Thin-Film Behavior of Poly(methyl methacrylates) (PMMA). 7. Stereocomplexation in Mixed Monolayers of Isotactic PMMA and Partially Hydrolyzed Syndiotactic PMMA

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Received October 25, 1991; Revised Manuscript Received June 23, 1992

ABSTRACT: In an attempt to find a monolayer stereocomplexing system in which phase separation phenomena are less restrictive than for the s-PMMA/i-PMMA couple, the monolayer behavior of partially hydrolyzed syndiotactic poly(methyl methacrylate) (s-PMMA) was studied. For low carboxyl group contents, the behavior of these materials is similar to that of the parent material, with an extra contribution of repulsive Coulombic forces originating from the ionized carboxyl groups when using basic subphases. The partially hydrolyzed materials are shown to retain their ability to exhibit a pressure-induced stereocomplexation in monolayer mixtures with isotactic poly(methyl methacrylate) (i-PMMA). When higher molecular weight parent materials for the syndiotactic component are used, aggregation processes can be observed to be suppressed for the partially hydrolyzed samples due to the aforementioned repulsive Coulombic forces, overcompensating the attractive cohesive interactions between the MMA segments and resulting in a high stereocomplexation efficiency. This efficiency is observed to strongly depend on the subphase pH, which regulates the degree of ionization of the incorporated acid groups.

Introduction

In previous publications of this series,[1-3] we discussed the behavior of mixed monolayers of i- and s-PMMA. On the basis of the anomalous pressure isotherms exhibited by these mixtures and of the characteristics of the layers transferred to solid substrates, we were able to identify a stereocomplexation process taking place in the monolayer upon compression, very similar to stereocomplexation processes involving i- and s-PMMA in melt or solution mixtures. In doing so, we encountered a complication pertaining to the phase behavior of these mixed systems: the monolayers appeared to exhibit a tendency for phase separation, especially when higher molecular weight s-PMMA samples were used, a phenomenon causing a significant impediment of the stereocomplexation process due to the resulting limited mutual acessibility of the components. In ref 3, the possibility of *compatibilization* of the monolayer mixtures was addressed: an approach using stereoblock PMMA additives to achieve a better dispersion of the s-PMMA chains in the monolayer was shown to be effective.

An alternative approach would include a modification of the interactions between the chains, which are responsible for the tendency for phase separation in the first place. These complications can specifically be attributed to the strong cohesive interactions between the segments of the s-PMMA chains. The challenge we face here is to try to modify the polymers in such a way that a better mixing is attained, without losing the possibility for stereocomplexation.

This latter boundary condition is fairly restrictive: modification of i-PMMA, e.g., by (partly) varying the ester group side chains, has been shown to effectively prohibit stereocomplexation,[4] since the methyl ester groups appear to play a crucial role in the subtle balance of interactions leading to the formation of the complex structures. The composition of the syndiotactic component allows for somewhat more flexibility: in this case, stereocomplexation was still observed upon exchanging the methyl ester group for ester groups with larger alkyl substituents, e.g., an isobutyl group.[4] Kitayama et al.[5] summarized a series of syndiotactic polymethacrylates with ester group substituents branched at the β-position, which were observed to exhibit stereocomplexation processes in mixtures with i-PMMA. The ester groups of the syndiotactic chains have been suggested to point outward in the double-helical structure, resulting in a high tolerance for variations.[4]

Syndiotactic poly(methacrylic acid) (s-PMAA) was also reported to form stereocomplex structures with i-PMMA: this system was extensively studied by Lohmeijer.[6] Mixtures of s-PMAA and i-PMMA exhibited complexation phenomena in dimethylformamide (DMF) solutions, although the complexing ability appeared to be low relative to the s-PMMA/i-PMMA couple. The complexed structures obtained exhibited X-ray diffraction patterns similar to those obtained from the s-PMMA/i-PMMA system, indicating that similar (double helical) structures were probably being formed.[7] Partially hydrolyzed s-PMMA was also investigated:[8] these materials also exhibited stereocomplexation phenomena in mixtures with i-PMMA, the characteristics of this process gradually changing with the composition of the copolymer.

Carboxyl groups along the polymer chains (as in partially hydrolyzed s-PMMA) would present a very versatile handle for changing the interactions in the monolayer. First, the composition of the material can easily be varied, the modification procedure being fairly simple. Second, and even more important, the effect of these acid groups will depend strongly on their degree of ionization, which in turn can easily be varied through a variation of the pH of the subphase. The effect of the presence of ionized acid groups can be imagined to be very strong, adding long-range Coulombic type interactions to the extensive set of more short-range forces already operative in the monolayer. These Coulombic forces may also be regulated by the ionic strength of the subphase, adding another tunable parameter. Finally, these materials are of interest since the acid group provides an easy handle for further modification of the structure.

Experimental Section

s-PMMA was partially hydrolyzed by dissolving it in 96% sulfuric acid, followed by stirring at room temperature (samples 1, 4, and 5, 10 h; sample 2, 72 h) or at 45 °C (sample 3, 6 days).

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Table I
Partially Hydrolyzed s-PMMA

sample no.	parent s-PMMA: triad tacticity (%) i	h	s	$\bar{M}_n$ (10^3)	D	% MAA
1	2	8	90	11	1.22	5
2	2	8	90	11	1.22	30
3	2	8	90	11	1.22	95
4	1	14	85	46	1.20	5
5	2	11	87	270	1.20	5

Table II
PMMA Characteristics

material	tacticity (%) i	h	s	$\bar{M}_n$ (10^3)	D
m4	>97			160	1.20
m13	>97			13	1.19

The solution was precipitated in an ice water mixture, filtered, dissolved (or, for low degrees of modification, suspended) in water with excess KOH, and heated to 100 °C for 45 min to remove anhydride functionalities. Concentrated HCl was added (to pH 1), and the resulting precipitate was extensively dialyzed with pure Milli-Q water. After this procedure, the product was reprecipitated from DMF solution into ether, washed, and dried.[8]

The carboxyl group content of the products was estimated from ^{1}H-NMR and infrared experiments. The degree of polymerization is assumed to remain unaffected by the modification procedure. The modification of s-PMMA has been reported to result in a more or less random structure, in contrast to i-PMMA, for which this modification procedure leads to a more blocklike character of the resulting copolymer.[9] Sample characteristics of the partially hydrolyzed s-PMMA samples are summarized in Table I. Remarkable is the fact that sample 3 appears to be hydrolyzed up to 95%; this value contrasts with claims in the literature[10] that only a limiting conversion of 85% can be attained using this procedure. IR spectra indicated that the resulting polymers did not contain any significant amount of anhydride groups. Characteristics of the PMMA samples used in the monolayer experiments are listed in Table II. These parent PMMA fractions were prepared through either an anionic polymerization in toluene at -90 °C, using a *t*-BuLi/triethylaluminum (1:5) initiating system[10] (samples 1-3), or through a Ziegler-Natta type polymerization[11] (samples 4 and 5). The monolayer behavior was studied using apparatus and procedures as described in ref 12. Polymers were spread from 0.3 g/L solutions of the materials in 35-65 (v/v) DMF/chloroform mixtures. This mixture was chosen as the spreading solvent, since it combines solubility for poly(methacrylic acid), as well as for the poly(methyl methacrylate) and the partially hydrolyzed PMMA samples, with a good water surface spreading behavior. The pH of the subphase was adjusted by adding either a HCl or NaOH solution to pure Milli-Q water; no extra salts were added to the subphase.

Results and Discussion

The effect of the presence of charged groups in monolayers is known to affect the behavior of these monolayers; much work has been done using ionized acid or amine group containing low molecular weight substances. An exact description of the effects of the charges on the monolayer behavior has proven to be extremely difficult[13] because of uncertainties with respect to the nature of the ionic double layer which is formed at the air-water interface. Davies[14] has tried to calculate the effect of the charges on the surface pressure (and the surface potential) on the basis of a (very simple) model for this ionic double layer, proposed by Gouy and Chapman. In this model,[15] the surface is considered as a uniformly charged plane, with ions present in the subphase behaving as point charges. The potential in the surface plane can then be described as a function of the temperature, the charge density in the monolayer, and the concentration of ions in the subphase.

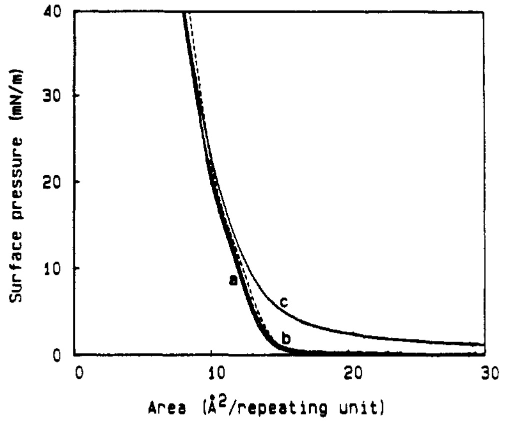

Figure 1. Pressure-area isotherms of s-P(MMA-*co*-MAA) sample 1; subphase pH 4.5 (a), 9.4 (b), and 11.4 (c). Dashed line represents parent s-PMMA. T = 22 °C.

The result is an extra contribution to the surface pressure, based on the Coulombic type forces: upon compression, the charges in the monolayer will come closer together, without being screened completely by the water molecules or the ions present in the subphase, leading to an increase of th free energy of the system and thus to the aforementioned contribution to the surface pressure. Using the Gouy-Chapman model, Davies calculated this extra contribution of the Coulombic forces to the surface pressure as

$$\Delta\Pi \propto c^{1/2}\left[\cosh\left(\sinh^{-1}\left(\frac{K}{Ac^{1/2}}\right)\right)-1\right]$$

with K being a constant, c representing the concentration of ions in the subphase, and A being the area available per unit charge in the monolayer.[13] This expression describes the increase of the surface pressure due to the Coulombic interactions upon compression (through A) or due to an increasing content of charged species in the monolayer. As stated before, this expression is based on a very simple model for the ionic double layer that may not describe the actual situation accurately: penetration of subphase ions into the surface monolayer may disturb the model situation, and, in reality, the nature of the counterions present in the subphase proves to be important in many cases.[13] For charged groups embedded in condensed polymer chains in the monolayer, the assumption of a homogeneous charge distribution may not be correct.

It is clear that the degree of ionization will be very important for the monolayer behavior of the partially hydrolyzed PMMA samples: more ionization will imply a higher contribution of repulsive Coulombic interactions to the surface pressure. The degree of ionization can be regulated through the pH of the subphase.

Monolayer Behavior of Partially Hydrolyzed s-PMMA. The monolayer behavior of the partally hydrolyzed s-PMMA samples was investigated as a function of the degree of hydrolyzation and as a function of the pH of the subphase. For this purpose, a series of samples (samples 1-3) was prepared from the same parent material (s-PMMA m41). The monolayer behavior of the nonhydrolyzed parent s-PMMA exhibited no effect of the pH of the subphase.

Figure 1 shows isotherms for s-P(MMA-*co*-MAA) sample 1 (carboxyl group content approximately 5%) for various pH values of the subphase. For pH values up to 7, the isotherms are very similar to the isotherms of the nonhydrolyzed material. At subphase pH 9.4, a slight tail

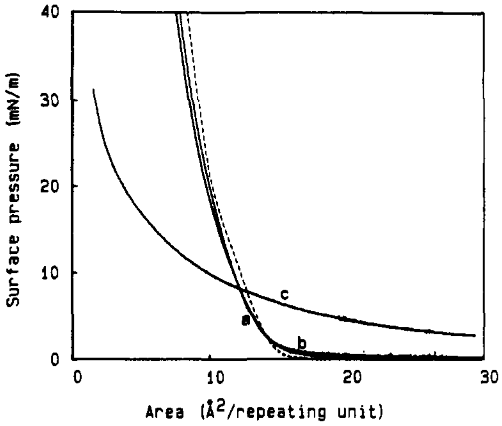

Figure 2. Pressure-area isotherms of s-P(MMA-*co*-MAA) sample 2: subphase pH 4.0 (a), 9.2 (b), and 11.3 (c). Dashed line represents parent s-PMMA. T = 22 °C.

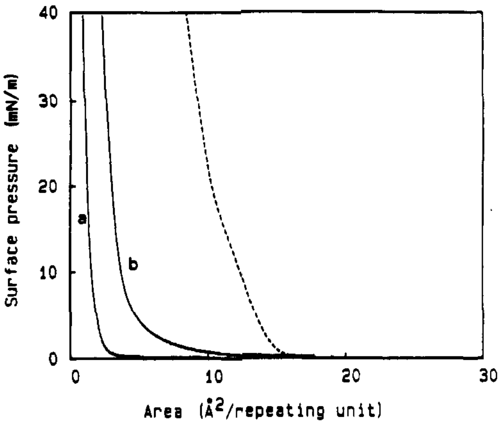

Figure 3. Pressure-area isotherms of s-P(MMA-*co*-MAA) sample 3: subphase pH 6.3 (a) and 1.9 (b). Dashed line represents parent s-PMMA. T = 22 °C.

becomes visible, extending to the high-area side in the isotherm. Raising the pH even further results in a strong enhancement of the contribution of this tail to the surface pressure; still, even at pH 11.4, the steep part of the isotherm (as present in the nonionized monolayers) remains almost unaffected. The interpretation of these effects may be obvious: at low pH values, the degree of ionization and the contribution of Coulombic interactions are low, with the polymers behaving similarly to the polymers with no carboxyl groups, forming thin "pancake-like" condensed structures located at the air-water interface. With a basic subphase, the acid groups become ionized, and the chains will start to feel the repulsive Coulombic forces even at large available areas, resulting in a surface pressure buildup. The segments of the chains remain all located in a very thin film at the interface, not much different from the nonionized monolayers, eventually leading to a steep pressure buildup when complete monolayer coverage is attained, at similar areas as observed for the s-PMMA parent material. s-P(MMA-*co*-MAA) samples 4 and 5, characterized by higher molecular weights than sample 1, but with comparable COOH contents, exhibit a similar monolayer behavior.

The deprotonation of the acid groups in the monolayer evidently occurs at fairly high values for the pH of the subphase. In this context, it is important to note that the degree of ionization will be determined by the *local* pH at the surface, instead of the bulk pH. The local pH at the surface will be different from this bulk pH, due to the deviating local potential: a negative potential (e.g., due to the presence of already ionized acid groups) will attract H^+ ions and lower the effective surface pH:[13]

$$\mathrm{pH}_{\mathrm{surface}} = \mathrm{pH}_{\mathrm{bulk}} + \frac{e\psi}{2.3kT}$$

with e as the unit charge and ψ as the potential difference between the subphase bulk and the surface layer.

Apart from charges in the monolayer, the dipole moment of the monolayer will also contribute to the effective potential experienced at the surface: this was, e.g., demonstrated by Möbius et al.[16] For a monolayer of mainly MMA segments, this contribution will also lead to a lowering of the surface pH. The deprotonation of the partially hydrolyzed s-PMMA samples is observed in a similar pH range as, e.g., the ionization of monolayers of stearic acid.[13]

An increase of the carboxyl group content to approximately 30% results in isotherms as shown in Figure 2. The isotherms for values of the subphase pH up to pH 7 are practically identical, with a small surface pressure tail extending to higher areas; this tail becomes somewhat more pronounced at a subphase pH of 9, due to a higher contribution of the repulsive Coulombic forces. On subphases with a bulk pH value of 11, this tail has become the dominant feature in the isotherm, extending up to areas of far over 100 Å^2 (monomeric unit)$^{-1}$; in this case, we no longer observe the steep pressure buildup at approximately 14 Å^2 (monomeric unit)$^{-1}$, characteristic for the s-PMMA chains and also observed for this material at lower degrees of ionization; instead, the monolayers remain highly compressible up to very low values for the specific area. Evidently, upon compression, parts of the polymer chains are pushed into the subphase, the solubility being higher due to the high content of COO^- groups present along the chain.

When the tail of the isotherms recorded for high subphase pH values is analyzed according to the expression as deduced by Davies and as discussed above, we only observe a moderate agreement. The behavior deviates somewhat from that predicted by this formula in that the experimentally observed surface pressure buildup upon compression falls behind that predicted theoretically. It is easy to speculate about possible causes for this discrepancy, e.g., the neglection of the contribution of the cohesive forces between the MMA segments, a partial submersion of the monolayer during compression, or a lowering of the degree of ionization upon compression.

The monolayer behavior of sample 3 is strongly deviating: with the hydrolysis completed to a high conversion, the monolayers only exhibit a pressure buildup at very low areas per monomeric unit (Figure 3). Pure s-PMAA spread from the DMF/chloroform solvent mixtures did not yield stable monolayers, not even when spread on acidic subphases. This observation stands in contrast with claims in the literature about monolayers of PMAA on acidic subphases being stable at low surface pressures;[17] this discrepancy might be caused by the different spreading procedure. The 95% hydrolyzed s-PMMA (sample 3) still forms some kind of monolayer, although the remaining number of methyl ester groups is low; the resulting films are only stable at low surface pressures. A pressure buildup is observed at higher areas in the case of spreading onto an acidic subphase as compared to a neutral subphase; no stable film can be observed on (even weakly) basic subphases. It is likely that even on neutral or acidic subphases, a considerable loss of monolayer material has occurred during spreading: the areas associated with a pressure buildup remain very small when compared with literature reports for PMAA. The difference observed between the neutral and acidic subphases is probably the

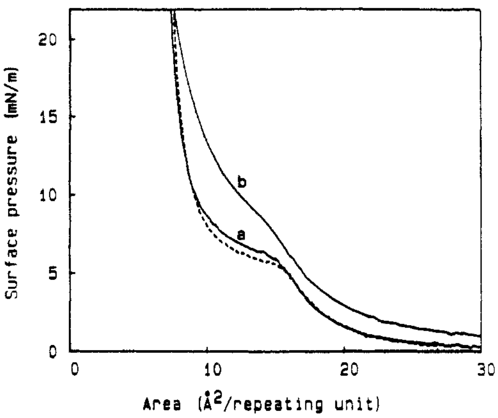

Figure 4. Pressure–area isotherms of a 2:1 mixture of s-P(MMA-*co*-MAA) sample 1 and i-PMMA (material m13, $\bar{M}_n$ = 13K): subphase pH 6.0 (a) and 11.0 (b). Dashed line represents a mixture based on parent s-PMMA. T = 45 °C, compression speed = 2 Å^2 (monomeric unit)$^{-1}$ min^{-1}.

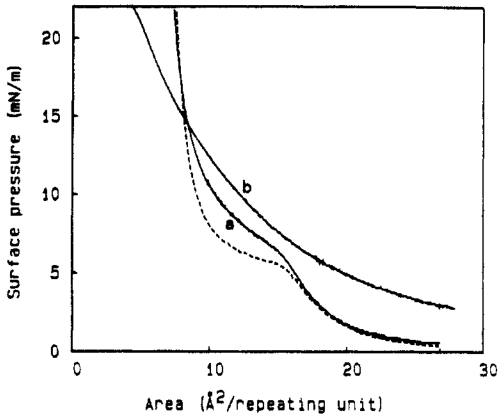

Figure 5. Pressure–area isotherms of a 2:1 mixture of s-P(MMA-*co*-MAA) sample 2 and i-PMMA (material m13, $\bar{M}_n$ = 13K): subphase pH 6.2 (a) and 11.0 (b). Dashed line represents a mixture based on parent s-PMMA. T = 45 °C, compression speed = 2 Å^2 (monomeric unit)$^{-1}$ min^{-1}.

result of such loss processes in the spreading stage: injection of concentrated acid into an almost neutral (pH 6) subphase under a monolayer of this material did not result in a film expansion.

Stereocomplexation of i-PMMA with Partially Hydrolyzed s-PMMA. The repulsive Coulombic forces which are caused by the partially dissociated acid groups may be advantageous with respect to the stereocomplexation processes in monolayers of mixtures of these materials with i-PMMA. If the repulsive interactions are large enough to overcome the cohesive interactions between the MMA segments in the syndiotactic copolymers, it is conceivable that the aggregation processes of the syndiotactic chains (as discussed in ref 3) can be suppressed. In the rest of this paper, this possibility will be investigated.

First, it is necessary to check whether stereocomplexation is still possible following the introduction of a significant amount of COOH groups in the syndiotactic polymers. As mentioned in the Introduction, Lohmeijer[8] has already studied the complexation behavior of syndiotactic copolymers of methacrylic acid and MMA and observed that stereocomplexation with i-PMMA was still feasible at all compositions.

In Figures 4 and 5 the compression isotherms are given for mixtures of low molecular weight (partially hydrolyzed) s-PMMA with a rather low molecular weight sample of i-PMMA. The molecular weights of the i-PMMA and the s-PMMA parent material were chosen so as to have no significant problems with phase separation phenomena.[3]

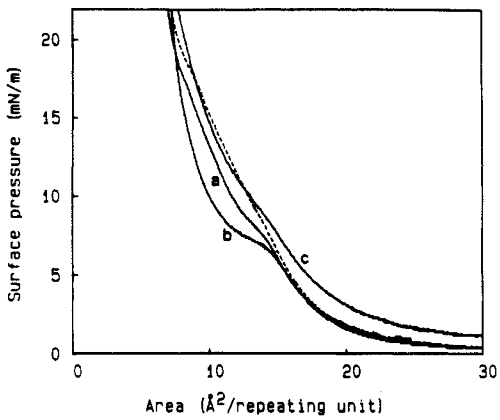

Figure 6. Pressure–area isotherms of a 2:1 mixture of s-P(MMA-*co*-MAA) sample 4 and i-PMMA (material m13, $\bar{M}_n$ = 13K): subphase pH 1.7 (a), 9.2 (b), and 11.3 (c). Dashed line represents mixture based on parent s-PMMA. T = 45 °C, compression speed = 2 Å^2 (monomeric unit)$^{-1}$ min^{-1}.

It can easily be seen that in the isotherms of the mixtures of i-PMMA with s-P(MMA-*co*-MAA) samples 1 and 2, the stereocomplexation transition, as elaborated on in previous papers,[1,2] is still clearly observable, similar to the mixture based on the nonhydrolyzed parent material. The onset pressure has shifted to slightly higher surface pressures with increasing COOH content; this is evidently the result of the slightly better interaction of these segments with the subphase, which has to be overcome for the double-helix formation to take place, and the presumably lower extent of intrinsic stabilization of the stereocomplex. For these compositions, monolayer stereocomplexation does still take place efficiently. A similar mixture based on sample 3 did not yield an isotherm with a clearly identifiable stereocomplexation transition.

An effect of the subphase pH on this stereocomplexation transition becomes visible only when basic subphases are used; as with the isotherms of poure monolayers of samples 1 and 2, no effect is observed up to a pH of 7. At higher pH values, the stereocomplexation transition is observed to shift to higher surface pressures, as is illustrated by the isotherms in Figures 4 and 5. This effect may be ascribed to the fact that upon stereocomplexation the average distance between the charged groups will decrease or to the effect of the enhanced interaction of the segments with the subphase in the "amorphous" conformation. Sample 2, containing 30% COOH groups, no longer exhibits a clear stereocomplexation process when the subphase pH is raised to 11: in this case the affinity of the water subphase for the highly ionized polymer chains is evidently too high.

Having established that stereocomplexation is still possible for s-PMMA samples containing up to moderate levels of COOH groups, we will now focus on the aggregation effect operative in mixtures with high molecular weight syndiotactic components.

In Figure 6, compression isotherms are shown for mixtures of i-PMMA m13 ($\bar{M}_n$ = 13K) with s-PMMA m45 ($\bar{M}_n$ = 46K) and with a fraction of this latter material hydrolyzed up to approximately 5%. The isotherm of the mixture with the nonhydrolyzed material clearly shows the effect of the stereocomplexation being suppressed by aggregation phenomena;[3] the behavior of this mixture does not change with variations of the subphase pH. In contrast, the monolayer behavior of the mixtures of the partially hydrolyzed s-PMMA with i-PMMA is strongly dependent on the subphase pH. On neutral subphases, stereocomplexation is still effectively possible, in contrast to

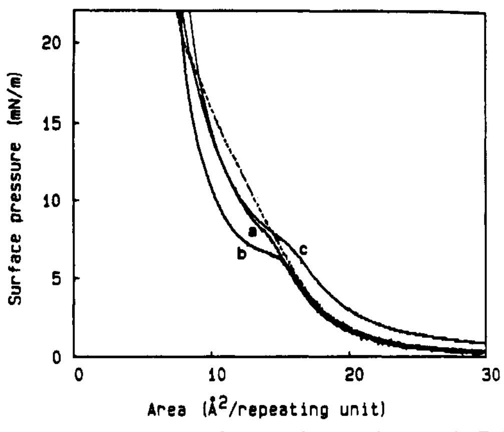

Figure 7. Pressure–area isotherms of a 2:1 mixture of s-P(MMA-*co*-MAA) sample 5 and i-PMMA (material m13, $\bar{M}_n$ = 13K): subphase pH 1.9 (a), 9.3 (b), and 11.0 (c). Dashed line represents mixture based on parent s-PMMA. T = 45 °C, compression speed = 2 Å² (monomeric unit)$^{-1}$ min^{-1}.

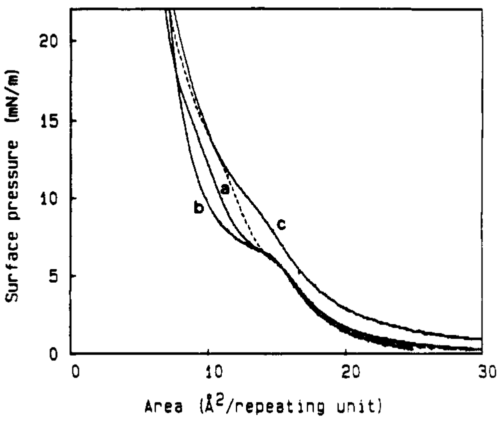

Figure 8. Pressure–area isotherms of a 2:1 mixture of s-P(MMA-*co*-MAA) sample 1 and i-PMMA (material m4, $\bar{M}_n$ = 160K): subphase pH 1.9 (a), 9.3 (b), and 11.3 (c). Dashed line represents mixture based on parent s-PMMA. T = 45 °C, compression speed = 2 Å² (monomeric unit)$^{-1}$ min^{-1}.

monolayers containing the nonhydrolyzed material. Upon lowering the pH of the subphase, we observe that, for the partially hydrolyzed s-PMMA, the efficiency of the stereocomplexation process process is also lowered, although, even at pH 1.7, the transition is still more clearly observable than in the mixture based on the parent material. The efficiency of the stereocomplexation process appears to be highest for a subphase pH of approximately 9; a stronger basicity leads to a suppression of the process similar to that observed for the low molecular weight materials in Figures 4 and 5. The fraction of charged segments, associated with the optimal stereocomplexation efficiency, is still very small: the fraction of hydrolyzed ester groups was only 5%, and the fraction of these groups deprotonated is also still limited at this subphase pH value.

In Figure 7, the same experiments are reported, but not for a syndiotactic parent material of even higher molecular weight (270K). Also in this case, at favorable subphase pH values, stereocomplexation is observed to occur up to high conversions.

The presence of a small amount of ionized COOH groups in the polymer chains is evidently responsible for the *compatibilization* of the monolayer mixtures. The repulsive Coulombic forces, resulting from the negatively charged deprotonated carboxylic acid groups in the monolayer, are strong enough to prevent the aggregation of the syndiotactic chains, which would be favorable from the point of view of the cohesive interactions between the MMA segments of the syndiotactic chains. Lowering the pH of the subphase lowers the average charge per chain and thus the repulsive interactions between the chains, a process resulting in a higher degree of aggregation and consequently a lower efficiency of the stereocomplexation process. Apart from the suppression of the aggregation of the individual chains, an additional effect may be the deformation of the *shape* of the individual monolayer coils. An isolated coil that is characterized by strong cohesive interactions and a high "perimeter energy"[3] can be imagined to assume a shape so as to minimize its borderline, an effect that will also be unfavorable with respect to its susceptibility for stereocomplexation. With the presence of a number of negatively charged groups within this coil, the mutual repulsion of these groups may lead to a deformation of the coil in order to accommodate the charged segments at relatively large average distances. Such a deformation may lead to a longer perimeter line over which the syndiotactic component can be in contact with the isotactic component. When using stereoblock additives to compatibilize the mixtures, we saw that for high molecular weight materials this approach was of limited efficiency, due to the fact that the domain sizes associated with the segregated individual coils became the limiting factor. The hydrolysis approach may also be able to partially overcome this latter effect due to a deformation of the individual coils. The high efficiency of the stereocomplexation process observed in Figure 7, despite the high molecular weight used, may be an indication for this last argument.

When studying mixtures of a low molecular weight s-PMMA sample with a fairly high molecular weight i-PMMA sample, we also observed that stereocomplexation was hindered (although not to the extent of the reversed combination). In ref 3, we discussed this effect in terms of the propensity of the chains to segregate, the high molecular weight of the isotactic PMMA imposing a rather large domain size, not competing with the tendency of the s-PMMA chains to aggregate. In this situation, extensive penetration of the i-PMMA chains is enthalpically unfavorable. If we replace the low molecular weight s-PMMA sample with a partially hydrolyzed sample (sample 1), we can observe that an efficient stereocomplexation process is possible: this is illustrated by Figure 8. Upon partial ionization, the repulsive Coulombic forces between the syndiotactic chains result in an aggregation of these structures being very unfavorable; from the isotherms in Figure 8, we can deduce that under these conditions a fairly intimate mixing of the isotactic and the syndiotactic components can be achieved. Again, we observe a clear effect of the pH of the subphase on the monolayer behavior, illustrating the fact that this behavior is dominated by the Coulombic repulsive forces. A combination of a high molecular weight i-PMMA sample with a high molecular weight partially hydrolyzed s-PMMA sample is less susceptible to the compatibilizing effect of the Coulombic interactions.

The enhancement of the miscibility of a mixture due to internal repulsive interactions within one component of the mixture is well-known from studies of regular three-dimensional blends and is sometimes described as the "*copolymer effect*".[18] The approach described here is based on an analogous concept, but with one remarkable difference: the copolymer effect is usually related to unfavorable interactions between *different* groups within the chains of one of the components, whereas in the case discussed here, internal repulsive interactions between *similar* functional groups are responsible for the enhanced miscibility.

Conclusions

Partial hydrolysis of s-PMMA yields a material whose monolayer behavior can be controlled by the COOH content and the degree of ionization of these groups, which is directly regulated by the subphase pH. For low levels of ionized COOH groups, the polymer chains form monolayers with a behavior comparable to s-PMMA; upon ionization of the carboxyl groups, the Coulombic interactions between the charged groups in the monolayers give rise to a surface pressure tail in the isotherms extending to lrge areas.

The partially hydrolyzed materials are still susceptible to stereocomplexation processes in mixtures with i-PMMA. Compared to regular s-PMMA, aggregation processes in high molecular weight materials can be suppressed by choosing the subphase pH in such a way that a Coulombic repulsive forces overcompensate the cohesive interactions between the MMA segments, resulting in an effective stereocomplexation process upon compression, even for molecular weight combinations that, for the unmodified materials, lead to phase separation phenomena suppressing the complexation process. The effects observed strongly support the suggestion that monolayer phase separation effects were responsible for the suppression of the stereocomplexation process.

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