is adequate. Similar phenomena have been reported for blends of block or graft copolymers with homopolymers having repeat units either identical[30,38–41] or able to interact exothermally[7–15] with those of one of the segments of the copolymer. Several experimental investigations[11,12,38–41] have shown that the extent of solubilization is strongly affected by the molecular weight of the homopolymer relative to that of the corresponding copolymer segment.

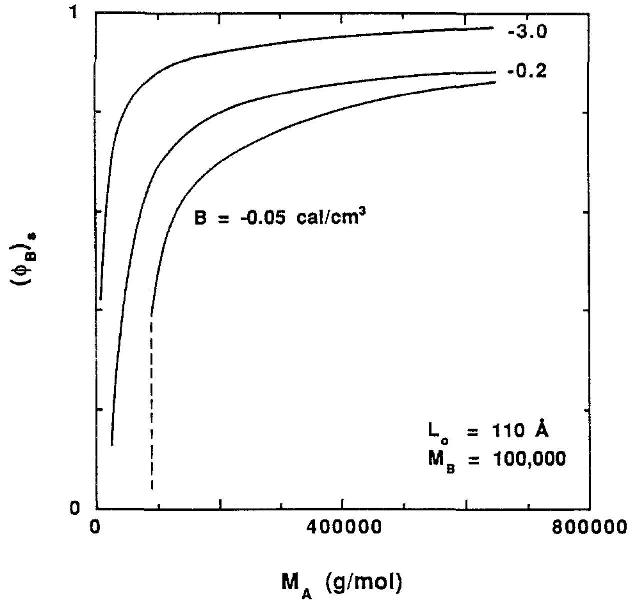

Figure 8 Effect of molecular weight of the grafted A chains, M_A, on the extent of solubilization for different values of the interaction energy density B when $L_0 = 110$ Å and $M_B = 100\,000$. The dashed line corresponds to regions yielding positive minima in ΔG_{total}

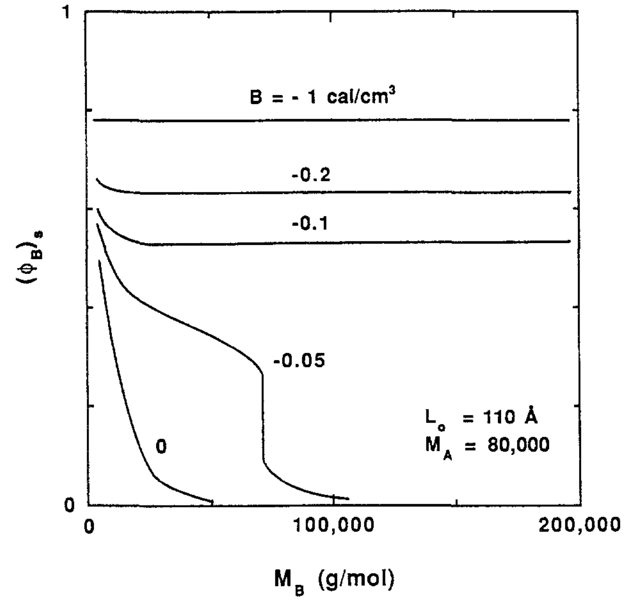

Figure 9 Effect of molecular weight of the added polymer B, M_B, on the extent of solubilization for different values of the interaction energy density B when $L_0 = 110$ Å and $M_A = 80\,000$

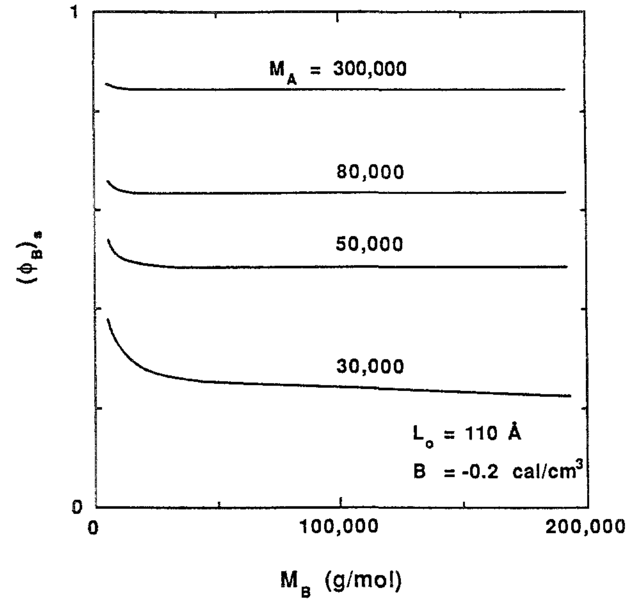

Figure 10 Effect of molecular weight of the added polymer B, M_B, on the extent of solubilization for different molecular weights of the grafted A chains, M_A, when $L_0 = 110$ Å and $B = -0.2\,\text{cal cm}^{-3}$

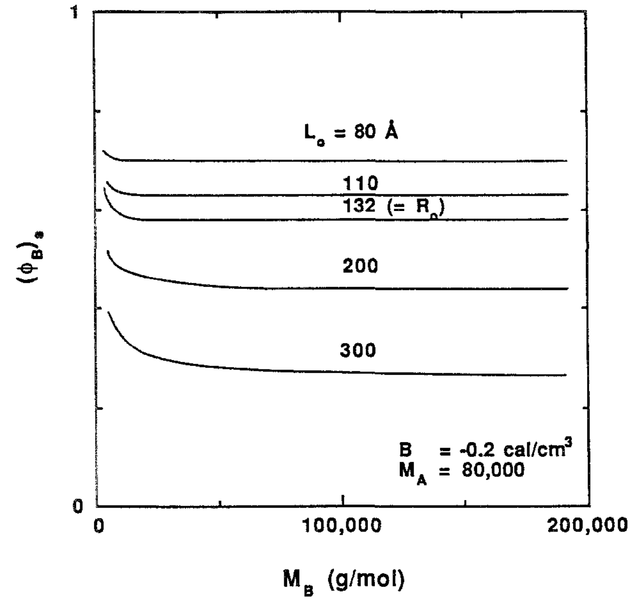

Figure 11 Effect of molecular weight of the added polymer B, M_B, on the extent of solubilization for various initial shell thicknesses, L_0, when $B = -0.2\,\text{cal cm}^{-3}$ and $M_A = 80\,000$

Free polymer molecular weight, M_B. *Figure 9* shows, for a fixed M_A and L_0, that when the interaction is very favourable, the extent of solubilization is not significantly affected by the molecular weight of the free B chains; on the other hand, when the interaction is less favourable, the molecular weight of B chains has a stronger effect on the solubilization. Note that for the case of $B = -0.05\,\text{cal cm}^{-3}$, when M_B becomes larger than 72 000, the contribution from the conformational change of B chains becomes so significant that there is an abrupt drop in the extent of solubilization. Increasing M_B reduces the favourable contribution from the entropy of mixing; however, entropy of mixing becomes less important for solubilization as B becomes more negative. For a modestly favourable interaction energy of $-0.2\,\text{cal cm}^{-3}$, the effect of M_B on solubilization is relatively unimportant compared with the effect of M_A as shown in *Figure 9*.

It is important to remember that the effects of the size of the B chains on solubilization are dependent on the size of the grafted chain A and the original thickness of the shell layer. *Figure 10* shows for $B = -0.2\,\text{cal cm}^{-3}$ and $L_0 = 110$ Å that when M_A is large, the extent of solubilization of polymer B in the grafted layer is high and not significantly affected by M_B; on the other hand, when M_A is small, the solubilization is lower and M_B has a somewhat stronger effect on its value. *Figure 11* shows the effect of M_B on solubilization for various original

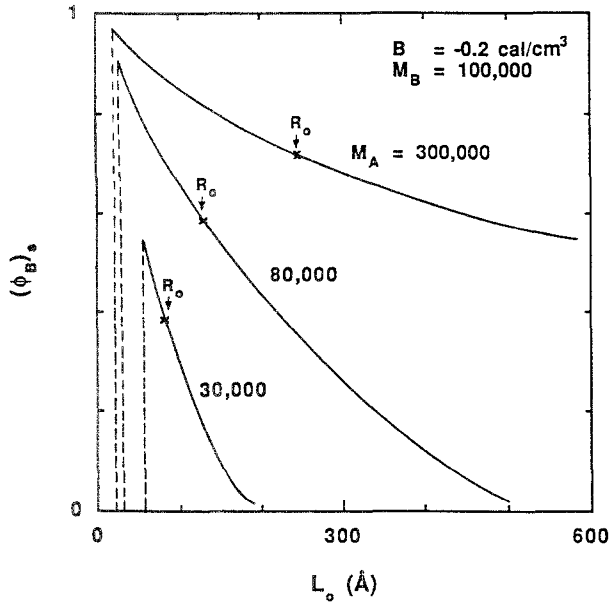

Figure 12 Effect of initial shell thickness, L_0, on the extent of solubilization for fixed molecular weights of the grafted A chains when $B = -0.2\,\mathrm{cal\,cm^{-3}}$ and $M_B = 100\,000$. The dashed lines correspond to regions where the minima in $\Delta G_{\mathrm{total}}$ are positive

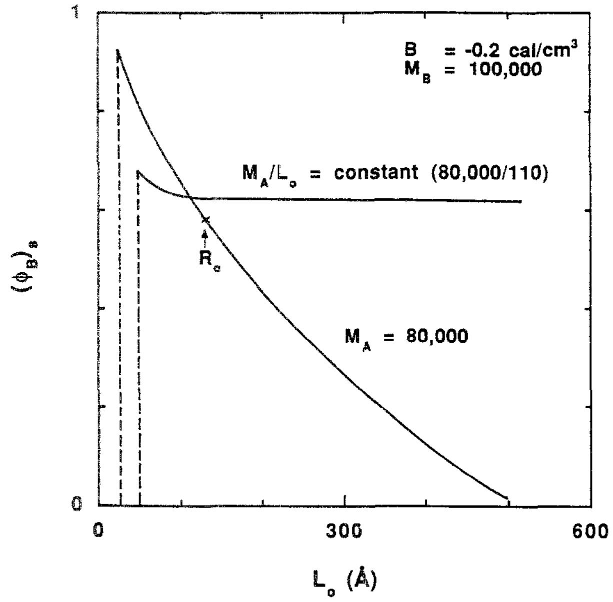

Figure 13 Effect of initial shell thickness, L_0, on the extent of solubilization when M_A is fixed at 80000 and when M_A varies in proportion to L_0, for the case $B = -0.2\,\mathrm{cal\,cm^{-3}}$ and $M_B = 100\,000$. The dashed lines correspond to regions where the minima in $\Delta G_{\mathrm{total}}$ are positive

shell thicknesses that span the values of the natural dimension of the grafted chains, R_0, defined earlier (i.e. $L_0 < R_0$, $L_0 = R_0$ and $L_0 > R_0$). It is interesting to note that a thicker original shell layer tends to absorb a smaller fraction of polymer B in the shell layer. The effect of the original shell thickness on the solubilization will be discussed more explicitly in the next section.

Shell thickness, L_0. In most of the above calculations, the original shell thickness, L_0, was assumed to be 110 Å. However, L_0 can be varied over a wide range as illustrated in *Table 1*. The extent of solubilization of B chains of fixed M_B into the shell layer, as predicted by equation (25), strongly depends on the choice of L_0, as shown in *Figure 12* for three values of molecular weight of the grafted chains, M_A, for the case where $B = -0.2\,\mathrm{cal\,cm^{-3}}$. As L_0 decreases, $(\phi_B)_s$ becomes larger, regardless of the values of M_A, contrary to what one might intuitively expect. The reason for this is that the conformational entropy term for the grafted chains A is a strong function of the original shell thickness relative to the natural dimension of the grafts, L_0/R_0, as seen in equation (25). When the grafted chains are initially stretched, i.e. $L_0/R_0 > 1$, they more strongly resist further stretching from swelling of the graft layer by imbibition of polymer B. When the graft chains are actually compressed in the thickness direction, i.e. $L_0/R_0 < 1$, swelling helps them achieve their more natural conformation. However, when L_0 becomes small in comparison with the coil dimensions of polymer B, the contribution from the conformational change of polymer B causes the minimum $\Delta G_{\mathrm{total}}$ to increase to positive values, leading to an abrupt drop in solubilization as seen in *Figure 12.*

One may visualize altering the shell thickness in two different ways. One is to graft more A chains of fixed molecular weight to the surface; this is the case shown in *Figure 12.* Alternatively, the molecular weight of the grafted polymer can be increased for a fixed number of grafted chains. *Figure 13* shows this case where the ratio of M_A to L_0 is fixed at 80000 to 100 Å. The extent of solubilization in this case is much less dependent on the absolute level of the initial thickness since the conformational state of the grafted chains does not vary with L_0.

CONCLUSIONS

A thermodynamic model for the solubilization of free polymer chains into the polymer brush formed by the grafted shell of core–shell impact modifiers has been developed using the approach employed by Tucker and Paul[14] for polymer solubilization into the microdomains of block copolymers. The extent of equilibrium solubilization reflects a balance between the favourable driving forces for mixing *versus* the unfavourable entropy associated with conformational changes of the grafted and added chains. Significant levels of solubilization only occur when the interaction energy between the two types of chain segments is sufficiently favourable, and this depends on the grafted chain molecular weight, the added polymer molecular weight and the initial shell thickness. In general, the model predicts for a given interaction energy density that higher extents of solubilization will be possible the higher the molecular weight of grafted chains and the thinner the original shell thickness, while the molecular weight of the added polymer is not so important except when the interaction is quite weak.

Some assumptions have been made to simplify the development of the model. The shell is approximated as planar because the L_0/R_s ratio is typically small. However, the convex curvature of the shell increases the packing space of the grafted chains with increasing distance from the surface, reducing the conformational restrictions[42]. This may lead to a higher extent of solubilization than predicted here when the shell is relatively thick. The model assumes uniform mixing and neglects concentration gradients that in reality must exist[14,27]. Considering these concentration gradients may lead to a higher prediction of the extent of solubilization as suggested by Xie *et al.*[27]. Finally, it has been assumed that both the grafted and added polymers are monodisperse. It is beyond the scope of this work to explore how polydispersity affects the extent of solubilization.

A companion paper[23] examines the extent to which SMA8 and SMA14 copolymers are imbibed into the grafted PMMA layer of core–shell impact modifiers by studying the glass transition behaviour of the hard phase and the morphology of the SMA/core–shell blends using transmission electron microscopy techniques.

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