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Effect of the molecular weight of the homopolymers on the morphology in ternary blends of polystyrene, polyisoprene, polystyrene-block-polyisoprene copolymer

Loïc Messé*[,1], Laurence Corvazier[2], Anthony J. Ryan

Department of Chemistry, University of Sheffield, S3 7HF Sheffield, UK

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Abstract

Three nearly symmetrical ternary systems made of ternary blends of polystyrene, polyisoprene, polystyrene—*block*—polyisoprene copolymer have been investigated by small angle X-ray scattering (SAXS). The molecular weights of the homopolymers were varied, keeping the diblock length constant, to obtain ratios of homopolymer to diblock length, α, of 0.19, 0.38 and 0.74. For all experimental phase diagrams determined, a phase transition from lamellar to bicontinuous microemulsion, and then macroscopic phase separation have been observed with increasing homopolymer content. In addition, for $\alpha = 0.38$ and 0.74, a region of coexistence of bicontinuous microemulsions and lamellae, between the periodically ordered phase (lamellar) and the channel of microemulsion is reported at low temperature, which transform into a pure bicontinuous microemulsions at a higher one. For $\alpha = 0.74$, the concentration at which the macroscopic phase separation occurs is lower than the one obtained with $\alpha = 0.19$ and 0.34, suggesting that, as the molecular weight of the two homopolymers is increased, the microemulsion morphology becomes less stable. The thermal fluctuations begin to destroy the microemulsion morphology in favour of macroscopic phase separated system. This observation is further confirmed by the study of the variation of the *d*-spacing for the lamellar phase, where no wetting of the diblock monolayers was noticed for $\alpha = 0.74$ as compared to $\alpha = 0.19$ and 0.38.

Keywords: ternary blends; bicontinuous microemulsion; SAXS

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1. Introduction

Block copolymers of strongly incompatible blocks exhibit a rich variety of morphologies in the melt state including cubic, hexagonal, lamellar and gyroid microstructures, according to the volume fraction of each of the constituents, f_v, and the product, χN, of the interaction parameter and the number of repeating units in the chains [1, 2]. Blends of block copolymers, with either one or two homopolymers of the same chemical structure as the diblock, generate swelling of the pre-existing morphologies and the formation of new microstructures or even macroscopic phase separation, depending upon the relative length of the polymers and the composition of the blends [3–6]. Indeed, at high block copolymer content and low molecular weight homopolymers, it was reported that the morphologies of the blends are essentially the same as the neat diblock, whereas the addition of a large amount of homopolymers results in the formation of new and complex morphologies.

Nearly symmetric ternary blends of block copolymer A–B with their corresponding homopolymers A and B ($\alpha = N_H/N_{A-B} = 0.20$; $N_H = (N_A \times N_B)^{1/2}$), have recently been the object of interest since the experimental determination of bicontinuous microemulsion structure [7–11]. At high block copolymer content, the homopolymers are essentially solubilised in the lamellar microdomains induced by the presence of symmetrical diblock. Increasing the homopolymers volume fraction generates the formation of bicontinuous morphology, similar in essence to the structure observed in the mixture of oil and water in

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* Corresponding author. Tel.: +44-1223-765-708; fax: +44-1223-765701.

E-mail address: messeloic@hotmail.com (L. Messé).

[1] Present address: BP Institute, Bullard Laboratories, University of Cambridge, Madingley Road, Cambridge CB3 0EZ, UK.

[2] Present address: Huntsman Advanced Materials, Duxford CB2 4QA UK.

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comparable amount with a surfactant [12], as more recently determined in ternary blends of two homopolymers and a block copolymer with as little as few percent of compatibilizer in the blends. Macroscopic phase separation is observed, in ternary blends, at very low concentration of diblock.

Phase diagrams confirming the existence of microemulsion for polyolefin/polyolefin, polyolefin/polyether and polyolefin/polydimethylsiloxane blends and lately, for ternary blends of polystyrene/polyisoprene/polystyrene-*block*-polyisoprene copolymer with $\alpha = 0.19$, have been reported elsewhere [7–11]. However, despite this, little effort has been devoted towards mapping out the bulk phase behaviour of ternary blends with different α values. According to theoretical calculation by Matsen et al., stable microemulsion can only be obtained when $\alpha < 0.8$ [13,14]. The purpose of the present contribution is to examine the influence of the increase of homopolymers molecular weight on the formation of microemulsion in ternary blends of polystyrene/polyisoprene/polystyrene-*block*-polyisoprene, keeping the diblock dimension the same. Results for $\alpha = 0.38$ and 0.74 are reported and compared with the one obtained for blends with $\alpha = 0.19$ [11]. The morphologies of the blends were determined by small angle X-ray scattering (SAXS).

2. Experiment

2.1. Samples and characterisation

Polystyrene, polyisoprene and polystyrene-*block*-polyisoprene were synthesised by anionic polymerisation under high vacuum using glass reactors and break-seals. The synthesis procedure is the same as previously described [11]. Gel permeation chromatography was used to determine the narrow chain length distributions and the molecular weights. MALDI-TOF technique was applied to confirm the chain lengths of the homopolymers. The molecular characteristics of the copolymer and homopolymers are given in Table 1.

Blends were prepared by dissolution of the appropriate amounts of polymer in toluene followed by co-precipitation in methanol. The samples were then allowed to dry under vacuum, at 40 °C, for at least two weeks (until no further change in weight was noticed) and two more days at 85 °C, before to be analyzed.

2.2. Small angle X-ray scattering

Experiments were conducted either at the synchrotron facility located at the CCLRC Daresbury Laboratory [15], Warrington, UK, and on beamline DUBBLE [16], at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Details of the beamline, storage ring, radiation, camera geometry and data collection electronics have already been described elsewhere [16]. Samples were placed in sealed aluminium pans (TA Instruments) equipped with thin mica windows, and held in a Linkam single-pan DSC cell. The thickness of the sample was kept constant using a (~1 mm) spacer. Temperature-controlled SAXS experiments were conducted from 80 up to 210 °C at a heating rate of 10 °C/min to avoid sample degradation, while SAXS profiles were recorded every 6 s. Prior to the SAXS measurements, samples were heated in the pan above the ODT to remove all thermal history.

Table 1
Molecular characteristics of the polymers used in this study

	M_n (kg mol^{-1})[a]	M_w/M_n[a]	N[b]	r_v[c]	f_{PS}[d]	α[e]
PS-PI	14.6	1.02	175	208	0.50	
PS	3.5	1.05	35	35		0.19
PI	2.2	1.05	32	42		
PS	7.2	1.03	69	69		0.38
PI	4.3	1.05	64	84		
PS	14.3	1.02	137	138		0.74
PI	8.5	1.03	125	165		

[a] Determined by GPC.

[b] N is the number-average degree of polymerisation.

[c] r_v is the overall length of the polymer in segments, normalised to a standard segment volume of 100 cm^3 mol^{-1}.

[d] f_{PS} is the volume fraction of polystyrene in the diblock, calculated from ^{1}H NMR.

[e] α is the ratio $r_{vH}/r_{vPS\text{-}PI}$ ($\sim N_H/N_{PS\text{-}PI}$, with $N_H = (N_{PS} \times N_{PI})^{1/2}$). The ODT temperature of the neat diblock, determined by SAXS and rheology, is 98 ± 1 °C.

3. Results and discussions

Morphologies of the blends and temperatures of order-disorder transition (ODT) have been identified by

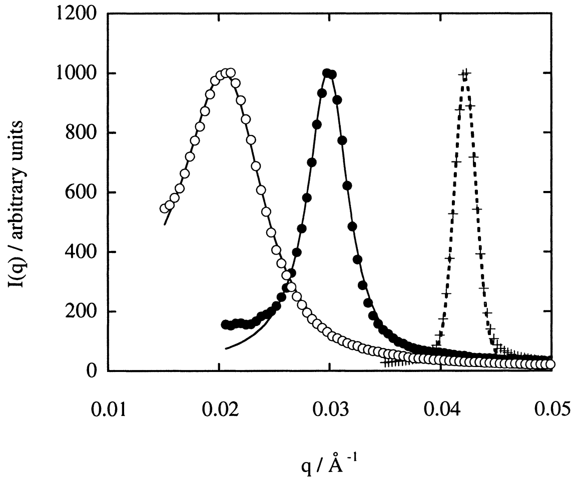

Fig. 1. SAXS profiles for PS/PI/PS-*b*-PI ternary blends ($\alpha = 0.74$) containing 0 (+), 0.35 (●) and 0.70 (○) volume fraction of homopolymers, as a function of scattering vector q, at 90 °C. The data (symbols) were fitted using the Gaussian equation (dotted line) for pure diblock, and the Teubner–Strey equation (line) for $\Phi_H = 0.35$ and 0.70.

temperature-controlled SAXS. Fig. 1 shows SAXS profiles, obtained at 90 °C, for three blends of concentration in homopolymers of 0, 0.35 and 0.70, respectively, for $\alpha = 0.74$. The maximum in the peak position is shifted towards lower q values as the homopolymers volume fraction is increased, indicating a swelling of the microdomains. The width of the peak, related to the correlation length between domains, also increases with the addition of homopolymers, suggesting a transformation in the morphology. Both observations are consistent with previous studies published on symmetrical ternary blends [9–11], where it was reported a modification of the morphology from lamellar to bicontinuous microemulsion, and an increase in the d-spacing, with the addition of homopolymers to the ternary blends. The presence of lamellar morphologies, for $\Phi_H = 0$ and 0.35, is characterised by the fit of the SAXS profiles using a Gaussian function, whereas, for the bicontinuous microemulsion ($\Phi_H = 0.70$), a Teubner–Strey equation is needed to model the diffraction peak. The lamellar systems are, furthermore, identified by the occurrence of a transformation in the SAXS profiles with increasing temperature, from a sharp Gaussian peak, below the ODT temperature, to a broad Lorentzian-like peak above it [17]. The microemulsion regime, however, is differentiated from the lamellar state by the only possible fit of the scattering profile with Teubner–Strey equation, at all temperatures.

Previous experiments have confirmed the efficiency of the Teubner–Strey equation to fit SAXS experimental data for various systems constituted of microemulsions, including complex bicontinuous microemulsions made of comparable amounts of oil and water with a surfactant [12] and, lately, of polymeric systems in their melt state [7–11]. Based on Ginsburg–Landau approach, the Teubner–Strey equation models scattering experimental data extremely well, using only three parameters [18].

$$I(q) \sim \frac{1}{a_2 + c_1 q^2 + c_2 q^4} \tag{1}$$

According to Teubner and Strey, the sole determination of the parameters a_2, c_1 and c_2 is sufficient to characterise the microstructure of a blend since, in the ordered state, microemulsions are described by $a_2 > 0$, $c_1 < 0$ and $c_2 > 0$, and for homogeneous isotropic liquids, by $a_2 > 0, c_1 > 0$ and $c_2 \sim 0$. The value $c_1 = 0$ is associated to the presence of the Lifshitz line. The correlation length of the domains ξ and the domain size d (associated with the peak position, q^*) are calculated from the knowledge of the values of a_2, c_1 and c_2.

$$\xi = \left[\frac{1}{2}\left(\frac{a_2}{c_2}\right)^{1/2} + \frac{1}{4}\frac{c_1}{c_2} \right]^{-1/2} \tag{2}$$

$$d = 2\pi\left[\frac{1}{2}\left(\frac{a_2}{c_2}\right)^{1/2} - \frac{1}{4}\frac{c_1}{c_2} \right]^{-1/2} \tag{3}$$

The characteristic length scales of the morphologies, d, as a function of homopolymers volume fraction, Φ_H, are shown in Fig. 2, for $\alpha = 0.19, 0.38$ and 0.74. For blends exhibiting a periodically ordered phase (lamellar), the values of the periodic spacing were defined at the ODT temperature, where the correlation length changes from strongly

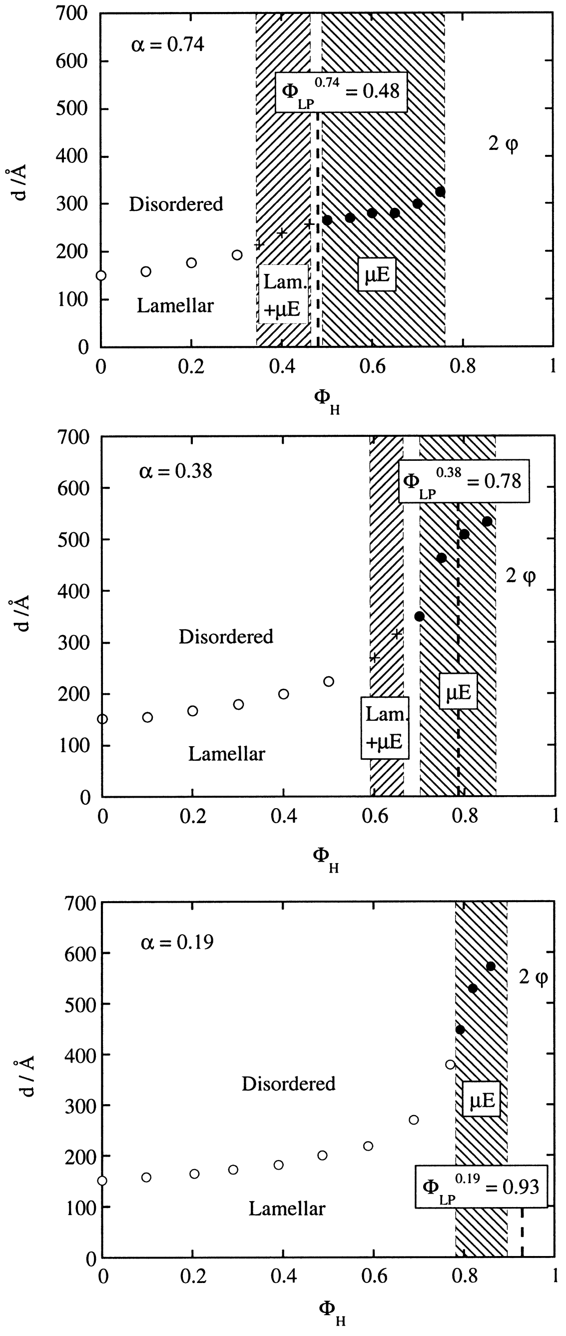

Fig. 2. Composition dependence of the PS/PI/PS-*b*-PI characteristic lengths, for the three systems investigated, determined (1) at the ODT for the lamellar systems, (2) when the correlation length decreases for the microemulsions. (○) d, periodic spacing of lamellar structure; (+) characteristic length at the transition from Lam. + μE → μE, (●) characteristic length of microemulsion; μE, channel of microemulsion; Lam. + μE, coexistence of lamellar and microemulsion morphologies; 2φ, region of macrophase separation. The theoretical Lifshitz point, Φ_{LP}, at a total homopolymer fraction is given for indication ($\Phi_{LP} = 1/(1 + 2\alpha^2)$).

correlated (ordered phase) to un-correlated (disorder) in few degrees. The boundary between the lamellar phase and the high temperature disordered state is often identified using a temperature-controlled experiments since it is well known to be associated with a discontinuity of the SAXS peak intensity and a change in the peak shape from a Gaussian to Lorentzian function [11,19,20]. Similarly, in the microemulsion regime, the values of the characteristic length, used to map out the phase diagrams, were taken where the correlation length between the domains starts to weaken and decrease towards zero (cf. Fig. 3). The SAXS peak for a microemulsion, which is described with the Teubner–Strey formula, slowly broadens and fades away as the temperature is increased. All the phase diagrams then determined were composed of regions of lamellar/disordered phase (at low homopolymer concentrations), bicontinuous microemulsion (at intermediate concentration) and macroscopic phase separation at high homopolymer content. In addition, the phase diagrams for $\alpha = 0.38$ and 0.74 show (1) a clear region of coexistence of bicontinuous microemulsions and lamellae between the periodically ordered phase (lamellar) and the channel of microemulsion, and (2) a shift in the position of the transitions. The volume fraction of homopolymers needed to develop a bicontinuous microstructure and macrophase separation is lower as the molecular weight of the homopolymers is increased. For $\alpha = 0.38$ and 0.74, only 70 and 50% of homopolymers in the blends are required to induce formation of microemulsions whereas 80% is necessary to generate a bicontinuous morphology, for $\alpha = 0.19$. Macroscopic phase separation occurs, for $\alpha = 0.74$, at 75% of homopolymers, 10% lower than the homopolymer concentrations reported for $\alpha = 0.19$ and 0.38 of, respectively, 86 and 84 %. This 10% decrease in the microemulsion stability might reflect the beginning of the disappearance of the microemulsion morphology in ternary blends since, according to Matsen et al. prediction, the attractive force between homopolymer domains will dominate the repulsive one, and, therefore, resulting in macrophase separation, for $\alpha > 0.8$.

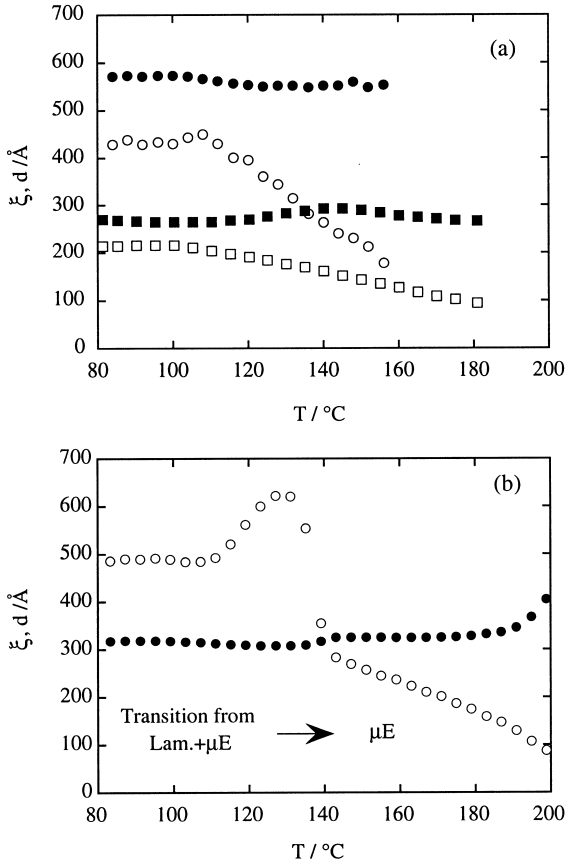

Fig. 3. Evolution of characteristic and correlation lengths, d (dark symbols) and ξ (light symbols), as a function of temperature. (a) pure microemulsion at $\alpha = 0.19$ ($\Phi_H = 0.86$), circle symbols/at $\alpha = 0.74$ ($\Phi_H = 0.55$), square symbols (b) coexistence of lamellar and microemulsion morphologies, $\alpha = 0.38$ ($\Phi_H = 0.65$).

The position of the theoretical Lifshitz point, calculated using Frederickson et al. equation [21,22], is also given on the phase diagrams for indication. It is clear that as α is increased, the position of predicted Lifshitz point moved to lower Φ_H values, to appear for $\alpha = 0.74$, between the region of coexistence of lamellae and microemulsions, and the pure microemuslions. Further studies are, however, needed to comment on the actual position of the Lifshitz point especially in regard of the most recent publications [23,24].

The coexistence of lamellae and microemulsions is revealed by the study of the variation of ξ and d, calculated from the values of a_2, c_1 and c_2, as a function of temperature T. The plots of ξ and d, shown in Fig. 3 for, respectively, $\Phi_H = 0.55$ ($\alpha = 0.74$), 0.86 ($\alpha = 0.19$) (Fig. 3(a)) and 0.65 ($\alpha = 0.38$) (Fig. 3(b)), contain information about both the persistence of the morphology and the development of the transition with temperature. For ternary blends where only microemulsions are present (Fig. 3(a): light symbols), ξ remains stable below 108 and 103 °C for, respectively, $\Phi_H = 0.55$ ($\alpha = 0.74$) and 0.86 ($\alpha = 0.19$), before decreasing linearly at higher temperatures. This constant decrease in ξ has previously been associated with the increase of thermal fluctuations at the interface between the microdomains, leading to a reduction of the length over which the microemulsions are correlated [11]. Meanwhile, d (dark symbols) remains roughly constant over the whole temperature range, suggesting a good stability of the microemulsion morphology even at elevated temperature. The values of d-spacing, at these temperatures (108 and 103 °C), were used to plot the phase diagrams. Only a small bump in the variation of d is observed for $\Phi_H = 0.55$ ($\alpha = 0.74$), which might be due to the re-organisation of the diblock at the interface to compensate for the increase in thermal fluctuations and the softening of the interface. On the other hand, the study of the variation of ξ with temperature for $\Phi_H = 0.65$ ($\alpha = 0.38$) (Fig. 3(b)), reveals a complex and different behaviour as the one observed for the $\Phi_H = 0.55$ ($\alpha = 0.74$) and 0.86 ($\alpha = 0.19$). From 80 to 110 °C, ξ stays constant at 490 Å before increasing unexpectedly up to 630 Å at 130 °C. Between 130 and 140 °C, ξ drops abruptly from 630 to 300 Å prior to decreasing linearly with temperature. If the behaviour of ξ, for $\Phi_H = 0.65$ ($\alpha = 0.38$), below 110 °C and above 140 °C, is consistent with the behaviour observed for ternary blends made of pure microemulsions with (1) a plateau at low temperatures and (2) a continuous decrease at higher temperatures (cf. Fig. 3(a) for $\Phi_H = 0.55$ ($\alpha = 0.74$) and 0.86 ($\alpha = 0.19$)), the increase and then drop in ξ between 110 and 140 °C reflects the presence of swollen lamellae in the mixture. Only the melting of lamellae, from an ordered to disordered state, can give such a sharp drop in ξ over a small temperature interval. For an ideal lamellar system, where the domains are perfectly well correlated, $\xi \to \infty$ (or ultimately to a high value constant), whereas, for a material with domains subject to strong thermal fluctuations, ξ decreases well below d. The transition associated to the ODT for lamellar systems is well understood and has previously been reported to be sharp [11,19,20]. The melting of the lamellae also corresponds a tiny increase of the d-spacing at 140 °C, back to its value at 80 °C. At 200 °C, the presence of the microemulsion morphology is still clearly visible, but is less well defined as ξ is approaching 0.

The stability of the microemulsions and the coexistence of the lamellar phase and microemulsion microstructure can be further investigated by plotting the variation of the amphiphilicity factor, f_a, as a function of temperature [12, 25]. The amphiphilicity factor is related to the coefficients a_2, c_1 and c_2 by the following expression:

$$f_a = \frac{c_1}{\sqrt{4\,a_2\,c_2}} \tag{4}$$

For very strong amphiphiles, where lamellar crystals are the dominant phase, $f_a = -1$. On the other hand, microemulsions are observed when f_a is between -1 and 0, with the strength of the microemulsion decreasing as f_a moves towards 0. The Lifshitz line is associated with $f_a = 0$ since $c_1 = 0$. Additional decrease in the amphiphilicity leads to the disorder line, where $f_a = +1$.

The evolution of the amphiphilicity factor as a function of temperature, is shown in Fig. 4, for two ternary blends exhibiting different behaviours. For $\Phi_H = 0.55$ ($\alpha = 0.74$) (Fig. 4(a)), where pure microemulsion morphology has been determined previously, f_a is roughly constant at -0.92 up to 108 °C, indicating that we are in presence of a 'good' microemulsion. However, at higher temperatures, f_a increases towards zero suggesting a weakening of the microemulsion through a loss of correlation between domains induced by thermal fluctuations (as clearly visible in Fig. 3 where ξ decreases but not d), but without reaching the theoretical Lifshitz line: at 180 °C, f_a is equal to -0.6. The variation of the amphiphilicity character and the value f_a found, undoubtedly confirm that we are going from a stable and good microemulsion at low temperatures to a less stable one at 180 °C. It is conceivable that the bicontinuous morphology persists even at higher temperatures but, because of the weak intensity of the diffracted peak and the samples leak out of the pans above 180 °C, it was impossible to determine at which temperature the mean-field isotropic phase is reached. The evolution of amphiphilicity factor for $\Phi_H = 0.65$ ($\alpha = 0.38$) (Fig. 4(b)) is, however, more complex with a jump-up of f_a from approximately -0.98, between 80 and 135 °C, to -0.92 at 145 °C. The value of f_a below 135 °C reveals a strong lamellar character for the blend since f_a is close to -1, confirming the presence of lamellae within the microemulsions suggested earlier. At around 145 °C, the lamellar phase disappears to give a microemulsion-based system, as f_a is similar (-0.92) to the values obtained for pure microemulsion morphologies (cf Fig. 4(a)). As the temperature is further increased above 160 °C, the amphiphilicity factor decreased exponentially towards zero. It can be alleged that, at roughly 200 °C, f_a reaches 0, which corresponds to the Lifshitz line. However, due to the difficulty of such experiments, the position of the Lifshitz line could not be determined for all compositions, which prevented us to define the position of the experimental Lifshitz point.

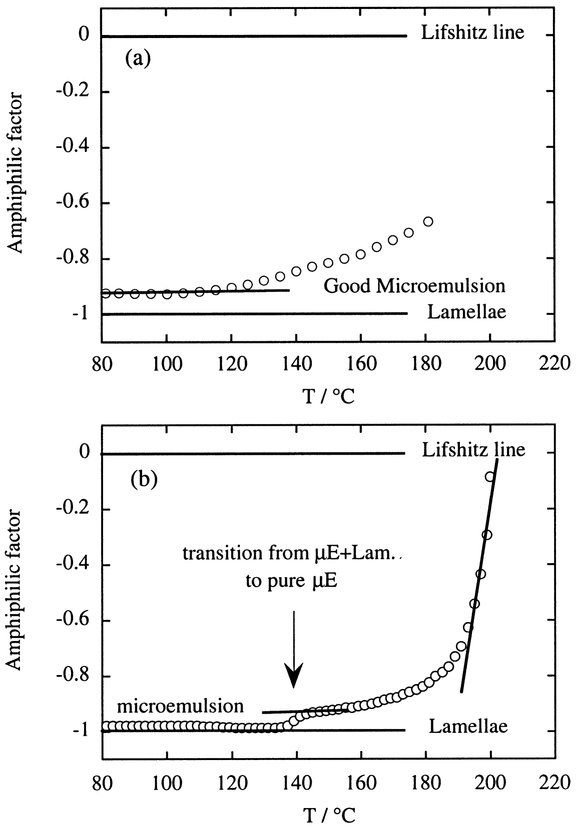

Fig. 4. Variation of the amphiphilicity factor as a function of temperature. (a) Pure microemulsion, $\alpha = 0.19$ ($\Phi_H = 0.86$), (b) region of coexistence of lamellar and microemulsion morphologies, $\alpha = 0.38$ ($\Phi_H = 0.65$).

It is also interesting to notice that upon the incorporation of homopolymers into the lamellar microstructure, the periodic spacing continuously increases from 152 Å in the original diblock, to a maximum value of 216, 234 and 379 Å for, respectively, $\Phi_H = 0.30$ ($\alpha = 0.74$), $\Phi_H = 0.5$ ($\alpha = 0.38$) and $\Phi_H = 0.77$ ($\alpha = 0.19$), without destruction of the lamellar morphology. The effectiveness of the homopolymers to swell the diblock clearly depends upon the molecular weight of two homopolymers, since blends made of homopolymers with the lowest α value ($= 0.19$) produce the highest swelling of the lamellar material. The evolution of the periodicity d, as a function of Φ_H is better shown in Fig. 5, for the three systems investigated, along with the variation of the d-spacing calculated using the surfactant/solvent model. In a lamellar surfactant/solvent system, where a bilayer of surfactant is stacked between layers of solvent, a simple relationship has been defined to calculate the periodicity of the overall membrane, d, from the knowledge of the bilayer thickness δ and the volume fraction of surfactant Φ_S, assuming that the thickness of the bilayer remains constant upon the addition of solvent [26].

$$d\,\Phi_S = \delta \tag{5}$$

Applying this model to our experimental data allows us to compare the behaviours of our ternary blends to the one exhibited by the surfactant/solvent system. For $\alpha = 0.74$, the experimental periodicities and the d values defined using the surfactant/solvent model are superimposable, at least up to $\Phi_H = 0.46$, suggesting that no homopolymer is penetrating the diblock layers (cf. Fig. 5). In a sense, the ternary blends behave exactly like a surfactant/solvent system despite their respective differences. In ternary blends, the homopolymers are located in the middle of the layers because of the unfavourable conformational entropy involved by the dissolution of the homopolymers into the diblock, whereas, in the surfactant/solvent system, a repulsive interaction parameter is responsible for the segregation of the surfactant and the solvent. The decrease in the stability of the microemulsion morphology observed in Fig. 2, for $\alpha = 0.74$, and assigned to the beginning of disappearance of the microemulsion morphology in ternary blends, is confirmed here since, according to Matsen's prediction, the strength of the repulsive force between homopolymer domains is proportional to the number of homopolymer molecules swelling the copolymer monolayers [13]. The smaller periodic spacings noticed in the polymer case for $\alpha = 0.38$ or 0.19, demonstrate that shorter homopolymers are easier solubilised in the diblock layers than longer ones. Indeed, upon the addition of homopolymers, the periodicity of the swollen lamellar morphology does not grow as much as it would do if it followed the surfactant/solvent prediction. The surfactant/solvent model can be applied only if the solvent does not penetrate the surfactant bilayer. The experimental d-spacing determined for $\alpha = 0.38$ and 0.19, are, within the experimental error, similar up to $\Phi_H = 0.3$, suggesting that the amount of homopolymers that can be dissolved in the diblock is also an important factor, not only the homopolymer chain length. Further increase of the homopolymer content reveals a difference between the evolution of d-spacing for $\alpha = 0.38$ and 0.19, probably because of the different degree of saturation of the diblock layers by the homopolymers. The diblock layers having solubilised as much homopolymers as they possibly can without losing too much conformational entropy, expulse the remaining homopolymers away from the swollen diblock layers. It might, as well, be possible to use the surfactant/solvent model to fit the experimental d-spacing data for $\alpha = 0.38$ and 0.19, considering that the homopolymers are located in the center of the lamellae for concentrations of homopolymers different from $\Phi_H = 0$.

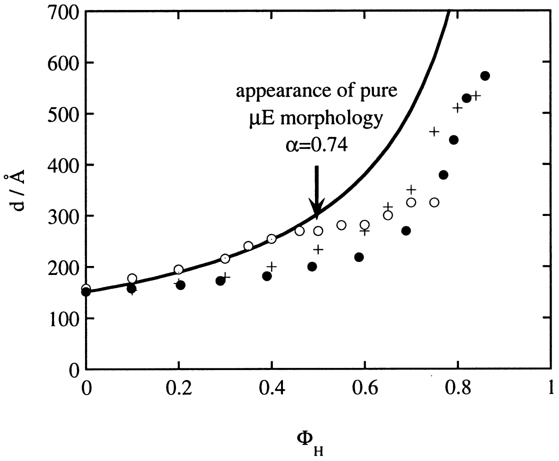

Fig. 5. Comparison of characteristic lengths determined experimentally for the three lamellar systems; (●) $\alpha = 0.19$, (+) $\alpha = 0.38$ and (○) $\alpha = 0.74$, with the value calculated using the lamellar surfactant/solvent system (solid line).

Above $\Phi_H = 0.46$ ($\alpha = 0.74$), the periodicity does not follow the surfactant/solvent prediction, probably because the morphology of the blends is not longer lamellar. At that concentration, bicontinuous microemulsions are observed, consisting of essentially pure homopolymer phases separated by a stretched copolymer layer.

4. Conclusions

The influence of the increase of the molecular weight of homopolymers on the phase behaviour in ternary blends of polystyrene/polyisoprene/polystyrene-*block*-polyisoprene has been investigated, keeping the diblock dimension constant. As the molecular weight of the homopolymers is increased closer to 0.8 (e.g. $\alpha = 0.74$), the macroscopic phase separation occurs at lower homopolymer concentration as the one observed for $\alpha = 0.19$ and 0.38, suggesting a disappearance of the microemulsion microstructure in favour of macrophase separation. Indeed, at $\alpha = 0.19$ and 0.38, macroscopic phase separation happens at the approximately same homopolymer content. The comparison of the variation of periodicity for lamellar phase with $\alpha = 0.74$, with the variation of the d-spacing calculated using the surfactant/solvent model indicates that, for this system, the homopolymers are located in the center of the bilayer, and do not swell the diblock interface. The absence of homopolymers in the lamellar monolayers is another indication of the instability of the microemulsion morphology for $\alpha = 0.74$, considering the theoretical prediction by Matsen et al. In all three systems studied, a phase transition from lamellar to bicontinuous microemulsion, and then macroscopic phase separation have been reported with addition of homopolymers, except for $\alpha = 0.38$ and 0.74 where a region of coexistence of bicontinuous microemulsions and lamellae, between the periodically ordered phase (lamellar) and the channel of microemulsion, has been identified.

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