Thin-Film Behavior of Poly(methyl methacrylates). 6. Monolayer Phase Behavior in Relation to Stereocomplexation in Mixed Monolayers of i- and s-PMMA

R. H. G. Brinkhuis and A. J. Schouten*

Laboratory of Polymer Chemistry, University of Groningen,
Nijenborgh 16, 9747 AG Groningen, The Netherlands

Received July 14, 1992; Revised Manuscript Received January 11, 1993

ABSTRACT: The stereocomplexation process in mixed monolayers of isotactic and syndiotactic poly(methyl methacrylate) is efficient only when low molecular weight samples are used. This phenomenon can be explained by an increasing tendency for phase separation in the monolayer upon using higher molecular weight samples, leading to larger domain sizes and a limited mutual accessibility: especially the use of high molecular weight syndiotactic PMMA appears to result in strong aggregation processes of these chains caused by the strong cohesive intersegment interactions at the air-water interface. This hypothesis is corroborated by the observation that addition of stereoblock PMMA strongly enhances the efficiency of the stereocomplexation process, thus acting as a compatibilizer, dispersing the s-PMMA chains in the monolayer.

Introduction

In previous publications,[1,2] we discussed stereocomplexation processes that can take place in monolayers of mixtures of isotactic and syndiotactic PMMA. Upon compression, the monolayers exhibit an isotherm transition that can be correlated to the formation of double helical stereocomplex structures of both components, similar to the formation of such complexes in solution and melt mixtures of these materials. Indications for stereocomplexation were inferred from, e.g., the stoichiometry, the tacticity dependence, the surface potential behavior, and IR measurements of transferred monolayers. The monolayer stereocomplexation was most effectively conducted at elevated temperatures, lower temperatures leading to incomplete conversions.[2] In this paper, we will focus on the relation between this stereocomplexation process and the phase behavior in the monolayer blends.

The behavior of monolayers of polymer mixtures has been the subject of many reports in the literature. Especially the group of Gabrielli dedicated much effort to studying mixed monolayers;[3-8] Kawaguchi recently also addressed the monolayer behavior of a series of polymer mixtures,[9] and many other authors reported on the miscibility behavior of specific polymers in monolayers. Most of these studies assess the miscibility of two components on the basis of deviations from addivity of the specific areas or the compressibility or on the basis of the collapse behavior of the mixed monolayers. The first approach may not be very sensitive in many cases, since often the effects are quite small; the latter approach gives information only about the collapse regime, with very high segment concentrations and strongly deformed conformations, and the results are not always unambiguous. In most cases, the mixtures are either classified as miscible or nonmiscible; more detailed information is usually not extracted. Phenomena such as the extent of segregation of the individual coils, limited interpenetration, and molecular weight effects have not been addressed in detail in these experimental studies; a direct correlation with theoretical results on the behavior of two-dimensional polymer mixtures is not often given.

Langmuir-Blodgett monolayers of polymers can be considered as a pseudo-two-dimensional system; for the poly(methyl methacrylates), with rather favorable amphiphilic interactions of the segments with the interface, combined with insolubility of the segments in the subphase, the monolayers can be expected to have a clear two-dimensional character at low surface concentrations. Although "defects" such as polymer chain crossovers cannot be completely excluded, their influence should be limited.

The phase behavior of two-dimensional polymer systems has received quite a lot of interest from a theoretical point of view. De Gennes[10] already predicted that in two-dimensional polymer systems, the individual polymer coils will tend to be *segregated.* Because of the two-dimensional topological constraints, crossovers and entanglements will not occur. In contrast to their three-dimensional analogues, the polymer chains do not readily interpenetrate; the only way to do so would be through a partial alignment of the chains, which would cost a substantial amount of conformational entropy and is only feasible when compensated by strong enthalpic effects (e.g. in a mixture with strongly favorable interactions between the different components).[11] Monte Carlo simulations have proven extremely useful in studying these two-dimensional polymer systems[12-14] and confirmed the tendency of the individual coils to segregate. The number of interchain segment-segment contacts is found to be clearly lowered with respect to intrachain contacts, relative to what would be expected for a random Flory-Huggins type mixing of the segments.[15]

For polymer mixtures with an *unfavorable* interaction energy (a situation that may well apply to monolayer mixtures of isotactic and syndiotactic PMMA), an additional effect, apart from a segregation of the individual coils, may be the aggregation of chains of similar segments, eventually leading to a macroscopic phase separation, in order to minimize the number of contacts between unlike segments. This phenomenon was observed in Monte Carlo simulations,[15] which were also used to investigate the kinetics of spinodal decomposition in these systems.[16,17]

The thermodynamic conditions for such macroscopic phase separation in two dimensions have been addressed by van Vliet and ten Brinke.[18] For athermal mixtures, and certainly for mixtures of polymers with an unfavorable segment-segment interaction enthalpy, the polymer chains will tend to be strongly segregated, without significant interpenetration. Using this assumption of complete chain segregation, van Vliet and ten Brinke applied a Flory type mean field approach to describe the free energy of mixing of the segregated chains, considering these chains as

0024-9297/93/2226-2514$04.00/0

separate impenetrable particles:

$$\Delta F_{\mathrm{mix}}/kT = \phi_{\mathrm{a}} \ln \phi_{\mathrm{a}} + \phi_{\mathrm{b}} \ln \phi_{\mathrm{b}} + \Gamma_{\mathrm{ab}}\phi_{\mathrm{a}}\phi_{\mathrm{b}}$$

where $\phi_{\mathrm{a,b}}$ represent the "area" fractions of both components, and Γ_{ab} is an exchange interaction parameter. This expression applies to the free energy of mixing of the segregated chains, and not to the mixing of the segments of these chains. Γ_{ab} is not equal to the segment–segment interaction parameter but represents the interaction between contiguous chains: this parameter will be determined not only by the strength of the segment–segment interactions but also by the number of segments in contact. Since these contacts will be limited to the perimeter of the segregated chains, Γ_{ab} will scale linearly with the number of segments in this perimeter, i.e. as $N^{1/2}$. This implies that a critical value for Γ_{ab} with respect to phase separation is more likely to be reached for higher molecular weights of the components, for a given segment–segment interaction energy. Unfavorable segment–segment energies that can be tolerated before phase separation occurs, will scale as $N^{-1/2}$.[18] Mixtures of long chains will therefore exhibit a stronger tendency for phase separation (beyond the segregation of the individual chains) than mixtures of short chains.

This mean field approach assumes a random distribution of the chains in the mixed state; in reality, this distribution will be affected by the interaction energies, e.g. leading to a higher number of contacts between unlike chains for favorable interaction energies, as was demonstrated by van Vliet and ten Brinke.[18] Alternatively, unfavorable interactions may lead to deviations from random mixing and to local aggregation of chains of the same components, even before macroscopic phase separation takes place; these arguments are similar to those used to describe deviations of random mixing on the segmental level due to enthalpic interactions.[19]

In the "real" systems under consideration, the LB monolayers, the fact that we are dealing with an excess surface area for low surface concentrations requires additional "voids" or solvent sites to be taken into account: the system is best described as a concentrated two-dimensional solution, so that a polymer mixture should in fact be treated as a *ternary* system, which considerably complicates the picture. It implies that the cohesive interactions, as well as the interactions between unlike segments, become important, e.g. distinguishing between condensed and expanded type monolayers, exemplified by syndiotactic and isotactic PMMA, respectively. Even a monolayer with only one component must be described as a two-component system. This is done, e.g., in the approach of Matuura and Motomura in their analytical description of the equation of state of polymeric monolayers.[20] In these systems, macroscopic phase separation is predicted to occur in the case of strong cohesive energies in condensed type monolayers. The tendency for phase separation is dependent on the molecular weight: the critical cohesive energy that can be tolerated before phase separation occurs is lower for longer chain lengths,[20] analogous to the predictions for two-dimensional polymer mixtures described above.

The aim of this investigation is to establish to what extent the stereocomplexation process in mixed monolayers of i- and s-PMMA can provide a handle to extract information about the phase behavior in this monolayer, as discussed above.

Experimental Section

Characteristics of the materials used are listed in Table I. Stereo(di)block PMMA was kindly provided by Professor Thieo Hogen-Esch (USC); the synthesis procedure was reported in ref 21. Mixed monolayers were spread from solutions of the mixed components in chloroform. The apparatus and procedures used for monitoring the monolayer behavior are described in ref 22. A standard compression speed of 2 Å^2/(monomeric unit (mmu)·min) at 45 °C was used for the monolayer stereocomplexation experiments.

Table I

material	triad tacticity i	h	s	$\bar{M}_n$ (10^3)	$\bar{M}_w/\bar{M}_n$
m2	>97			770	1.32
m5	>97			95	1.20
m8	>97			36	1.17
m11	>97			21	1.16
m13	>97			13	1.19
m41	2	8	90	11	1.22
m42	1	4	95	9.0	1.20
m43	2	4	94	87	1.35
m44	2	11	87	270	1.20
m45	1	14	85	46	1.20
m46	1	14	85	32	1.11
m47	1	14	85	25	1.09
m48	1	13	86	18	1.14
stereoblock	29	12	59	10	1.12

Results and Discussion

Before focusing our attention to the stereocomplexation process, it is useful to first address the area vs composition behavior of the mixed monolayers in the regime preceding the stereocomplexation process. When the specific area associated with a constant surface pressure corresponding to the pretransition region is plotted as a function of the monolayer composition, no, or only very small, deviations from additivity are found for a series of molecular weight combinations examined. The results of this conventional approach are evidently no basis for detailed speculations about the phase behavior, and the main conclusion is that in all cases the amount of s–i segmental contacts is low in this regime, in agreement with the picture of a chain-segregated monolayer.

Molecular Weight Effects. In the previous publication of this series,[2] we extensively discussed the characteristics of the stereocomplexation process in mixed monolayers of isotactic and syndiotactic PMMA. In doing so, we already suggested that the segments of the isotactic and syndiotactic chains are probably not intimately mixed but are subject to a segregation of the chains, as discussed in the introduction. This segregation may be responsible for the fact that, in many cases, the conversion of the stereocomplexation process is limited due to a limited accessibility of the "internal" regions of the domains formed by the segregated coils. Stereocomplexation requires two contiguous strands of isotactic and syndiotactic PMMA, and so is essentially limited to the periphery of the individual chains, where the two components may be in direct contact. Upon stereocomplexation, the isotactic and syndiotactic chains may be screened by the newly formed complex structure; for further progress of the stereocomplexation (either by a lamellar growth of the complex already formed or by the formation of an independent newly complexed section) some reorganization of the system is required, in order to generate some fresh contact area. These reorganizations will be possible up to a point where the system becomes immobilized due to a high concentration of short complexed sections (formed at high surface pressures).[2] For higher molecular weight materials, segregating to form larger domains, the stereocomplexation efficiency will be lower due to the limited contact between isotactic and syndiotactic chains, and the immobilization stage is reached long before complete conversion is attained.

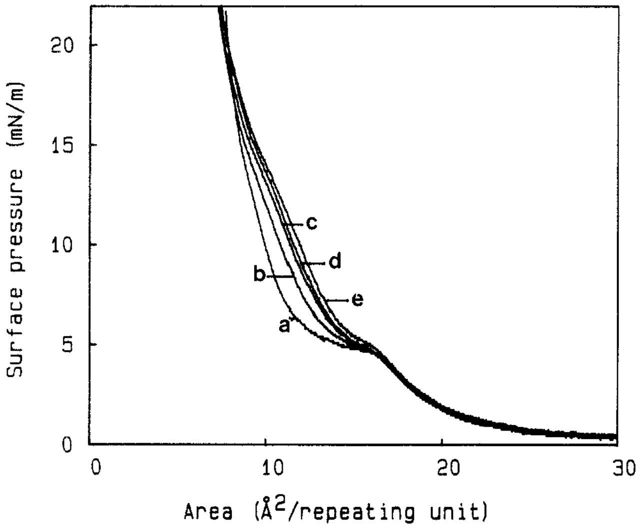

Figure 1. Pressure–area isotherms for 2:1 mixtures of s-PMMA m42 and i-PMMA m13 ($\bar{M}_n$ 13 000, a), m11 (21 000, b), m8 (36 000, c), m5 (95 000, d), and m2 (770 000, e). Compression speed 2 Å^2/(mmu·min), T = 45 °C.

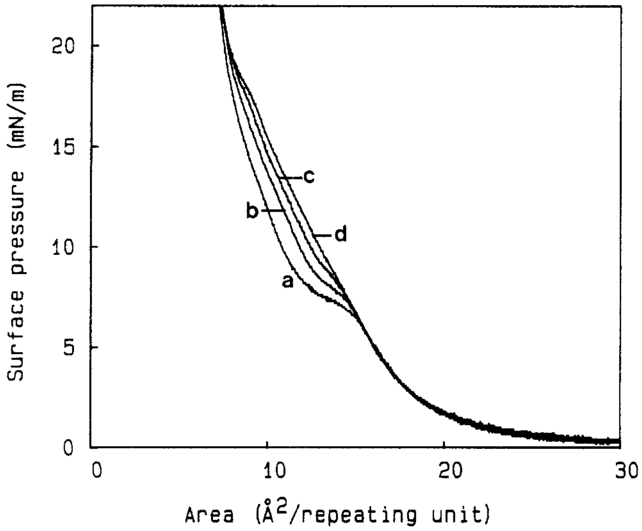

Figure 2. Pressure–area isotherms of 1:2 mixtures of i-PMMA m13 and s-PMMA m48 ($\bar{M}_n$ 18 000, a), m47 (25 000, b), m46 (32 000, c), and m45 (46 000, d). Compression speed 2 Å^2/(mmu·min), T = 45 °C.

Variation of the molecular weight of the isotactic PMMA (for a constant (rather low) molecular weight of the syndiotactic component) results in a behavior that, at first sight, appears to be compatible with this interpretation (Figure 1). When varying the molecular weight of the syndiotactic component (with constant (low) molecular weight of the isotactic component), we see that the restrictive effect of the molecular weight is even more pronounced than for high molecular weight samples of isotactic PMMA (Figure 2). Raising the molecular weight from 18 000 to 46 000 (only a factor 2.5) results in an almost complete suppression of the stereocomplexation process, much stronger than the analogous effect for i-PMMA in combination with low molecular weight s-PMMA. In the system of low molecular weight i-PMMA with the 46K syndiotactic material, we no longer see a clear onset of the stereocomplexation process, prior to an immobilization of the system, as we observed for the reversed combination. The behavior of the syndiotactic component upon raising the chain length is clearly different from that of the isotactic component and cannot be completely explained simply on the basis of chain segregation phenomena.

Two differences are obvious with respect to the syndiotactic and the isotactic components in the stereocomplexing system: the segmental stoichiometry (s:i = 2:1) and the cohesive interactions between the segments, these being much stronger for s-PMMA than for i-PMMA.[22] The stoichiometry will probably not be very relevant: both components occupy a similar area at the surface pressure associated with the onset of the stereocomplexation process. The strong cohesive interactions in syndiotactic PMMA are more likely to form an important factor, since they may cause a tendency of the syndiotactic chains to *aggregate* in the monolayer, increasing the dimensions of the domain structure. The very favorable segment–segment interactions for the syndiotactic chains will cause a high free energy to be associated with segments, in contact not with other syndiotactic segments but with isotactic segments, or with "empty" sites in the monolayer. The interfacial energy (or for the two-dimensional monolayer preferably the "perimeter" energy) of the syndiotactic chains will be much higher than that of the isotactic chains, which experience good solvent conditions in the monolayer,[22] implying a much stronger susceptibility for chain aggregation processes for the first material. The tendency for aggregation is also reflected in the negative values determined for the second virial coefficient in monolayers of atactic PMMA, as reported by Poupinet.[23]

As discussed in the Introduction, the propensity for chain aggregation will be stronger for higher molecular weights. Considering the segregated chains as separate particles with normal translational degrees of freedom, the interactions between two neighbouring s-PMMA chains will be stronger for higher molecular weights, because of the higher number of interchain segmental contacts per chain. This molecular weight dependent tendency for s-PMMA chain aggregation (which may eventually lead to a macroscopic phase separation but may also be responsible for local aggregation phenomena on a smaller scale) will result in larger domain dimensions in the monolayer, the number of contacts between isotactic and syndiotactic chains being lowered beyond an initial chain segregation effect as discussed earlier, and thus be responsible for the almost complete inhibition of stereocomplexation upon using a 46K s-PMMA sample.

The chain aggregation effect can be argued to be stronger for higher molecular weights but may also be operative for the lower molecular weight samples of s-PMMA. Considering this, the situation for the monolayers of mixtures of this material with i-PMMA of various molecular weights may be more complex than suggested before: the extent of aggregation of these syndiotactic chains can be imagined to be affected by the molecular weight of the i-PMMA, shorter chains suppressing this effect more (due to a more favorable entropy of mixing) than longer chains; the phase behavior may thus be determined by the molecular weights of both components. The rather large effect observed when the molecular weight of the isotactic component is raised from 13K to 36K (Figure 1) may be related to this effect. Support for this hypothesis will be discussed later on in this paper.

Apart from determining the domain dimensions, the molecular weights may also be relevant with respect to the susceptibility toward immobilization effects and the efficiency with which domain reorganizations may be conducted in the monolayer.

Bimodal Molecular Weight Distributions. Considering mixed monolayers of 2:1 mixtures of s- and i-PMMA, with the syndiotactic component consisting of two narrow molecular weight fractions (one of low molecular weight and one of higher molecular weight), we can observe that the behavior of the mixtures upon stereocomplexation is not additive with respect to both these fractions, as illustrated in Figure 3. If no s-PMMA

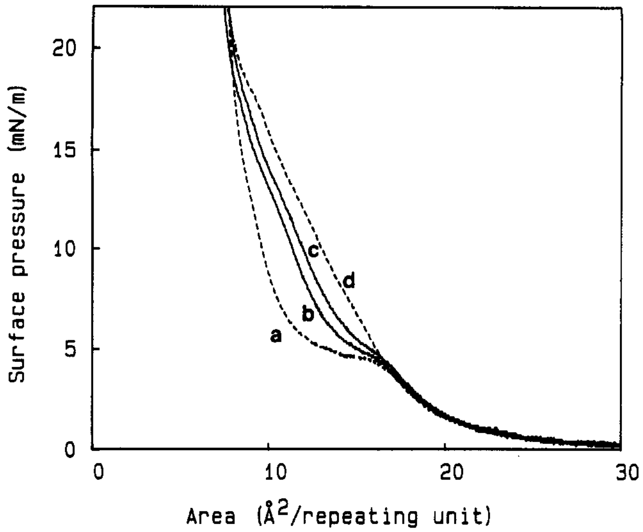

Figure 3. Pressure–area isotherms of ternary mixtures of i-PMMA m13 ($\bar{M}_n$ 13 000) with s-PMMA m42 ($\bar{M}_n$ 9000) and s-PMMA m44 ($\bar{M}_n$ 270 000). Overall stoichiometry s:i = 2:1. Ratio s-PMMA m44: s-PMMA m42: 0:1 (a), 0.16:0.84 (b), 0.3:0.7 (c), 1:0 (d). T = 45 °C.

chain aggregation phenomena were operative in the monolayer, a more or less additive behavior can be expected, each chain contributing individually to the stereocomplexation process. Instead, we see that addition of high molecular weight s-PMMA to the low molecular weight s-PMMA leads to a limited stereocomplexation conversion, this effect being significantly stronger than what is to be expected on the basis of the composition (additive behavior). Evidently, the high molecular weight s-PMMA chains present tend to aggregate and to include an amount of low molecular weight chains in these larger domains. The short chains themselves are not able to initiate the formation of extensive aggregated phases, but with the longer chains present, they may simply distribute themselves over the two phases present: the large aggregated s-PMMA domains and the "mixed monolayer". Only the short chains in this latter phase are well exposed to the isotactic components and will contribute significantly to the stereocomplexation process.

Compatibilization. It is clear that the suggested aggregation of the syndiotactic chains may severely limit the possibilities for stereocomplexation in the monolayer, restricting useful materials to low molecular weights. It is an interesting challenge to attempt to change the phase behavior of the monolayers, enhancing the miscibility of the isotactic and syndiotactic components. There are several strategies that can be used to achieve this goal, analogous to those used for compatibilization of conventional three-dimensional polymer blends. The first approach would be to modify the syndiotactic and isotactic chains so that strongly favorable interactions between the two components are operative; it is difficult to see how this can be done without losing the possibility for stereocomplexation. Another approach would be to induce strongly unfavorable interactions within the s-PMMA chains, making aggregation less favorable (analogous to the "copolymer effect"[24]). This concept is pursued in another publication.[25]

Finally, addition of "surface active" (or better "perimeter active") compounds to lower the interfacial ("perimeter") energy of the s-PMMA domains could result in a suppression of the aggregation processes in the monolayer and a better dispersion of the components. For conventional three-dimensional blends of two components, diblock copolymers of both components, segregating to the interface of the domains, may be used for this purpose.[26] The projection of this approach onto mixed monolayers of syndiotactic and isotactic PMMA would be the use of *stereoblock PMMA*, with each chain consisting of one syndiotactic and one isotactic block.

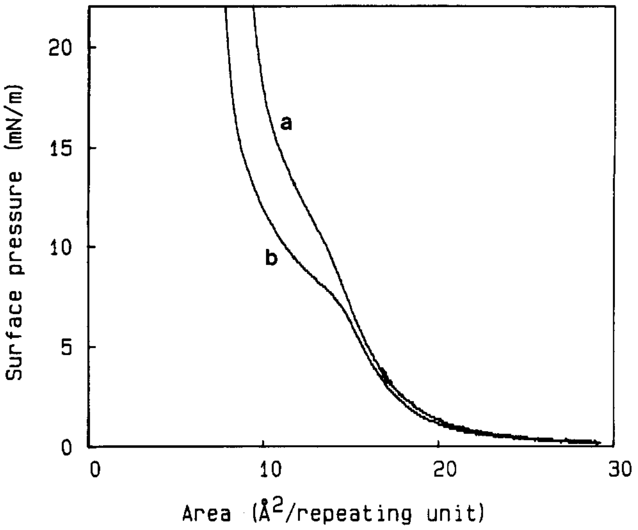

Figure 4. Pressure–area isotherms of stereoblock PMMA: (a) T = 22 °C; (b) T = 45 °C. Compression speed 2 Å²/(mmu·min).

Stereoblock PMMA. The stereoblock material we used is a diblock copolymer characterized by a narrow molecular weight distribution, with the syndiotactic block approximately twice as long as the isotactic block, corresponding to the overall stoichiometry of the mixtures studied. The block lengths are relatively short (Table I).

Compression isotherms of stereoblock PMMA are shown in Figure 4. The characteristic stereocomplexation transition is clearly present in the isotherm; the onset of the transition is associated with surface pressures a little higher than, e.g., observed for the mixtures reported in Figure 1. This is probably caused by the nonperfect stereoregularity of the blocks[21] and their relatively short length, in the regime where critical chain length effects may raise the stereocomplexation surface pressure.[2] The characteristics of the stereocomplexation process in the stereoblock monolayers are similar to those of the mixed homopolymer monolayers: the transition shifts to lower surface pressures at higher temperatures and is not completely reversible upon decompression and subsequent recompression (Figure 5). It is interesting to note that Beredjick and Ries[27] already reported anomalous isotherms for a PMMA material, which they claimed to have a stereoblock character; the material was not well characterized, though, and stereocomplexation was not mentioned as a possible cause for the observed deviations, an omission which can hardly be held against the authors, since, at that time, the concept of stereocomplexation was not yet introduced.

Stereoblock PMMA as Compatibilizer. The effect of mixing the stereoblock polymer with mixtures of syndiotactic and isotactic homopolymers, is shown in Figure 6. A syndiotactic component was chosen with a molecular weight of approximately 46 000, exhibiting an almost complete suppression of the stereocomplexation, presumably due to the aggregation of the chains in the monolayer. Upon adding the stereoblock polymer, we can see that the resulting isotherm exhibits an efficient stereocomplexation process, the isotherm transition being much clearer than what is to be expected on the basis of additive behavior; the three-component mixture shows a more pronounced transition than either the pure stereoblock monolayer or the mixture without the stereoblock added. Clearly, stereoblock PMMA, segregating to the "interface" of the domains, functions as a *compatibilizer*,

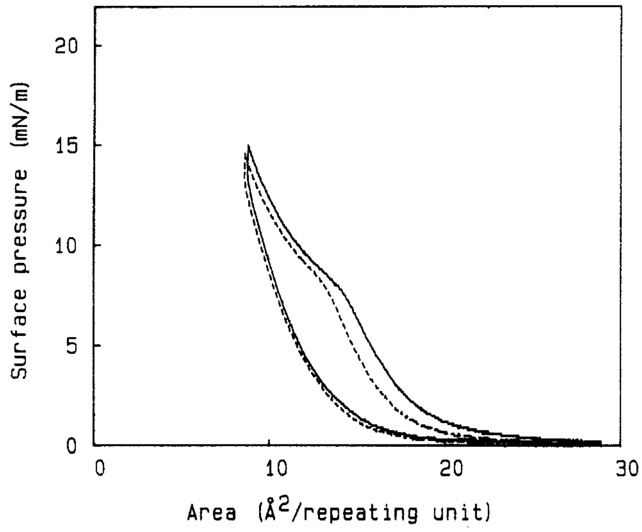

Figure 5. Hysteresis isotherms of stereoblock PMMA, T = 45 °C, compression and decompression speed 2 Å^2/(mmu·min). The solid line represents the first cycle, and the dashed line represents the second cycle.

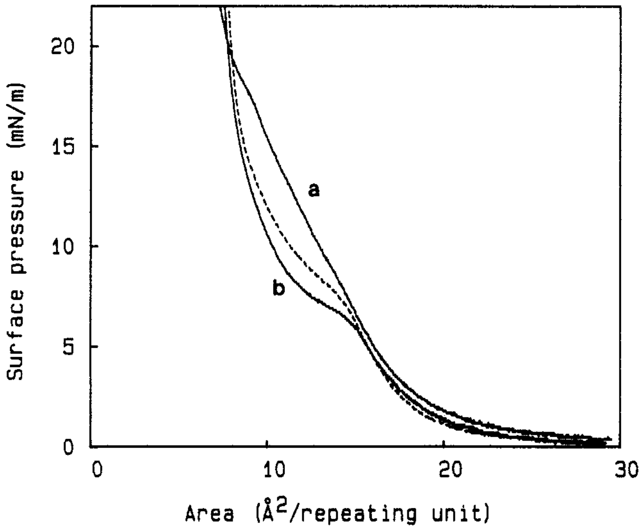

Figure 6. Pressure–area isotherms of (a) a 2:1 mixture of s-PMMA m45 ($\bar{M}_n$ 46 000) and i-PMMA m13 ($\bar{M}_n$ 13 000) and (b) the same mixture with 30 wt % stereoblock PMMA. The dashed line represents the pure stereoblock PMMA. T = 45 °C.

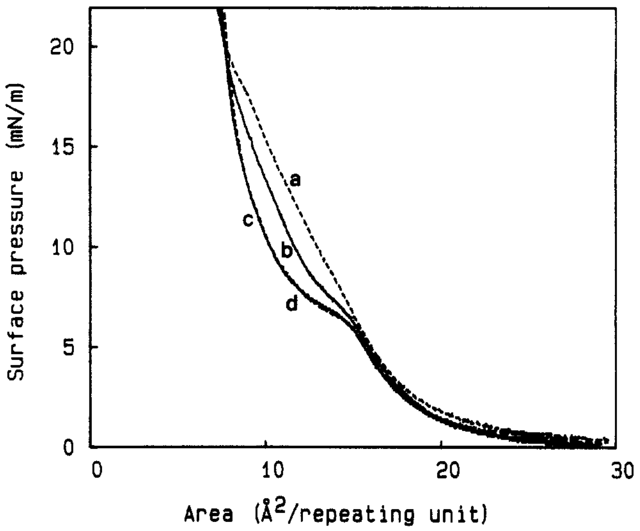

Figure 7. Pressure–area isotherms of ternary mixtures of s-PMMA m45 ($\bar{M}_n$ 46 000), i-PMMA m13 ($\bar{M}_n$ 13 000), and stereoblock PMMA. Overall stoichiometry s:i = 2:1. Stereoblock content: 0% (a, dashed), 16% (b, solid), 30% (c, solid), 46% (d, dashed). T = 45 °C.

dispersing the syndiotactic chains into smaller domains, which are better accessible for stereocomplexation. Varying the amount of the stereoblock PMMA, we see that the compatibilizing effect is optimal for a weight content of approximately 30%, higher concentrations not leading to a further improvement of the situation (Figure 7). The large amount of stereoblock material needed reflects the small domain sizes necessary for an efficient stereocomplexation process. Using s-PMMA fractions of somewhat lower molecular weights, a maximum efficiency can be achieved with smaller amounts of stereoblock PMMA; in case of a combination of low molecular weight s- and i-PMMA, addition of stereoblock PMMA only has an adverse effect.

The stereoblock material appears to efficiently suppress the aggregation of the syndiotactic chains but will probably not be able to alter the segregation of the individual coils: the domain size probably has an intrinsic bottom limit defined by the molecular weight of the material. In Figure 8, the effect of the addition of stereoblock PMMA is shown for a series of mixtures with varying molecular weights of the syndiotactic PMMA component. When the molecular weight of the s-PMMA is raised, the stereocomplexation process becomes less effective, even after addition of stereoblock PMMA, presumably due to the higher intrinsic domain size.

Considering mixed monolayers of rather low molecular weight s-PMMA with i-PMMA of an intermediate molecular weight (36K), we observe that also in this case, the addition of stereoblock PMMA enhances the efficiency of the stereocomplexation process; this is illustrated in Figure 9. This experiment indicates that also for these mixtures, chain aggregation effects were important in limiting the stereocomplexation efficiency, as was suggested before, the higher molecular weight i-PMMA being less effective in suppressing the s-PMMA aggregation. Addition of the stereoblock PMMA disturbs this aggregation process, resulting in a more intimate mixing (a better dispersion) of the isotactic and the syndiotactic components. When the molecular weight of the i-PMMA samples is raised further (with similar amounts of stereoblock PMMA added), the efficiency of the stereocomplexation is observed to slowly decrease, as was found for high molecular weight s-PMMA. This effect is even stronger for mixtures of two high molecular weight components.

It is interesting to note that when highly stereoregular polymers are used, with a possible onset of the stereocomplexation process at surface pressures lower than those for the stereoblock component, the onset pressure in the compatibilized mixture is determined by the highly stereoregular components rather than by the stereoblock PMMA (Figures 8 and 9).

Conclusions

Summarizing, we can conclude that the mixtures of syndiotactic and isotactic PMMA are probably subject to phase separation processes (if not macroscopic, then at least aggregation on a smaller scale) caused by strong cohesive interactions of the syndiotactic component, an effect that strongly affects the efficiency of the stereocomplexation process. This aggregation process is responsible for the fact that when mixtures of i-PMMA with a blend of high and low molecular weight s-PMMA are studied, these mixtures are observed not to behave according to what would be expected on the basis of additivity, with all s-PMMA chains contributing independently. Addition of stereoblock PMMA, as a perimeter active agent, suppresses the aggregation process and enhances the efficiency of the stereocomplexation process

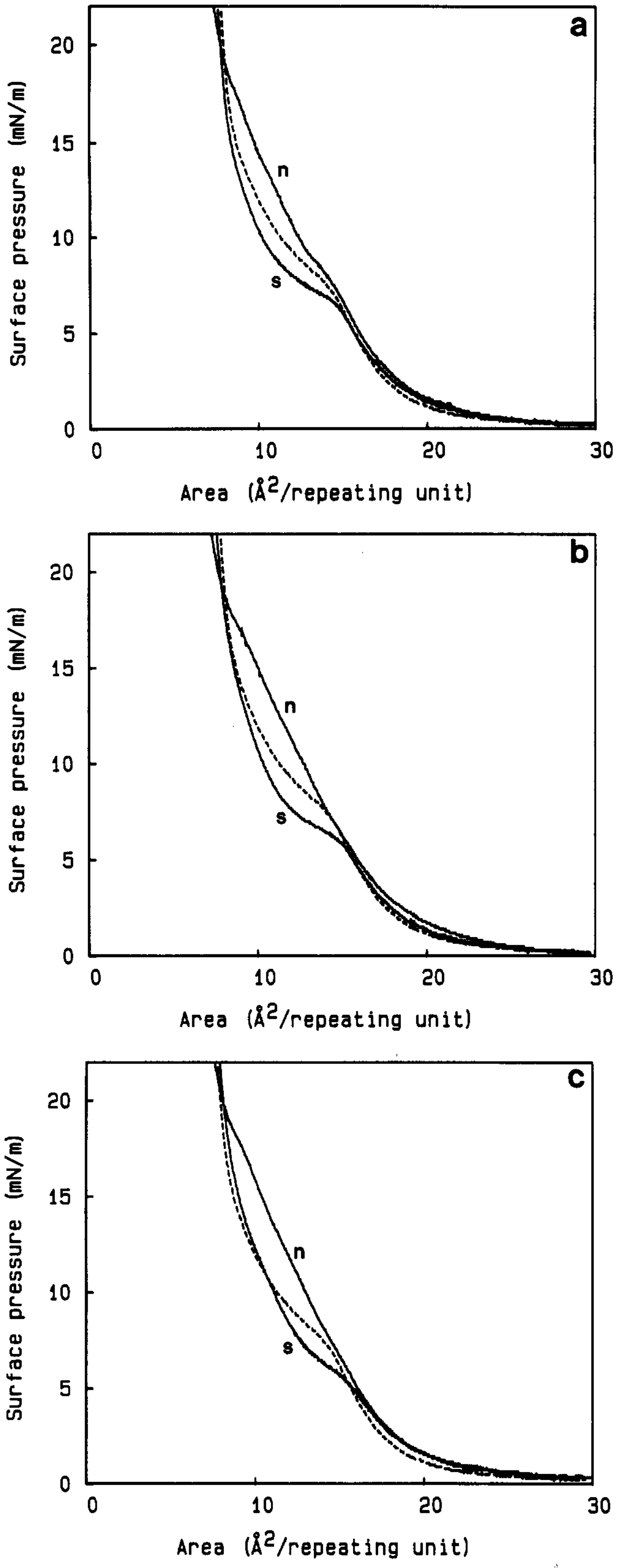

Figure 8. Pressure–area isotherms of 1:2 mixtures of i-PMMA m13 ($\bar{M}_n$ 13 000) with s-PMMA m46 ($\bar{M}_n$ 32 000, a), s-PMMA m43 ($\bar{M}_n$ 87 000, b), and s-PMMA m44 ($\bar{M}_n$ 270 000, c), before (n) and after (s) addition of approximately 30 wt % stereoblock PMMA. The dashed line represents pure stereoblock PMMA. T = 45 °C.

in the mixed monolayers, thus exhibiting a clear compatibilizer function. This latter observation strongly supports the hypothesis that phase separation processes are responsible for the observed limitation of the stereocomplexation process when higher molecular weight samples are used.

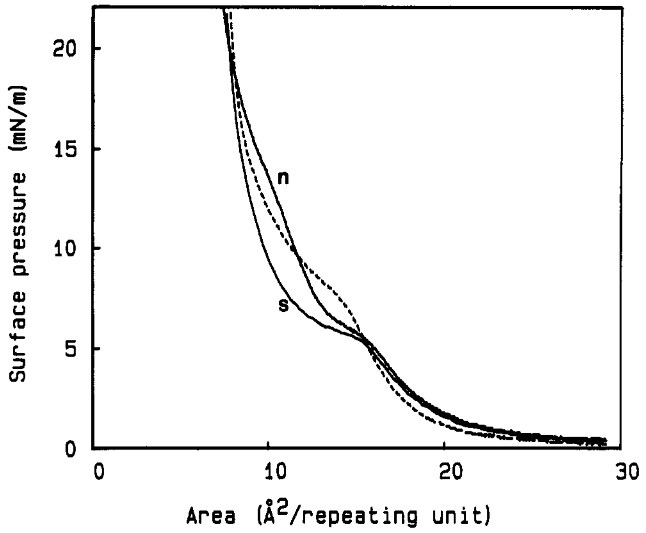

Figure 9. Pressure–area isotherms of a 2:1 mixture of s-PMMA m41 ($\bar{M}_n$ 11 000) and i-PMMA m8 ($\bar{M}_n$ 36 000), before (n) and after (s) addition of 26 wt % stereoblock PMMA. The dashed line represents pure stereoblock PMMA. T = 45 °C.

The information about the monolayer phase behavior that can be extracted from the efficiency of the stereocomplexation process cannot be obtained from conventional area vs composition plots at surface pressures corresponding to the pretransition condition of the monolayer: these plots exhibited no, or only very small, deviations from additivity in all cases and did not permit any detailed speculations about the phase behavior.

References and Notes

(1) Brinkhuis, R. H. G.; Schouten, A. J. *Macromolecules* **1992**, *25*, 2725.
(2) Brinkhuis, R. H. G.; Schouten, A. J. *Macromolecules* **1992**, *25*, 2732.
(3) Gabrielli, G.; Pugelli, M.; Faccioli, R. *J. Colloid Interface Sci.* **1971**, *37*, 213.
(4) Gabrielli, G.; Pugelli, M.; Ferroni, E. *J. Colloid Interface Sci.* **1974**, *47*, 145.
(5) Pugelli, M.; Gabrielli, G. *J. Colloid Interface Sci.* **1977**, *61*, 420.
(6) Gabrielli, G.; Pugelli, M.; Baglioni, P. *J. Colloid Interface Sci.* **1982**, *86*, 485.
(7) Caminati, G.; Gabrielli, G.; Ferroni, E. *Colloids Surf.* **1989**, *41*, 189.
(8) Caminati, G.; Gabrielli, G.; Puggelli, M.; Ferroni, E. *Colloid Polym. Sci.* **1989**, *267*, 237.
(9) Kawaguchi, M.; Nishida, R. *Langmuir* **1990**, *6*, 492.
(10) De Gennes, P. G. *Scaling concepts in polymer physics*; Cornell University Press: Ithaca, NY, 1979.
(11) Carmesin, I.; Kremer, K. *J. Phys. Fr.* **1990**, *51*, 915.
(12) Baumgärtner, A. *Polymer* **1982**, *23*, 334.
(13) Tobochnik, J.; Webman, I.; Lebowitz, J. L.; Kalos, M. H. *Macromolecules* **1982**, *15*, 549.
(14) Bishop, M.; Michels, J. P. J. *J. Chem. Phys.* **1985**, *83*, 4791.
(15) Cifra, P.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1988**, *21*, 446.
(16) Baumgärtner, A.; Heermann, D. W. *Polymer* **1986**, *27*, 1777.
(17) Ariyapadi, M. V.; Haus, J.; Nauman, E. B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (2), 92.
(18) van Vliet, J. H.; ten Brinke, G. *Macromolecules* **1989**, *22*, 4627.
(19) Howe, S. E.; Coleman, M. M. *Macromolecules* **1986**, *19*, 72.
(20) Motomura, K.; Matuura, R. *J. Colloid Sci.* **1963**, *18*, 52.
(21) Doherty, M. A.; Hogen-Esch, T. *Makromol. Chem.* **1986**, *187*, 61.
(22) Brinkhuis, R. H. G.; Schouten, A. J. *Macromolecules* **1991**, *24*, 1487.
(23) Poupinet, D.; Vilanove, R.; Rondelez, F. *Macromolecules* **1989**, *22*, 2491.
(24) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(25) Part 7: Brinkhuis, R. H. G.; Schouten, A. J. *Macromolecules* **1992**, *25*, 6173.
(26) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Tang, W. *Macromolecules* **1990**, *23*, 4780.
(27) Beredjick, N.; Ries, H. E., Jr. *J. Polym. Sci.* **1962**, *62*, 864.