Thin Film Behavior of Poly(methyl methacrylates). 9. Crystallization of Isotactic Poly(methyl methacrylate) in Mixed Monolayers

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ABSTRACT: The crystallization behavior of isotactic poly(methyl methacrylate) (i-PMMA) in monolayers of mixtures with a noncrystallizable component was investigated. The monolayer crystallization process in mixtures with high molecular weight condensed type polymers such as syndiotactic poly(methyl methacrylate) (s-PMMA) can be completely explained on the basis of additive behavior, as expected for monolayers with large phase-separated domains present, when compression speed effects are taken into account. When i-PMMA is mixed with noncrystallizable diluents, forming expanded monolayers, the monolayer crystallization of the i-PMMA component is shown to be a function of the molecular weight of the diluent. Whereas for high molecular weights crystallization approximately takes place as in an undiluted monolayer, low molecular weights of the diluent give rise to a suppressed monolayer crystallization, presumably the result of the demixing process that must take place upon crystallization.

Introduction

In previous papers, monolayers of isotactic poly(methyl methacrylate) (i-PMMA) were shown to exhibit a crystallization process in which monolayer structures were formed, presumably consisting of two-dimensional crystallites of double-helical structures, similar to those reported for the melt crystal structure.[1-3] We recently found that, in mixed monolayers of isotactic and syndiotactic PMMA (s-PMMA), stereocomplexation processes between these components can be induced upon compression.[4-7] This stereocomplexation process was observed to suffer from phase separation phenomena in the monolayer, resulting in a limited stereocomplexation conversion, evident in the compression isotherms. In this respect, the monolayer stereocomplexation process can serve as a sensitive indicator for the monolayer phase behavior.[6,7] Next to this stereocomplexation process, the monolayer crystallization of isotactic PMMA can also be expected to be sensitive to the phase behavior in polymer mixtures. It is therefore tempting to study such systems, since the crystallization process may offer information about the monolayer phase behavior which cannot easily be extracted from conventional area vs composition plots. The phase behavior of monolayers of polymer mixtures is especially interesting because of their two-dimensional character, and the complications that this might imply, e.g., a possible segregation of the individual chains.[8]

Experimental Section

Monolayer experiments were performed using a computer-controlled Lauda film balance FW2. Surface pressure was recorded with an accuracy of approximately 0.05 mN/m. The subphase was pure water, purified by reverse osmosis and subsequent filtration through a Milli-Q purification system. Monolayers were spread from 0.3 g/L chloroform solutions. A standard compression speed of 2 Å²/(monomeric unit·min) was used; all isotherms were recorded at 22 °C.

Characteristics of the PMMA materials used are listed in Table I; synthesis procedures are listed in ref 1. The poly(methyl acrylate) (PMA) and poly(vinyl acetate) (PVAc) materials are the products of conventional radical polymerizations in toluene solutions at 60 °C, followed by a rough fractionation procedure; characteristics are summarized in Tables II and III.

Table I
PMMA Characteristics

material	tacticity (%)			$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
	i	h	s		
m6	>97			63	1.30
m8	>97			36	1.17
m21	89	8	3	2.8	1.35
m22	>97			1200	1.45
m44	2	11	87	270	1.20

Table II
PMA Characteristics

sample	i	h	s	$\bar{M}_n \times 10^{-3}$	D
1		nd		4.1	1.72
2		nd		1100	4.7

Table III
PVAc Characteristics

sample	i	h	s	$\bar{M}_n \times 10^{-3}$	D
1		nd		1.7	1.37
2		nd		73	3.7

Results and Discussion

On the basis of our present insight in the monolayer crystallization process of i-PMMA, the level of mixing in a mixture containing i-PMMA and a noncrystallizable component level can be argued to be important. When isotactic PMMA is mixed with a polymer that does not exhibit this crystallization process, additive behavior can be expected if large domains are present with respect to the average crystallite size to be formed; the i-PMMA chains will not notice the presence of the other component. In the case of interpenetration of polymer chains, resulting in mixing up to close to the segmental level, the crystallization process, as depicted in ref 1, can be anticipated to be affected: this mixing process would be associated with a favorable free energy of mixing. Crystallization of the crystallizable component will necessarily result in a demixing process, so that the overall free energy change of the crystallization process will contain an *unfavorable* contribution from the free energy of demixing. Kinetic factors due to the necessary diffusion processes of the noncrystallizable components during crystallization may also play a role.
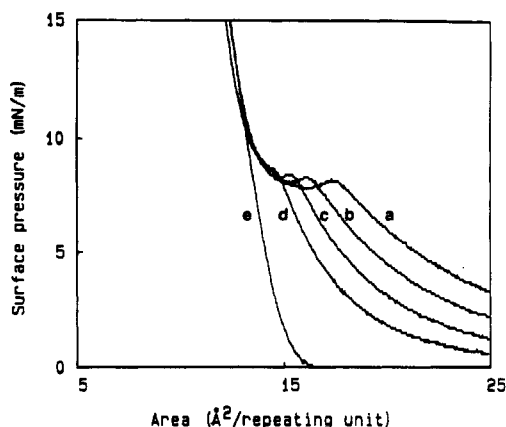
Figure 1. Pressure–area isotherms of mixtures of i-PMMA m6 ($\bar{M}_n$ 63K) and s-PMMA m44 ($\bar{M}_n$ 270K) as a function of composition. Weight fraction isotactic PMMA: 1 (a), 0.70 (b), 0.50 (c), 0.28 (d), 0 (e). Overall compression speed 2 Å²/(monomeric unit·min). T = 22 °C.

For a situation in which we do not have complete interpenetration of the chains, but a domain structure (e.g., due to segregated chains[6,8]) with the domains being of the same order of magnitude, or smaller than the average size of the crystallites to be formed,[1,2] the overall crystallization rate may also be affected. In this case, kinetic restrictions can also contribute: for a relatively low nucleation density, many growing crystallites will be stopped by domain boundaries, where, in a continuous monolayer of isotactic PMMA, they would continue to grow. This limitation of the overall crystallization rate due to geometric constraints is analogous to, e.g., the suppression of the three-dimensional crystallization in very thin films, the film thickness being small with respect to the average crystallite size determined by the nucleation density.[9] From these arguments, we can conclude that the average crystallite size will be an important parameter, about which, unfortunately, we do not have direct information. In ref 1, we suggested that the nucleation density and the average crystallite size will be a clear function of the surface pressure during crystallization. For the compression speeds used, the orientation characteristics of the monolayers following transfer indicated that the average crystallites were not very large, their long axis coinciding with the helix axis. More extensive crystallites were suggested to be formed during stabilization at lower surface pressures.[1]

Mixtures of Syndiotactic and Isotactic PMMA. The first system that we will address is a monolayer blend of isotactic and syndiotactic PMMA. For both materials, relatively high molecular weight fractions were chosen, so as to avoid interference from stereocomplexation phenomena.[4] As argued in ref 6, this combination presumably leads to a phase separation in large domains in the monolayer, resulting in a low level of s–i contacts, and consequently in an almost completely suppressed stereocomplexation. In Figure 1, isotherms are drawn for mixtures of varying composition, with a fixed compression speed of 2 Å²/(monomeric unit·min) at 22 °C. We see that the onset of crystallization transition upon compression is observed at progressively higher pressures as the fraction of syndiotactic PMMA is raised. At first sight, this may seem puzzling considering the fact that we anticipated a large-scale phase separation, without a significant direct influence of the syndiotactic component on the i-PMMA component. The presence of the syndiotactic component can be argued to indirectly influence the crystallization process, though.

To assess whether deviations from additivity occur in mixed monolayers, we must first define what we can expect on the basis of additive behavior. Additive behavior cannot be deduced from a simple superposition of the isotherms of the individual components: the reason for this fact lies in the sensitivity of the isotactic PMMA crystallization process with respect to the compression speed. In ref 1, the effect of a variation of the compression speed on the isotherms of i-PMMA monolayers was extensively discussed; the mechanism of the crystallization process, requiring a nucleation stage and subsequent crystallite growth, with a thermodynamic driving force strongly dependent on the surface pressure, is responsible for the strong kinetic effects observed in the isotherms in the transition region. In order to directly compare the compression isotherms, it is essential that the compression speed for the isotactic PMMA component is approximately equal.

In mixed monolayers, even in the case of complete macroscopic phase separation, the *effective compression speed* that the isotactic PMMA domains experience is not equal to the overall compression speed imposed on the mixed monolayer, but will also be determined by the compressibility of the complementary component. The reason for this is that, in a mixed monolayer, the surface pressure in the domains of the different components will necessarily be equal. If the components have different compressibilities, the effect of the area consumed by the mechanical compression will not be divided equally over the domains, but, instead, in such a way that the rise in surface pressure due to the effective compression of both domains is identical for both components.

If we consider two components A and B, with base mole fractions x_A and x_B, occupying specific areas A_A and A_B, in a completely phase-separated monolayer, we can see that

$$A_{tot} = x_A A_A + x_B A_B \tag{1}$$

Upon compression we find

$$\delta A_{tot}/\delta t = x_A(\delta A_A/\delta t) + x_B(\delta A_B/\delta t) \tag{2}$$

The total area decrease upon compression is divided between the two components

$$\delta A_{tot} = x_A \delta A_A + x_B \delta A_B \tag{3}$$

in such a way that the rise in surface pressure is equal for both components

$$(\delta\Pi_A/\delta A_A)\delta A_A = (\delta\Pi_B/\delta A_B)\delta A_B \tag{4}$$

relating the effective compression speed to the mole fractions and compressibilities of the two individual components. These expressions can be used to deduce a relation for the effective compression speed that one of the components experiences in a mixture, as a function of the overall compression speed and the compressibilities of both components. This relation is

$$\delta A_A/\delta t = (x_A + (1 - x_A)(K_B/K_A))^{-1}(\delta A_{tot}/\delta t) \tag{5}$$

with $K_{A,B}$ representing the "compressibility" of the components at a given surface pressure:[10]

$$K_i = \delta A_i/\delta\Pi \tag{6}$$

When isotactic PMMA is mixed with another component with a lower compressibility (characterized by a steep isotherm, e.g., syndiotactic PMMA), the effective compression speed that the isotactic component experiences will be higher than the overall compression speed, and this effective compression speed will increase with higher

fractions of the other component present, so that the crystallization transition can be expected to shift to higher surface pressures. When isotactic PMMA is mixed with a component of similar compressibility, the effective compression speed will be similar to the overall compression speed. It may be obvious that the compressibilities at surface pressures in the region of the onset of the crystallization process are most relevant. The rise in surface pressure observed in Figure 1 for the onset of the crystallization of i-PMMA in monolayer blends with s-PMMA is in perfect quantitative agreement with an increase in the effective compression speed of the isotactic component, on the basis of the relations given above, and with the picture of a strongly phase separated monolayer.

During the transition itself, additional effects cause further deviations from a first-order additivity: the fact that the overall crystallization rate is limited to the domains of the isotactic PMMA makes the absolute rate that is achieved lower with respect to monolayers of pure i-PMMA: the amount of area "generated" by the crystallization process will be lower, so that the drop in surface pressure exhibited by a monolayer of pure i-PMMA, experiencing the same initial effective compression speed, will be more pronounced than in a mixed monolayer. Figure 1 also illustrates this effect. Mixtures of isotactic PMMA with syndiotactic poly(ethyl methacrylate) exhibit a similar additive behavior.

Mixtures of Isotactic PMMA with Other Polymers Exhibiting Expanded Monolayer Behavior. In the rest of this paper, we will address monolayers of isotactic PMMA, mixed with other expanded noncrystallizable components: i-PMMA oligomers, poly(methyl acrylate), and poly(vinyl acetate). For these monolayers, we observe that the compressibilities do not differ strongly in the 5–9 mN/m regime, so that the effective compression speed which the isotactic PMMA experiences in an additive mixture will be approximately equal to the overall compression speed. The effect of the absolute conversion rate being lower in a mixed monolayer, resulting in a less pronounced pressure drop upon crystallization, remains operative though. For these expanded monolayers, all components are characterized by weak cohesive interactions, and low "perimeter energies",[6] so that no large-scale phase separation effects are to be expected a priori. All systems discussed in this section exhibit an approximately additive behavior at low surface pressures in the regime preceding the i-PMMA crystallization transition, as can be judged from area vs composition plots.

The first system that we will address is a mixture of a crystallizable isotactic PMMA sample with i-PMMA of low molecular weight, far under the critical chain length, not able to participate in the crystallization process.[1] In Figures 2 and 3, the isotherms are shown of a series of compositions with compression speeds of 12 and 2 $Å^2$/(monomeric unit·min), respectively. We can clearly see that addition of low molecular weight i-PMMA results in a severe suppression of the crystallization process. The oligomeric i-PMMA chains do not participate directly in the crystallization process: this can be inferred from stabilization experiments at 12 mN/m, which eventually yield an approximately additive value for the specific area. Simultaneously, the crystallization of the longer chains in the mixed monolayer is hindered by the presence of the oligomeric chains: the onset of the crystallization is clearly shifted to higher surface pressures, although the compressibilities of the crystallizable and the noncrystallizable components are approximately equal. The molecular
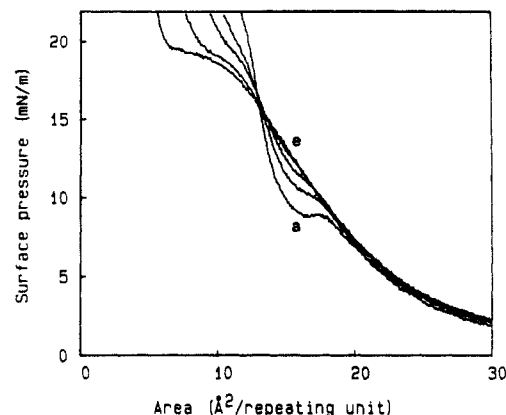
Figure 2. Pressure–area isotherms of mixtures of i-PMMA m8 ($\bar{M}_n$ 36K) with oligomeric i-PMMA m21 ($\bar{M}_n$ 2800). Weight fraction low molecular weight component: 0 (a), 0.26, 0.45, 0.69, 1 (e). Compression speed 12 $Å^2$/(monomeric unit·min). $T = 22$ °C.
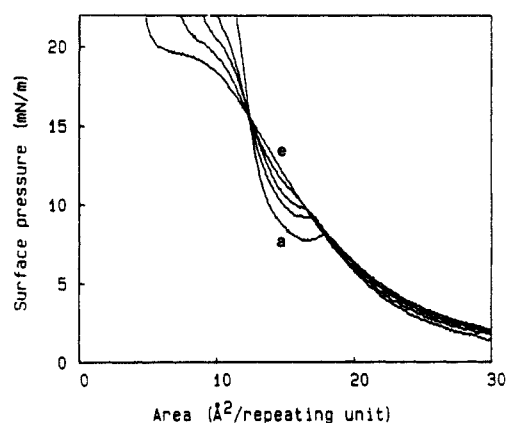

Figure 3. The same as Figure 2. Compression speed 2 $Å^2$/(monomeric unit·min).

weight ($\bar{M}_n$) of the long-chain component was 36 000; if this component is replaced by a sample with a very high molecular weight (1.2 million), the effects are practically identical.

Evidently, in this case, we are dealing with a mixing of the long and the short chains, leading to a situation in which domains of the crystallizable component with dimensions large with respect to the average crystallite size to be formed during the experiment no longer exist: for crystallization of the high molecular weight component, the oligomeric chains will have to be "squeezed out". Considering the analogous effects observed for the 36K and the 1.2 million molecular weight material, and the high nucleation density (and small crystallites) anticipated for the high compression speeds used,[1,2] it is probable that the mixture is characterized by an extensive chain interpenetration or, rather, a penetration of the long chains by the oligomers. The free energy of the demixing process associated with crystallization contributes unfavorably to the overall free energy of crystallization.

The chain segregation restriction in a two-dimensional mixture can be expected to be less severe in the case of short chains. In polydisperse systems, the longest chains have been argued to expand due to partial penetration by smaller chains present in the system.[8,11] In the limit of a solventlike molecule, a complete swelling of the long chains by these small molecules is obviously not restricted by the two-dimensional character of the monolayer.

The lowering of the thermodynamic driving force for crystallization results in a relatively low nucleation density, and consequently in "broader" crystallites, an effect which
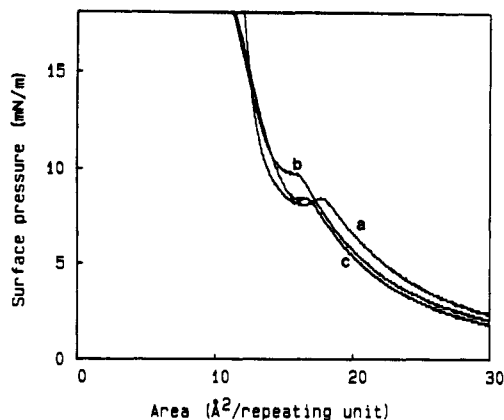
Figure 4. Pressure–area isotherms of i-PMMA m6 ($\bar{M}_n$ 63K): pure (a) and mixed with poly(methyl acrylate) of low molecular weight (1, $\bar{M}_n$ 4.1K) (b) or high molecular weight (2, $\bar{M}_n$ 1100K) (c), in an approximately 1:1 (base mole) ratio. Compression speed 2 Å²/(monomeric unit·min). T = 22 °C.
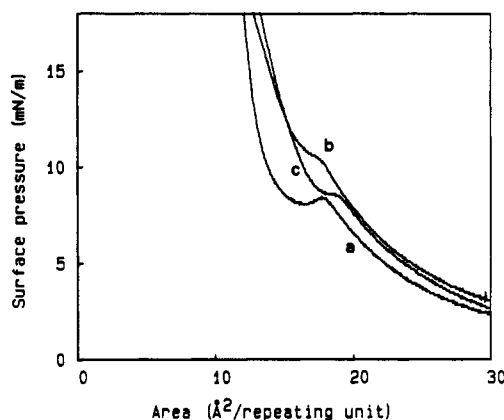


Figure 5. Pressure–area isotherms of i-PMMA m6 ($\bar{M}_n$ 63K): pure (a) and mixed with poly(vinyl acetate) of low molecular weight (1, $\bar{M}_n$ 1.7 K) (b) or high molecular weight (2, $\bar{M}_n$ 73K) (c), in an approximately 1:1 (base mole) ratio. Compression speed 2 Å²/(monomeric unit·min). T = 22 °C.

is illustrated by an orientation of the crystallites helices perpendicular to the dipping direction upon transfer to solid substrates; the underlying mechanism for this phenomenon is extensively discussed in ref 2.

The monolayer crystallization behavior of isotactic PMMA in mixtures with poly(*methyl acrylate*) and poly(*vinyl acetate*) was also investigated. Mixtures of a sample of isotactic PMMA with samples of PMA or PVAc of relatively high molecular weights, in an approximately 1:1 (base mole) ratio, exhibit an onset of the crystallization process upon compression at surface pressures similar to that in the pure i-PMMA monolayer (Figures 4 and 5). Probably, in this case, no extensive chain interpenetration takes place, the segregation of the individual chains leading to fairly large domains, large relative to the average crystallite size to be formed under the conditions of the experiment, so that, locally, the isotactic strands do not feel the effect of the presence of the noncrystallizable component. In this situation, the effect of the entropy of a demixing process would be low anyway due to the high molecular weight of the noncrystallizable component, so that this experiment cannot serve as an absolute proof for the absence of chain interpenetration. Still, in the case of such extensive chain interpenetration, kinetic effects associated with the demixing process would be expected to lead to deviations from additivity, especially at higher crystallization rates.

If an isobaric stabilization experiment is performed on these mixtures at low surface pressures (6.7 mN/m), we
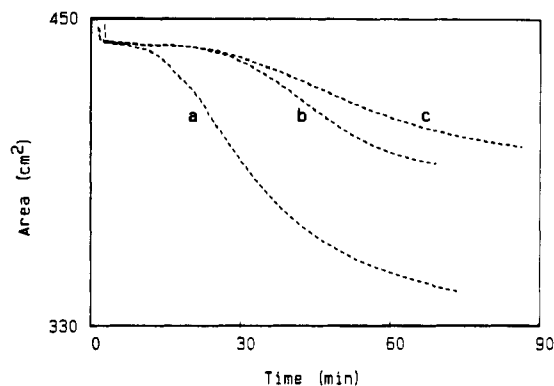
Figure 6. Isobaric stabilization experiments for pure i-PMMA m6 ($\bar{M}_n$ 63K) (a) and i-PMMA mixed with high molecular weight PMA (2) (b) or PVAc (2) (c). Mixing ratio 1:1. T = 22 °C, Π = 6.7 mN/m.

do observe that crystallization (related to the amount of i-PMMA present) is somewhat slower than in a pure i-PMMA monolayer (Figure 6). Under these more subtle conditions, this lowering of the crystallization rate does not necessarily have a thermodynamic origin; an interpretion in terms of a kinetic suppression due to the constraints of the domains limiting the growth of the crystallites formed is also possible.

Replacing the high molecular weight PMA and PVAc in the mixtures with low molecular weight samples of the same materials, and performing the same compression experiments, we now observe that the onset of the monolayer crystallization clearly shifts to higher surface pressures, similar to the mixtures of i-PMMA with its own oligomers (Figures 4 and 5). Probably, the long chains of isotactic PMMA can swell in these short chains of PMA and PVAc present in the monolayer, the entropy of mixing associated with this process responsible for this phenomenon thermodynamically suppressing the crystallization of the i-PMMA. The fact that the isotherms of the mixtures containing the PMA oligomers exhibit a smaller surface pressure shift than those of the mixtures containing the PVAc oligomers is probably related to the lower molecular weight of the latter material and the resulting higher entropy of mixing.

Conclusions

The results reported here for mixed monolayers containing i-PMMA can be explained on the basis of the proposed mechanism for the monolayer crystallization of this component. Monolayer mixtures of isotactic PMMA with high molecular weight s-PMMA samples exhibit an approximately additive behavior, in agreement with the model of large domains being present in the monolayer, as can be concluded after taking into account the deviating effective compression speed that the i-PMMA domains experience. For mixtures of isotactic PMMA with oligomeric noncrystallizable components (i-PMMA, PMA, or PVAc), also exhibiting an expanded monolayer behavior, we observe a clear suppression of the crystallization of the isotactic PMMA, suggesting extensive chain interpenetration, or rather a swelling of the longest chains, with the short oligomeric chains almost behaving as a two-dimensional solvent. Chain interpenetration probably does not occur on a similar scale when using high molecular weight noncrystallizable diluents; in this case, upon compression and crystallization, the monolayer behavior is approximately additive, with deviations only being observed during isobaric stabilization experiments at low surface pressures.

The monolayer crystallization process of isotactic PMMA in mixed monolayers provides information about the miscibility with other substances, which cannot easily be obtained, e.g., from conventional area vs composition plots. This approach can easily be extended to mixtures of i-PMMA with other polymeric or low molecular weight substances, offering an extra tool to assess their monolayer miscibility.

References and Notes

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