Thin Film Behavior of Poly(methyl methacrylates). 8. Monolayer Behavior of Mixtures of Poly(methyl methacrylate) and Poly(isobutyl methacrylate)

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ABSTRACT: In view of recent observations of stereocomplexation processes in mixed monolayers of isotactic and syndiotactic poly(methyl methacrylate) (i-PMMA and s-PMMA) monolayers of mixtures of isotactic PMMA and syndiotactic poly(isobutyl methacrylate) (s-PiBMA) were studied in search of an alternative system exhibiting stereocomplexation at the air–water interface. An anomalous transition observed in the isotherms of these mixtures is shown not to correspond to such a stereocomplexation process, but rather to a pressure-induced mixing, which is responsible for a suppression of the crystallization of the i-PMMA component in the monolayer. Miscibility is also observed (even without a required surface pressure buildup) for mixtures of s-PiBMA and s-PMMA. The large effects observed indicate that mixing must occur up to close to the segmental level. The observation that random copolymers of these monomers exhibit smaller effects than homopolymer mixtures suggests that the two-dimensional character of the monolayer, prohibiting random segmental mixing of the homopolymer mixtures, is favorable with respect to the adhesive interactions. For the mixtures of s-PiBMA and i-PMMA, clear molecular weight effects are found, both with respect to the kinetics of the lateral interdiffusion process upon mixing, as well as in terms of the thermodynamics of the mixing process.

Introduction

In previous papers,[1-4] the opportunities for stereocomplexation of isotactic and syndiotactic poly(methyl methacrylate) (i-PMMA and s-PMMA) in mixed monolayers at the air–water interface were addressed. So far, we limited ourselves to mixtures of i- and s-PMMA, with the exception of the partially hydrolyzed s-PMMA that was shown to form monolayer stereocomplex structures with isotactic PMMA in ref 4. In an attempt to find other systems exhibiting monolayer stereocomplexation processes, and thus to broaden the scope of the characteristics that can be introduced in thin films using this approach, we will address the couple isotactic PMMA/syndiotactic *poly(isobutyl methacrylate)* (s-PiBMA) in this paper.

Syndiotactic poly(isobutyl methacrylate) was reported to engage in stereocomplexation processes in mixtures with isotactic PMMA. The first report was published by Bosscher et al.,[5] and a more elaborate study was later published by Kitayama et al.[6] In the latter paper, stereocomplexation was claimed to occur both in solution as well as in melt mixtures of these materials. The stereocomplex structure itself is probably strongly related to that of the s-PMMA/i-PMMA system, the bulky ester side groups of the syndiotactic component pointing outward from the double helical structure without disturbing it.[5,7,8]

The monolayer behavior of syndiotactic poly(isobutyl methacrylate) was discussed in ref 9. The pressure–area isotherms for this material indicate a significantly higher area pro monomeric unit associated with the s-PiBMA materials, compared to s-PMMA, both polymers yielding condensed monolayers. The resulting larger separation of the polymer backbones may imply a lower level of cohesive forces between the segments: if stereocomplexation were to occur in monolayers of mixtures of s-PiBMA and i-PMMA, problems due to aggregation of the syndiotactic component in the monolayer (a direct result of these strong cohesive interactions, as discussed for s-PMMA in ref 3) may be less restrictive. In this paper we will discuss the behavior of monolayer blends of stereoregular poly(isobutyl methacrylate) and poly(methyl methacrylate), and focus on the interactions of these polymers in the monolayer.

Table I
PMMA Characteristics

material	tacticity (%) i	h	s	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
m1	>97			1200	1.35
m10	>97			24	1.21
m13	>97			13	1.19
m26	81	15	4	18	1.13
m28	66	28	6	28	1.21
m33	3	33	64	18	1.15
m42	1	4	95	9.0	1.20

Table II
PiBMA Characteristics

sample	i	h	s	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
b1	95	5		3.2	4.8
b2	5	30	65	390	1.27
b3	6	28	66	30	1.31
b4	3	6	91	450	1.18
b5	2	7	91	22	1.59
b6	0	3	97	16	1.09

Table III
PnBMA Characteristics

sample	i	h	s	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
nb1		nd		28	1.51

Experimental Section

The characteristics of the materials used are listed in Tables I–III. Synthesis procedures used for the preparation of the PMMA samples are listed in ref 10. Syndiotactic PiBMA was prepared either according to the procedure introduced by Hatada[11] (sample b6), or through a Ziegler–Natta type polymerization[12] followed by a fractionation procedure (samples 4 and 5). Atactic PiBMA (as well as PnBMA) was a product of a conventional radical polymerization in toluene at 70 °C; the MMA–iBMA copolymers were also prepared according to this procedure, using three different monomer feed ratios: these polymerizations were stopped at 20% conversion. Isotactic

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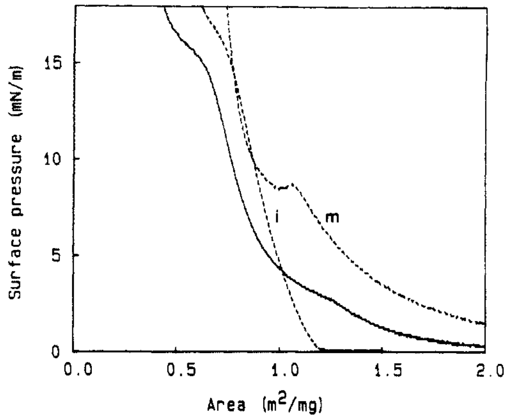

Figure 1. Pressure–area isotherms of i-PMMA m10 (m, dashed), s-PiBMA b6 (i, dashed), and a mixture of these materials (weight fraction s-PiBMA 0.57, base mole fraction 0.49) (solid line). T = 22 °C.

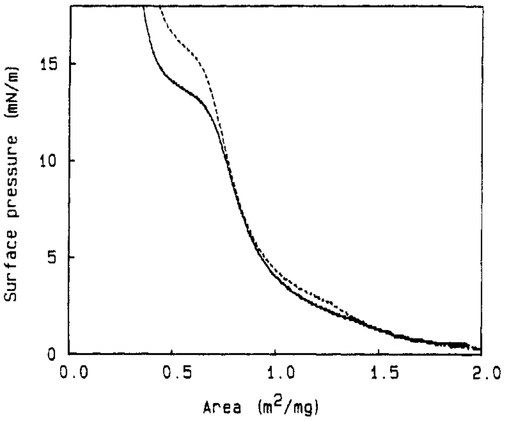

Figure 2. Pressure–area isotherms of a mixture of i-PMMA m10 and s-PiBMA b6. Composition as in Figure 1. T = 22 °C (dashed line) and 41 °C (solid line).

PiBMA was prepared with a phenylmagnesium bromide initiator in toluene at room temperature.[13]

The monolayer behavior of the mixtures was studied using the procedures and apparatus as described in ref 10; polymers were spread from dilute (mixed) chloroform solutions. Unless stated otherwise, a standard compression speed of 2 Å^2/(monomeric unit·min) was used. The IR apparatus and techniques used to acquire infrared spectral information of the transferred LB layers of these materials are discussed in ref 14. Surface potential measurements were performed at the MPI für Biophysikalische Chemie in Göttingen, BRD, in collaboration with Prof. D. Möbius, using the vibrating plate technique.[15]

Results and Discussion

In Figure 1, pressure–area isotherms are shown of monolayers of isotactic PMMA (m10, $\bar{M}_n$ 24K), syndiotactic PiBMA (b6, $\bar{M}_n$ 16K), and a mixture of these two materials in an approximately 1:1 (base mole) ratio. From these isotherms, it may be evident that the monolayer of the mixture does not exhibit additive behavior: only up to a surface pressure of about 3 mN/m, the isotherm appears to follow an approximately additive curve, until an anomalous transition is observed. Beyond this transition, the specific area of the mixed monolayer is clearly lower than the average value for the monolayers of the two individual components. The isotactic PMMA monolayer crystallization transition[10,14] is no longer visible in the isotherms and appears to be completely suppressed. The collapse pressure of the mixed monolayers is slightly lower than that of pure s-PiBMA.

Temperature Dependence. Figure 2 shows pressure–area isotherms of the monolayer mixture from Figure 1 as a function of temperature. The anomalous behavior observed at room temperature is also evident in the isotherms at other temperatures. Over the entire temperature range studied, from 10 to 41 °C, the monolayer crystallization of the isotactic PMMA component is suppressed, and the anomalous low surface pressure transition can be observed. The onset of this transition shifts to lower pressures at higher temperatures. So far, these phenomena are strongly reminiscent of the behavior of the stereocomplexing mixtures of isotactic and syndiotactic PMMA, discussed in refs 1 and 2.

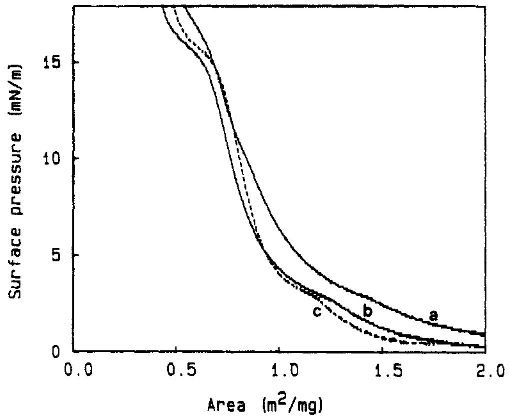

Figure 3. Pressure–area isotherms for mixtures of i-PMMA m10 and s-PiBMA b6. Weight fraction s-PiBMA (base mole fraction): 0.38 (0.30) (a), 0.57 (0.49) (b), and 0.76 (0.69) (c, dashed line). T = 22 °C.

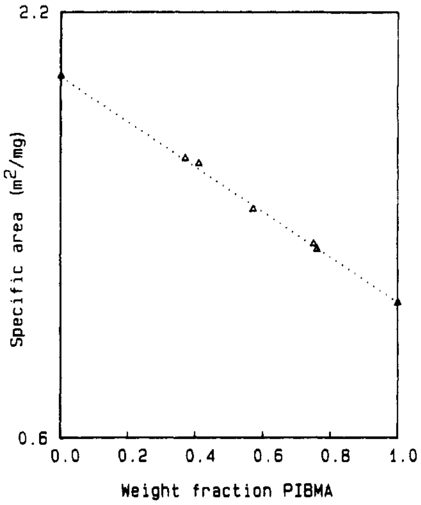

Figure 4. Specific area (Π = 1.6 mN/m, T = 22 °C) for mixtures of i-PMMA m10 and s-PiBMA b6, as a function of composition.

Stoichiometry. Varying the composition of the i-PMMA/s-PiBMA mixtures results in pressure–area isotherms as reported in Figure 3. For all mixing ratios, a transition can be seen at low surface pressures, the onset pressure being independent of the monolayer composition. Only for the mixture with a (base mole) mixing ratio of 2:1 (i-PMMA:s-PiBMA), there is a slight inflection detectable in the isotherm that may reflect the "normal" i-PMMA monolayer crystallization process; in the other mixtures, this process has not left any marks in the isotherms.

In the low surface pressure regime of the isotherms, the mixtures exhibit *additive behavior*, as is illustrated by Figure 4, representing the specific areas associated with constant low surface pressures as a function of mixture composition. The compressibility of the monolayers also follows the additive line in this pretransition region closely. Additivity was also observed for these parts of the

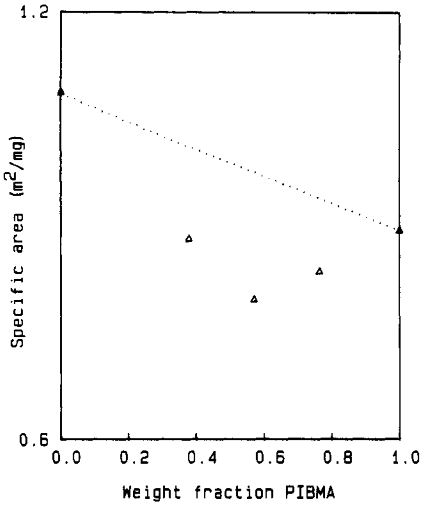

Figure 5. Specific area (Π = 8.5 mN/m, T = 22 °C) for mixtures of i-PMMA m10 and s-PiBMA b6, as a function of composition.

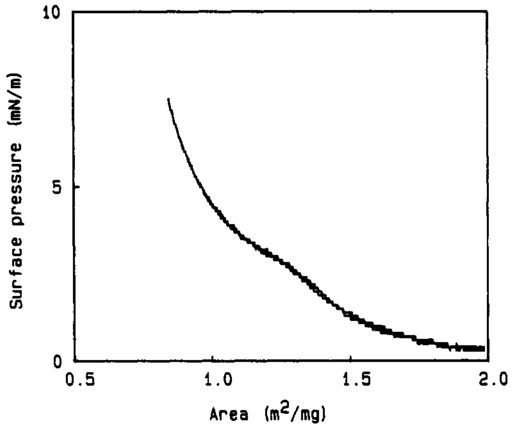

Figure 6. Hysteresis experiment with a mixture of i-PMMA m10 and s-PiBMA b6. Composition as in Figure 1. Compression and decompression speed 2 Å^2/(monomeric unit·min). T = 22 °C.

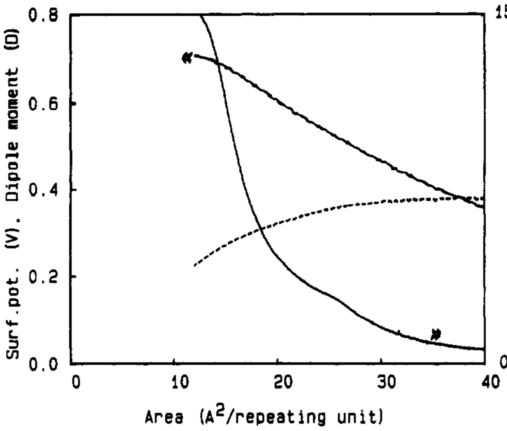

Figure 7. Surface potential (solid), $\mu_\perp$ (dashed), and surface pressure upon compression of a monolayer of a mixture of i-PMMA m13 and s-PiBMA b6. Weight fraction s-PiBMA 0.59, base mole fraction 0.51. T = 22 °C.

isotherms at other temperatures. The specific areas directly beyond the transition clearly deviate from the additive line (Figure 5): from the mixtures studied, the one with the 1:1 (base mole) composition exhibits the largest deviation. This apparent 1:1 stoichiometry marks a first discrepancy with the behavior of the i-PMMA/s-PMMA monolayer mixtures.[1]

Compression Speed Dependence and Hysteresis. The isotherms of the s-PiBMA/i-PMMA mixture, reported in Figure 1, surprisingly do not exhibit a clear compression speed dependence in the surface pressure regime up to the collapse of the monolayer. The monolayer is instantaneously stable when compression is paused, even in or beyond the transition region of the isotherm. Hysteresis experiments (Figure 6) indicate that the monolayer compression is perfectly reversible, even if the monolayer is compressed beyond the transition region: the decompression isotherm exactly follows the compression isotherm, and so does a second compression isotherm, following decompression. The monolayer appears to remain in thermodynamic equilibrium during compression, without any kinetic effects being significant during the monolayer transition, using a compression speed of 2 Å^2/(monomeric unit·min). Only when the isotherm is recorded at low temperatures, a small hysteresis loop can be observed, which disappears upon lowering the compression speed. The behavior of these mixed monolayers stands in sharp contrast with that of monolayers of s-PMMA/i-PMMA mixtures, or of pure i-PMMA, in which during the stereocomplexation or the i-PMMA crystallization process, respectively, kinetic effects proved to be very important, and in which strong hysteresis effects were observed, for the PMMA stereocomplexation process even resulting in an incomplete melting of the complexed structures upon complete decompression.[2,10]

Surface Potential Measurements. An experiment performed on a mixture of i-PMMA and s-PiBMA, in which the surface potential of the monolayer was recorded simultaneously with the surface pressure, yields information as reported in Figure 7. At low surface pressures, the dipole moment pro monomeric unit ($\mu_{\perp,\Pi\to 0}$) that can be extracted from the surface potential data yields a perfectly additive value (0.38 D, versus 0.35 and 0.415 D for i-PMMA and s-PiBMA, respectively). During the transition, evident in the pressure–area isotherm, no discontinuity in the surface potential or the slope of the surface potential curve is observed. In both the water surface crystallization of isotactic PMMA as well as the monolayer stereocomplexation in mixtures of i- and s-PMMA, the onset of the double helix formation process was accompanied by a sudden stop in the rise of the surface potential upon further compression (with a corresponding onset of a sharp fall of $\mu_\perp$).[1,9] For these systems, this effect is illustrative for the conformation change in the monolayer from a more or less amphiphilic orientation to the helical conformation, characterized by a lower value for $\mu_\perp$. For mixed monolayers of i-PMMA and s-PiBMA, the initial amphiphilic orientation does not seem to be changed drastically during the transition, the surface potential remaining at an approximately additive value.

Considering these results, a stereocomplexation process as the cause for the isotherm transition for mixtures of i-PMMA and s-PiBMA appears unlikely.

Infrared Experiments. In order to obtain more information about the nature of the isotherm transition, infrared spectra were recorded from LB layers of these mixtures, transferred to solid substrates at surface pressures corresponding to the situation before and beyond the isotherm transition (2.5 and 8 mN/m, respectively). The mixed monolayers can be easily transferred to ZnS and gold substrates, with typical transfer ratios of 0.3 (downstroke) and 1.0 (upstroke). The multilayers built this way were studied by IR transmission and grazing incidence reflection (GIR) techniques.

The spectra obtained for the as-deposited multilayers are reported in Figures 8 and 9 (transmission and GIR spectra, respectively). In both figures, spectra are shown for the same i-PMMA/s-PiBMA mixture, transferred at

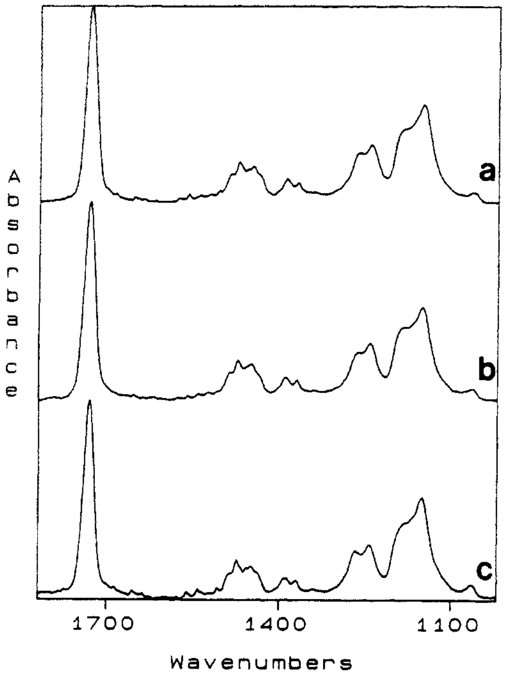

Figure 8. Transmission IR spectra of multilayers on ZnS, built from a mixture of i-PMMA m10 and s-PiBMA b6 (composition as in Figure 1): (a) as-deposited, transfer pressure 2.5 mN/m; (b) as-deposited, transfer pressure 8 mN/m; (c) after annealing at 70 °C for 2 h.

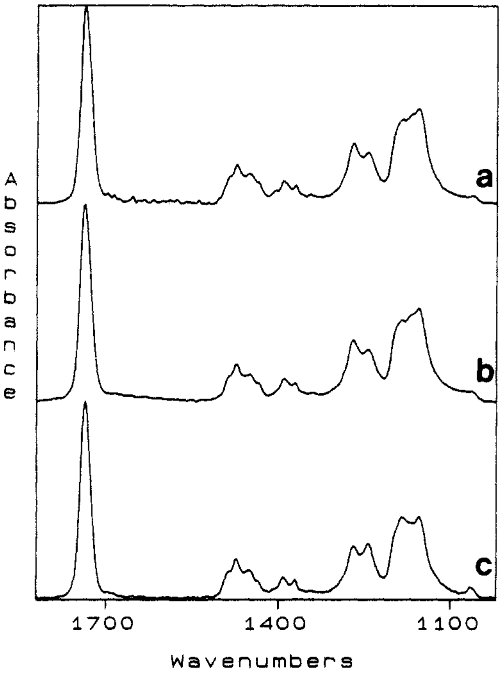

Figure 9. Grazing incidence reflection IR spectra of multilayers on gold substrates, built from a mixture of i-PMMA m10 and s-PiBMA b6 (composition as in Figure 1): (a) as-deposited, transfer pressure 2.5 mN/m; (b) as-deposited, transfer pressure 8 mN/m; (c) after annealing at 70 °C for 2 h.

two different surface pressures. The similarity of the spectra related to the pre- and posttransition condition of the monolayers is striking. There are differences between the transmission spectra and the GIR spectra, indicating that there is some kind of orientation difference between the *X* and *Y* directions in the plane of the substrate on one side, and the *Z* direction perpendicular to the substrate on the other side. These spectral differences are qualitatively similar to those observed in monolayers of pure s-PiBMA (reported in ref 9), and are indicative of a remaining amphiphilic orientation in the as-deposited multilayers. It appears that, upon traversing the transition region of the isotherm, this amphiphilic orientation of the segments is simply retained, a conclusion that can also be drawn from the surface potential measurements discussed in the previous paragraph. A more detailed interpretation of these spectra is difficult to give, since it is hard to separate the contributions from the i-PMMA and the s-PiBMA components.

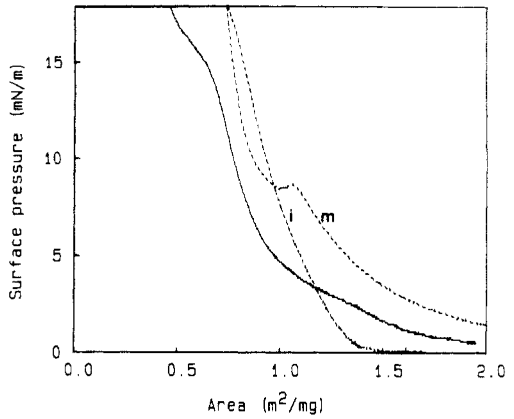

Figure 10. Pressure–area isotherms of a-PiBMA b3 (i, dashed), i-PMMA m10 (m, dashed), and a mixture of these materials (weight fraction PiBMA 0.59, base mole fraction 0.51) (solid line). T = 22 °C.

When polarized IR radiation is used to probe the samples in the transmission mode, no preferential orientation in the XY plane can be detected: the spectra obtained with the electrical field vector parallel to, or perpendicular to, the transfer direction are identical. For multilayers built both from the water surface crystallized LB layers of isotactic PMMA as well as from the stereocomplex structures formed in monolayer mixtures of s- and i-PMMA, a clear anisotropy within in the *XY* plane parallel to the substrate was observed.[1,14] For these systems, this lateral orientation is the result of the flow associated with the transfer process in combination with the presence of anisotropic rigid structures (the (crystallites built from the) double helices present in the monolayer). The fact that no such effect is observed in mixed monolayers of i-PMMA and s-PiBMA is another indication against the presence of helical stereocomplex structures.

When the as-deposited multilayers are heated to 70 °C (just above the glass transition temperature of either component), the amphiphilic orientation of the PiBMA segments can be observed to disappear, and the multilayer attains isotropic characteristics (Figures 8c and 9c); again, there is no indication for the presence of crystalline-like structures with higher melting points.

Tacticity Dependence. A final check before definitely rejecting a stereocomplexation process as the cause for the isotherm transition must be a study of the effect of the tacticity of both components on this process: in the case of stereocomplexation, lower tacticities must be observed to result in a suppression of this transition, or in a shift to higher surface pressures (as was found for the s-PMMA/i-PMMA monolayer stereocomplexation process in ref 1).

Figure 10 shows the pressure–area isotherm of a mixture of isotactic PMMA with "atactic" (conventional) PiBMA (sample b3). The isotherm of this mixture is very similar to that of the mixture based on the highly syndiotactic material (Figure 1): again, at low surface pressures, additive behavior is observed, followed by a transition in the isotherm and a subsequent region characterized by specific areas significantly smaller than the additive value. The onset of the transition is observed at a surface pressure

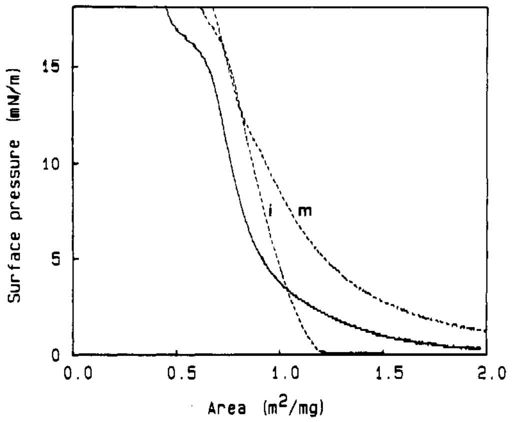

Figure 11. Pressure–area isotherms of s-PiBMA b6 (i, dashed), i-PMMA m26 (81% i-triads, m, dashed), and a mixture of these materials (weight fraction PiBMA 0.58, base mole fraction 0.50) (solid line). T = 22 °C.

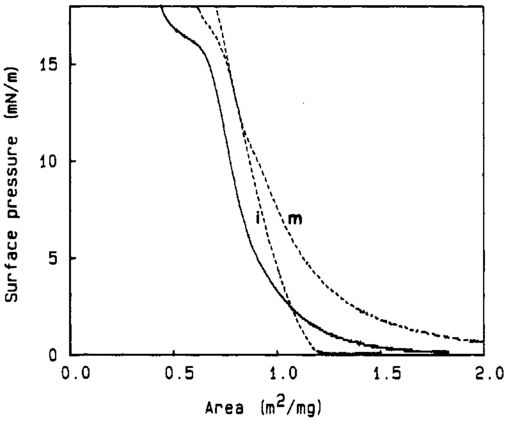

Figure 12. Pressure–area isotherms of s-PiBMA b6 (i, dashed), i-PMMA m28 (66% i-triads, m, dashed), and a mixture of these materials (weight fraction PiBMA 0.61, base mole fraction 0.52) (solid line). T = 22 °C.

similar to that in the isotherms of the analogous mixture based on highly syndiotactic PiBMA. Evidently, a high stereoregularity of the PiBMA component is not required for the transition process.

Variation of the tacticity of the PMMA component in the mixtures yields interesting results. In Figure 11, the isotherms are shown of a mixture of s-PiBMA with i-PMMA m26, triad tacticity 81%, and of the individual components of this mixture; in Figure 12, the same is done for a mixture of s-PiBMA with i-PMMA m28, with an even lower triad tacticity of 66%. In both cases, it can be seen that the isotherm recorded for the mixture deviates significantly from that calculated for additive behavior, with lower specific areas observed. The transition is less clear, because it appears to have shifted to *lower* surface pressures, so that no clear regime of additive behavior preceding such a transition can be observed in these mixtures. The shift of the transition to lower surface pressures indicates that, upon lowering the stereoregularity of the i-PMMA component, the posttransition condition of the monolayer becomes relatively more favorable compared to the condition reflecting additive behavior, clearly opposite of what would be expected for a stereocomplexation process.

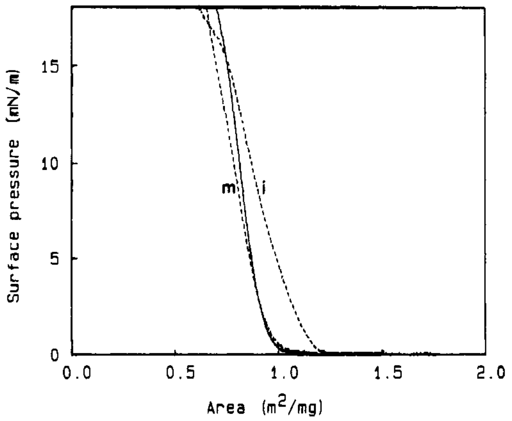

Figure 13. Pressure–area isotherms of s-PMMA m42 (m, dashed), s-PiBMA b6 (i, dashed), and a mixture of these materials (weight fraction PiBMA 0.55, base mole fraction 0.46) (solid line). T = 22 °C.

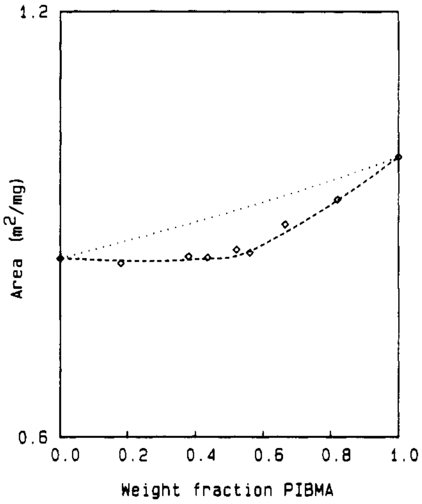

Figure 14. Specific areas (Π = 5.0 mN/m, T = 22 °C) for mixtures of s-PMMA m42 and s-PiBMA b6, as a function of composition.

When the i-PMMA samples are exchanged for predominantly *syndiotactic* PMMA samples, we also observe that the mixtures with s-PiBMA clearly deviate from what is to be expected for additive behavior. Both with conventional (atactic) as well as with highly syndiotactic PMMA, the mixtures form condensed monolayers, but with specific areas deviating significantly from the additive values. Especially at low surface pressures, the monolayers can be observed to occupy a smaller surface area; the experimental isotherms are also steeper than hypothetical additive isotherms (Figure 13). The influence of the composition on the specific areas in mixtures of s-PiBMA with s-PMMA is illustrated by Figure 14. As in the mixtures with i-PMMA, we observe that a maximum deviation from the additive line is attained for an approximately 1:1 (base mole) ratio. For mixtures of conventional a-PiBMA with conventional a-PMMA, these data are included in Figure 17 and yield identical conclusions. The specific areas obtained for the 1:1 mixtures are of a magnitude similar to the magnitude of those observed for the posttransition region of the mixtures of s-PiBMA and i-PMMA.

Similar deviations of the monolayer behavior, leading to smaller values for the specific areas, relative to the additive value, have been reported for mixtures of conventional PMMA with poly(n-butyl methacrylate)[16] and with poly(propyl methacrylate),[17] two polymers which are fairly similar in structure to the poly(isobutyl methacrylate) studied here. Therefore, the observations reported here may not be limited to the PiBMA/PMMA system, but may apply to a broader range of polymers. In Figure 15, an isotherm is reported for a mixture of i-PMMA and poly(n-butyl methacrylate). Indeed, also in this mixture, a deviation from additive behavior is observed, characterized by smaller values for the specific areas, and a

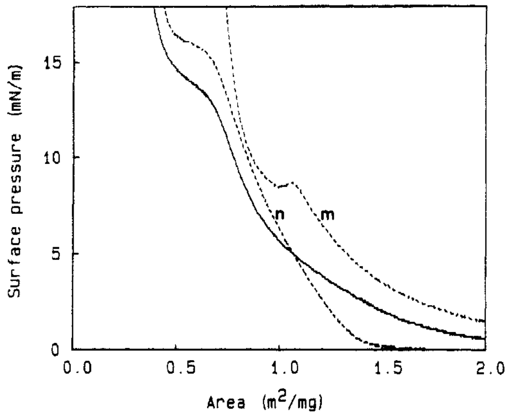

Figure 15. Pressure–area isotherms of PnBMA (n, dashed), i-PMMA m10 (m, dashed), and a mixture of these materials (weight fraction PnBMA 0.59, base mole fraction 0.51) (solid line). T = 22 °C.

complete suppression of the crystallization of the i-PMMA component, similar to the mixtures with PiBMA; the onset of the departure from additivity is not as clear as in these latter mixtures. The collapse characteristics of the PnBMA/i-PMMA mixed monolayers are also different from those of a pure PnBMA monolayer.

From the results reported so far, we can definitely conclude that the transition observed in the mixtures of i-PMMA and s-PiBMA is not associated with a stereocomplexation process. Instead, it appears that PMMA and PiBMA tend to form monolayers that are intimately mixed, with a high number of MMA–iBMA segment contacts, and an orientation of the segments with respect to the water phase which is not strongly different from that in a nonmixed situation. We will first address the s-PMMA/s-PiBMA mixtures.

Mixtures of s-PMMA and s-PiBMA. Mixtures of s-PMMA and s-PiBMA (or poly(propyl methacrylate) or poly(n-butyl methacrylate)) form condensed monolayers, which occupy an area significantly lower than that calculated as the average of the two individual components in nonmixed monolayers, even at zero surface pressure. The only way to explain these strong deviations is to assume that there are strong favorable interactions between the MMA and the iBMA segments, which induce a contraction of the monolayer with respect to a situation with only contacts between identical segments; the number of contacts must be high in order to be able to cause deviations as large as those observed. The first aspect that needs to be clarified is the nature of these favorable interactions: why is the interaction between the MMA segments and the iBMA (or PMA or nBMA) segments more favorable than the combination of the interactions between the segments of the same component, and why does this result in a lower area occupied by the chains in the monolayer?

The interactions between the segments in monolayers of PMMA and PiBMA were already addressed in ref 9. Monolayers of syndiotactic PMMA are characterized by strong cohesive interactions between the segments, an effect that was attributed to the difficulty for the syndiotactic backbone to assume an amphiphilic conformation. The polymer backbones are closely packed in the monolayers to optimize these interactions. The interactions in monolayers of PiBMA will be strongly affected by the presence of the bulky isobutyl groups, which will prevent a close approach of the backbones, reflected in the observation that PiBMA occupies an area per monomeric unit that is almost twice that of PMMA. The backbone–backbone interactions may be frustrated by the large separation imposed by the steric hindrance between the large side groups. This argument is also valid for poly(n-butyl methacrylate) and poly(propyl methacrylate): in all cases, the monolayer packing will be determined by a balance between the attractive backbone–backbone interactions and the repulsive forces resulting from the steric hindrance from the ester alkyl substituents.

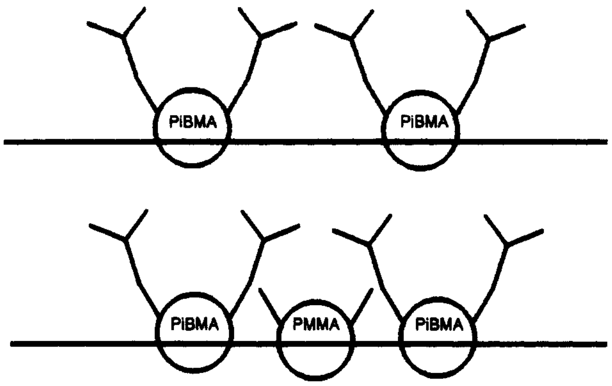

Figure 16. Schematic representation of the suggested interaction between s-PiBMA and s-PMMA strands.

Let us now consider the situation in which we have a strand of PiBMA located on the water surface, parallel to a neighboring strand of PMMA. If we imagine the strands to be separated by a distance which is the average of the distances in the individual components ("additive" behavior), it is not difficult to see that the balance of the repulsive force and the attractive forces is not necessarily zero. The steric repulsion effects between the chain with the isobutyl groups and the chain with the short methyl side chains will probably be less than in the case of two contiguous PiBMA chains, whereas the attractive forces between the backbones may be higher as a result of the smaller separation. The result of the unbalance will be an effect in which the backbones are brought closer together, resulting in more favorable backbone–backbone interactions, until the steric repulsive forces between the PMMA and the PiBMA chain again balance these attractive interactions. This process can also be imagined to be accompanied by a variation in the degree of submersion of one of the polymers, e.g., a slight "lifting" of the PiBMA chain in order to accommodate the approaching PMMA chain more efficiently. As a net result, the PMMA may be "shoved" under the "umbrella" formed by the isobutyl groups of the PiBMA chain. This speculative mechanism is illustrated in Figure 16; it may rationalize the fact that contacts between the segments of PMMA and PiBMA (or PPMA or PnBMA) are enthalpically favorable, especially with respect to the interactions in pure PiBMA monolayers, and that they lead to an effective contraction of the monolayer. Moreover, it predicts a 1:1 stoichiometry on the monomeric unit level to be optimal for the contraction process, a ratio that can indeed be deduced from the results reported here. The observation that the compressibility of the mixed monolayer is lower than expected for additivity can also be explained along these lines.

When syndiotactic PiBMA is replaced by *isotactic* PiBMA, we do not observe this type of mixing: up to the collapse regime, the monolayers exhibit approximately additive behavior in mixtures with s-PMMA; this observation is in agreement with the aforementioned interpretation. In contrast to its syndiotactic analogon, isotactic PiBMA forms an *expanded*-type monolayer, the contribution from the backbone interactions to the segmental cohesion being weak.[9] Evidently, in this case, the idea of backbone interactions being frustrated by the steric repulsions of the side groups will not apply; at low surface pressures, the distance between the backbones tends to be larger than that associated with the steric repulsion of the side groups.

Langmuir–Blodgett monolayers can be considered to form a pseudo-two-dimensional system. This two-dimensional character may have some restrictive implications with respect to mixing processes: in bidimensional polymer mixtures, a random mixing of the segments, as conceivable for a three-dimensional system, cannot be expected due to the topological constraints of the monolayer. For athermal mixtures (or for mixtures with an unfavorable interaction energy), the individual polymer chains will tend to be segregated to form isolated coils,[18] since interpenetration of the coils would require a large sacrifice of conformational entropy. In the case of strongly attractive interactions between the segments of the different components, Cifra et al.,[19] using Monte Carlo simulations, demonstrated that interpenetration of the polymer coils can occur. In this case, the mixtures are characterized by *locally parallel* contiguous strands of both components. The mixture cannot be described in terms of *randomly* mixed segments: random segmental mixing is not feasible, since this would require an unprohibited crossing of the chains in the two-dimensional layer. The results reported by Cifra apply to fairly short chains; in the case of longer chains, interpenetration may become less easy.[20] In the present case, when high molecular weight samples of syndiotactic PiBMA and PMMA are used, instead of the rather low molecular weights used so far, mixing is still observed, to an extent similar to that for the low molecular weight samples. In this context, is important to note that, in the actual monolayer under consideration, escape routes are available to relieve the effects of the chain segregation: if the contact enthalpy gain is very high, crossovers may be allowed to some extent so as to optimize the number of contacts.

iBMA/MMA Copolymers. As outlined in the previous paragraph, the segment mixing in the PiBMA/PMMA mixed monolayers cannot be expected to have a random character, but may be more properly described in terms of a locally parallel alignment of the chains, causing favorable interactions over some length along the parallel chains. In this context, it is interesting to study the behavior of monolayers of random copolymers of isobutyl methacrylate and methyl methacrylate, in which a more or less random mixing of the segments must be anticipated. Figure 17 shows the areas occupied by these copolymers, and by mixtures of conventional PMMA and PiBMA homopolymers, as a function of the overall monolayer composition. In this plot, we can clearly see that the copolymers occupy significantly larger areas compared to the homopolymer mixtures of the same overall composition, with only small deviations from additivity. Random segmental mixing in the monolayer is evidently less favorable than the type of mixing involving two homopolymers.

The explanation for this intriguing observation can be found in the fact that, for two parallel homopolymer strands in contact, some sort of cooperative mechanism may be effective in optimizing the interactions between the chains: e.g., for the optimization of the contact interaction, an entire strand can be moved into a position with respect to the other chain (both in terms of the lateral backbone–backbone distance as well as in terms of the degree of submersion) that is most favorable for the interaction of all segments along this strand. In contrast, in random copolymer chains, such a cooperative motion is not effectively possible: if an optimization of the interaction between an iBMA segment with a neighboring MMA segment would require a closer approach of these segments, or a different degree of submersion of one of the segments, this would be accompanied by a similar translation of the segments to which they are covalently connected: the segments cannot independently assume the most favorable position. In this case, it is very likely that a specific relocation of one segment can be disturbed by the neighboring segments within the same copolymer chain. If a close approach of an iBMA and an MMA segment would also require a closer approach of two contiguous iBMA segments, it is easy to see that the steric repulsions of the latter segments may prohibit the approach of the first two segments.

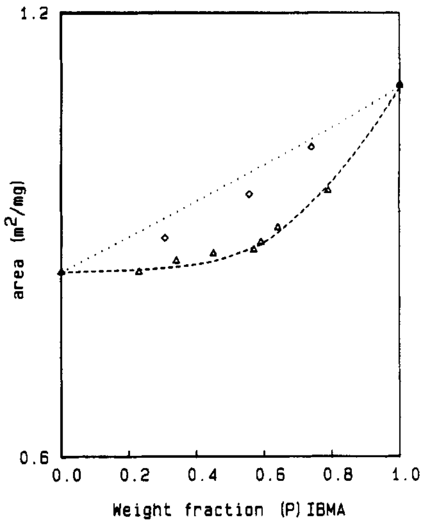

Figure 17. Specific areas ($\Pi = 5.0$ mN/m, $T = 22$ °C) for mixtures of a-PiBMA b3 and a-PMMA m33 (△), and for atactic copolymers P(MMA-*co*-iBMA) (◇), as a function of composition.

Mixtures of PiBMA and i-PMMA. Returning to the mixture that we initially started to investigate, syndiotactic PiBMA and isotactic PMMA, we see that mixing does not occur at low surface concentrations: the mixture is characterized by a low level of MMA–iBMA contacts, without extensive chain interpenetration, with possibly some kind of aggregation of chains of the same component,[3] leading to additive behavior. As discussed in ref 10, isotactic PMMA experiences "good solvent conditions" in the monolayer. This results in an entropically favorable expansion of the two-dimensional polymer coils in the available surface area. In mixtures with s-PiBMA, at low surface concentrations, the formation of a condensed mixture with a high number of MMA–iBMA contacts is not as favorable as for the s-PMMA/s-PiBMA system, since this would require the isotactic PMMA to give up its favorable expanded conformation, something that is evidently not compensated by a large enough enthalpy gain. The adhesive interactions in these mixed monolayers of i-PMMA and PiBMA may also be less favorable than in the case of the s-PMMA/s-PiBMA mixtures: here, the same arguments may apply as for the cohesive interactions in i-PMMA monolayers.

When the mixed monolayers are compressed, a surface pressure builds up due to the restriction of the expanded i-PMMA chains to smaller areas. Upon further compression, the expanded condition for the i-PMMA chains becomes less and less favorable, until the chains will start to interpenetrate and form a more condensed mixed monolayer with a high number of MMA–iBMA contacts, as in the s-PMMA/s-PiBMA mixtures: we are dealing with a *pressure-induced miscibility*. An interpretation of the monolayer transition along these lines appears to be in agreement with the absence of large conformational changes, as illustrated by the surface potential and the IR experiments, and, e.g., with the observed 1:1 stoichiometry, and the deviating collapse characteristics. The nature of the mixed phase can be assumed to be similar to that of the mixtures with syndiotactic PMMA, the i-PMMA chains located to some extent under the isobutyl groups of the PiBMA chains.

The nature of the mixing transition is completely different from the crystallization-type phenomena in monolayers of i-PMMA, or the stereocomplexation phenomena in mixed monolayers of s- and i-PMMA: in this situation, there is no critical nucleation stage, the transition almost instantaneously follows thermodynamic equilibrium, and no hysteresis is observed. In the mixed condition, the isotactic PMMA is no longer able to crystallize. This behavior is different from that of monolayer mixtures of i-PMMA with low molecular weight, noncrystallizable polymers forming expanded monolayers.[21] In this latter situation, where mixing merely has an entropic origin, crystallization can still occur, albeit at higher surface pressures, by a squeezing out of the oligomeric noncrystallizable component. In the mixtures with PiBMA, no such process is possible: the i-PMMA in the condensed mixture is stabilized by the favorable enthalpic interactions with the PiBMA strands. Moreover, crystallization would be accompanied by an unfavorable $\Pi\Delta A$ contribution to the free energy.

A lowering of the tacticity of the isotactic PMMA results in a higher level of cohesive interactions,[10] which can also be expected to be more favorable with respect to the interactions with the PiBMA chains in the mixed condition. Simultaneously, the tendency for these polymers to be in the expanded state is lowered (the "solvent quality" of the interface environment has decreased), so that the transition from the nonmixed expanded state into the mixed condensed state will take place at lower surface pressures, as was observed experimentally.

An effect that remains to be explained is the shift of the mixing transition to lower surface pressures at higher temperatures (Figure 2). A first argument that may be raised is the fact that the entropy of mixing will be positive, and could be responsible for this effect. The overall entropy change associated with the mixing process is hard to predict though, since it may also contain negative contributions from the conformational adjustments necessary in the two-dimensional mixed condition, and because the expanded, nonmixed condition was favored at low surface pressures for entropic reasons in the first place. Another important effect may be the promotion of the cohesive intercations between the i-PMMA segments at higher temperatures, as discussed in ref 9, the result of a disturbance of the amphiphilic orientation. In this respect, raising the temperature has the same effect as lowering the tacticity.

It is interesting to compare the miscibility behavior of s-PiBMA with stereoregular PMMA in the monolayer with that in bulk mixtures. In the monolayers, at low surface pressures, s-PiBMA appears to be intimately mixed with s-PMMA, and not with i-PMMA. In contrast, for bulk mixtures, s-PiBMA was reported to be miscible with i-PMMA,[5] whereas DSC results indicate that blends with s-PMMA are phase separated. The correlation between bulk and monolayer miscibility, suggested by Kawaguchi,[22] does not hold for this system.

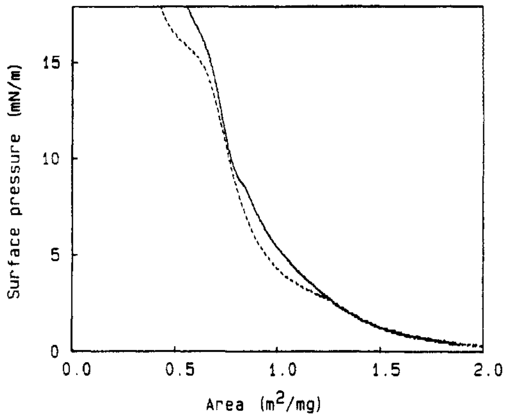

Figure 18. Pressure–area isotherms for a mixture of i-PMMA m10 ($\bar{M}_n$ 24K) and s-PiBMA b6 ($\bar{M}_n$ 16K) (dashed line), and for a mixture of i-PMMA m1 ($\bar{M}_n$ 1200K) and s-PiBMA b4 ($\bar{M}_n$ 450K) (solid line). Weight fraction s-PiBMA 0.57, base mole fraction 0.49. Compression speed 2 Å^2/(monomeric unit·min). T = 22 °C.

Molecular Weight Effects. For mixtures of PiBMA with predominantly syndiotactic PMMA, we have already noted that high molecular weights do not appear to disturb the mixing process, the adhesive interactions being very strong. Mixtures of PiBMA with isotactic PMMA, in which the mixing process is the result of a more subtle balance between various effects, do exhibit variations in their monolayer behavior with variations of the molecular weight of the components.

During the mixing transition, the monolayer changes from a situation without extensive chain interpenetration into a situation in which the polymer chains are mixed up to close to the segmental level. For this to happen, a lateral interdiffusion process must take place within the monolayer. For the combinations of the rather low molecular weight samples discussed so far, this interdiffusion process was almost instantaneous. The use of high molecular weight samples of either component introduces *kinetic* effects in the monolayer isotherms: in this case (small) hysteresis phenomena are observable for compression speeds of 2 Å^2/(monomeric unit·min), and the transition region of the isotherms varies somewhat with this compression speed: the interdiffusion process no longer takes place instantaneously on the time scale of the experiments. In the isotherms, recorded with compression speeds of 2 Å^2/(monomeric unit·min), there is even some evidence of i-PMMA crystallization in the monolayer. The surface pressure associated with these crystallization phenomena is similar to that observed in monolayers of pure i-PMMA, indicating that it is limited to the remains of the rather large undisturbed phases of i-PMMA in the monolayer blend (Figure 18). At higher temperatures, this interdiffusion process is much faster, resulting in a less pronounced (or absent) hysteresis effect. The kinetic problems associated with the mixing process of the high molecular weight samples are somewhat similar to those observed in the stereocomplexation of syndiotactic and isotactic PMMA.

Figure 19 shows an effect of the molecular weight of the isotactic PMMA on the *thermodynamics* of the mixing process. With a constant molecular weight of the s-PiBMA component, the onset of the mixing transition in the isotherm is a function of the molecular weight of the isotactic PMMA: upon lowering the molecular weight, this onset shifts to lower surface pressures. This observation is not related to kinetic phenomena as discussed in the previous paragraph, since upon decompression, the same effect is observed. A possible explanation for this effect

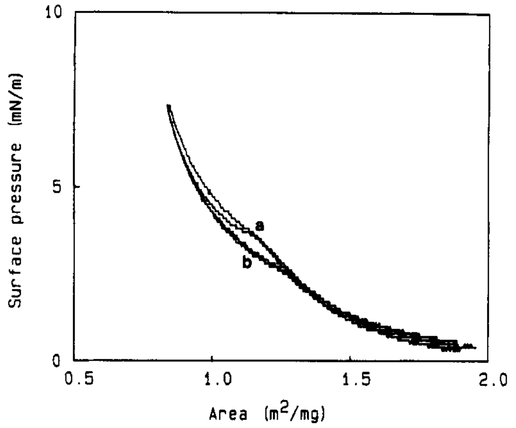

Figure 19. Hysteresis experiments with a mixture of s-PiBMA b6 with i-PMMA m1 ($\bar{M}_n$ 1200K) (a) and with i-PMMA m13 ($\bar{M}_n$ 13K) (b). Weight fraction s-PiBMA 0.61, base mole fraction 0.52. Compression and decompression speeds 2 Å²/(monomeric unit·min). $T = 22$ °C.

can be found in a higher favorable entropy of mixing contributing to the transition free energy for low molecular weights, whereas the ease of interpenetration of the polymer chains in the two-dimensional mixture may also be higher for lower molecular weight materials, requiring a smaller sacrifice in conformational entropy.

The variation in the transition pressure with variation of the molecular weight of the isotactic PMMA stands in contrast to the absence of such an effect in the stereocomplexation processes in mixed monolayers of i- and s-PMMA[2] (with only the opposite effect being observed for very low molecular weights). In this case, the transition pressure is only related to the local formation of a small complexed structure and does reflect the two-dimensional mixing of the complete chains.

Conclusions

Mixed monolayers of s-PiBMA and i-PMMA were found to exhibit a characteristic transition, reminiscent of the stereocomplexation process observed in mixed monolayers of i- and s-PMMA. The transition was shown not to correspond to such a stereocomplexation phenomenon, but instead to reflect a *pressure-induced mixing* of the components of the mixture. Stereocomplexation does not occur in the monolayer, an observation that may be explained by the fact that the larger hydrophobic side chains of PiBMA will extra stabilize the normal more or less amphiphilic orientation, relative to a conformation in a helix structure, which would be characterized by a rather hydrophobic shell in contact with the water subphase.

Monolayer mixtures of s-PiBMA and predominantly syndiotactic PMMA can also be characterized as mixed on a scale close to the segmental level. In general, there appears to be a strong favorable enthalpy of mixing in these monolayers, something which was speculatively attributed to a relatively low level of steric repulsions between the PiBMA and PMMA chains, resulting in an enthalpically favorable dense packing of the backbones. The interactions between the chains appear to be extra favorable due to a local parallel alignment of the strands of the homopolymer chains; random MMA–iBMA copolymers, characterized by a more random mixing of the segments in the monolayer, exhibited smaller deviations from additivity.

The characteristics of the mixing process of i-PMMA and s-PiBMA vary with the molecular weight of the components; kinetic effects become important using high molecular weights, whereas the molecular weight of the components also has an effect on the thermodynamics of the process.

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Registry No. PMMA (isotactic homopolymer), 25188-98-1; s-PiBMA (syndiotactic homopolymer), 26814-03-9; α-PiBMA (homopolymer), 9011-15-8; α-PMMA (homopolymer), 9011-14-7; P(MMA)-*co*-iBMA) (copolymer), 26044-94-0; s-PMMA (syndiotactic homopolymer), 25188-97-0; PnBMA (homopolymer), 9003-63-8.