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Thin-Film Behavior of Poly(methyl methacrylates). 5. Characteristics of the Poly(methyl methacrylate) Monolayer Stereocomplexation Process

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ABSTRACT: Characteristics of the stereocomplexation process in mixed monolayers of isotactic and syndiotactic poly(methyl methacrylate) (i- and s-PMMA), as introduced in the preceding paper in this series, are addressed. The surprising shift of the stereocomplexation transition to lower surface pressures upon raising the temperature appears to be caused by dominating effects of the segmental mobility. The observation that, in many cases, an incomplete conversion is attained can be attributed to the combination of a limited mutual accessibility of the components in the monolayer, caused by chain segregation effects in the pseudo-two-dimensional system formed and immobilization effects that may become operative upon compression. Especially when using higher molecular weight samples, the effect of this limited extent of mixing appears to be a strongly limiting factor. The kinetics of the monolayer process suggest the existence of a lamellar growth regime only at low surface pressures and high temperatures, similar to mechanisms suggested for solution and melt mixtures. In general, the length of the complexed sections formed during the monolayer stereocomplexation process appears to be (much) shorter than that of the helical structures formed in monolayer crystallized i-PMMA. Attempts to spread preformed stereocomplexes from a solution in a complexing solvent were not successful.

Introduction

In the preceding publication in this series,[1] we established the possibility to induce stereocomplexation processes in mixed monolayers of isotactic and syndiotactic poly(methyl methacrylate) (i- and s-PMMA). This stereocomplexation process, taking place under the influence of the surface pressure buildup upon compression, appeared to be strongly analogous to the crystallization process observed in monolayers of i-PMMA:[2,3] in both cases, double-helical structures were formed, lying flat at the air–water interface. The previous paper dealt with the identification of the process, its stoichiometry, the dependence on the tacticity of the components, and the characteristics of multilayers built from these stereocomplex monolayers: in this paper, we will more specifically address the characteristics of the monolayer process itself.

The characteristics of the stereocomplexation process in solution and bulk mixtures have been the subject of extensive research efforts over the last 25 years and are complicated by an overlap of complexation, aggregation, and crystallization processes.[4,5] It is interesting to try and establish in what respect the monolayer stereocomplexation behavior is analogous to these three-dimensional processes on one side and the monolayer crystallization process of i-PMMA on the other side and in which respects these processes differ.

A final parameter that will be addressed in this paper is the spreading solvent: PMMA mixtures spread from complexing solvents may well behave differently compared to monolayers spread from solutions in noncomplexing solvents like chloroform.

Experimental Section

The apparatus and procedures used to monitor the monolayer behavior of the PMMA mixtures were described in ref 2. If not explicitly mentioned, a standard compression speed of 2 Å^2/monomeric unit (mmu)·min was used. Table I lists the sample characteristics of the materials used in the experiments reported in this paper. Synthesis procedures were addressed in ref 2. All polymers were spread from chloroform solutions, unless stated otherwise.

Table I

material	tacticity i	tacticity h	tacticity s	$\bar{M}_n$, ×10^{-3}	D
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
m17	95	5		7.8	1.23
m18	96	4		7.0	1.14
m20	90	7	3	4.0	1.20
m21	89	8	3	2.8	1.35
m33	3	33	64	18	1.15
m41	2	8	90	11	1.22
m42	1	4	95	9.0	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

Results and Discussion

Temperature Dependence. In the previous publication,[1] it was shown that the anomalous transition that can be observed in monolayer isotherms of mixtures of (fairly low molecular weight) s- and i-PMMA can be attributed to the formation of stereocomplex structures. The temperature dependence of this stereocomplexation process was already shortly indicated.[1] In Figure 1, isotherms are given for the mixed monolayers at temperatures ranging from 10 to 45 °C. Evident from these compression isotherms is that (1) at higher temperatures, the onset of the stereocomplexation transition can be observed at lower surface pressures and (2) at lower temperatures, the conversion of the stereocomplexation process upon compression appears to be lower than at higher temperatures.

Stabilization experiments (stabilization surface pressure 12 mN/m; Figure 2) also suggest an incomplete limiting conversion for these low-temperature experiments, when

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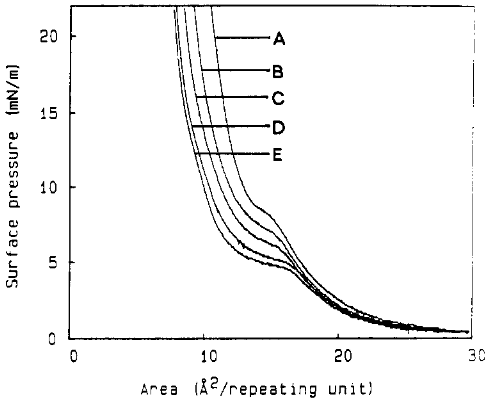

Figure 1. Pressure–area isotherms of a 2:1 mixture of s-PMMA m42 and i-PMMA m13. Compression speed 2 Å²/mmu·min, T = 10 °C (A), 22 °C (B), 30 °C (C), 38 °C (D), and 45 °C (E).

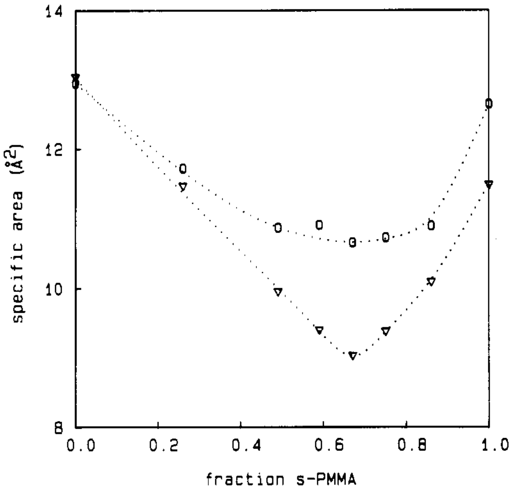

Figure 2. Specific area upon stabilization at 12 mN/m for mixtures of s-PMMA m42 and i-PMMA m13, as a function of composition. Compression speed 1.5 Å²/mmu·min, T = 22 °C (○) and 45 °C (▽).

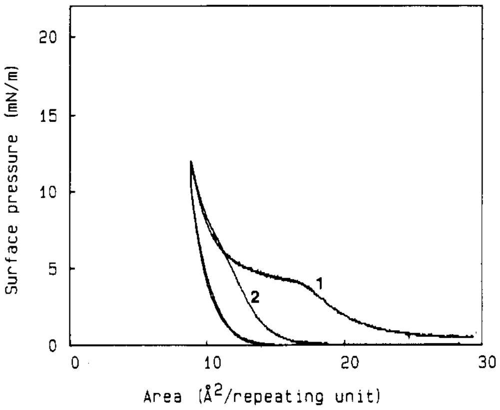

Figure 3. Hysteresis isotherms for a 2:1 mixture of s-PMMA m42 and i-PMMA m13. Compression speed 1 Å²/mmu·min, T = 45 °C: (1) first and (2) second hysteresis cycles.

compared to experiments performed at higher temperatures. Even at 22 °C, the monolayers stabilize within 1 h; the minimum observed in the limiting area as a function of the composition of the monolayer is less pronounced than at 45 °C but is still clearly located asymmetrically with respect to both components, at the syndiotactic-rich side, in accordance with the proposed 2:1 (s–i) stoichiometry.[1,6]

The lowering of the transition surface pressure with increasing temperatures, as observed in the isotherms, is opposite to the effect observed for the monolayer crystallization of i-PMMA,[2] in which similar double-helical structures are formed, and opposite to what might be expected for this complexation process: one would anticipate a negative complexation entropy. Although it is not impossible that, at higher temperatures, the noncomplexed condition of the mixed monolayer has a relatively higher free energy than at lower temperatures. Another explanation may be that, especially at lower temperatures, the transition ("crystallization") rate is to a large extent controlled by the mobility of the segments and thus by a transport term rather than by the free energy gain upon complexation. Stereocomplexation at low surface pressures can be thermodynamically more favorable at lower temperatures, but the segmental mobility may be too low for a reasonable rate of complexation to be observed in the monolayer. This situation is analogous to a melt complexation or crystallization process at low temperatures: in this regime, the rate is also dominated by the segmental transport process, leading to higher conversion rates with increasing temperatures. The difference with the i-PMMA monolayer crystallization process may be caused by the condensed character of the s-PMMA component involved and the accompanying lower mobility.

Hysteresis. Hysteresis experiments on a 2:1 monolayer mixture of s- and i-PMMA indicate that the stereocomplexation is, to a large extent, not reversible: upon decompression, the surface pressure rapidly falls to zero, and upon recompressing the layer after a decompression up to 40 Å²/mmu, the isotherm strongly deviates from the original compression isotherm in the region before stereocomplexation takes place: evidently, even at zero surface pressure, the stereocomplex structures did not completely decompose (Figure 3). At higher surface pressures (beyond the stereocomplexation transition), the recompressed film occupies a similar area as in the first run, indicating that no irreversible three-dimensional collapse has occurred. The transition observed upon compression clearly does not reflect thermodynamic equilibrium and can indeed be controlled by the segmental mobility, as was suggested in the previous paragraph. This behavior, of complexed structures not "melting" at surface pressures comparable to the pressure at which they were formed, is analogous to the hysteresis phenomena observed in the monolayer crystallization process of i-PMMA and, e.g., to stereocomplexation phenomena in the melt, the complexed structures melting at higher temperatures than the complexation temperature: the complexation process behaves as a one-dimensional crystallization.[4]

Performing the same experiments with i-PMMA m29 (66% isotactic triads), instead of the sample of high stereoregularity, also leads to an incomplete decomplexation upon decompression, although the second compression isotherm follows the original isotherm closer than in the case of the mixture based on the highly isotactic sample. A mixture of highly isotactic PMMA (m13) with a conventional atactic poly(methyl methacrylate) (a-PMMA) sample (m33, 64% syndiotactic triads) also exhibits a large hysteresis cycle, but, in this case, complete decomplexation is attained at zero pressure: upon recompression, the isotherm follows an identical curve as the first compression isotherm (Figure 4). The less perfect stereoregularity evidently lowers the stability of the stereocomplexes formed.

Figure 5 shows the results of an experiment, performing several hysteresis cycles on the same monolayer at 22 °C. We see that, in the first compression run, the stereocomplexation only reaches a low conversion: subsequent stabilization at 12 mN/m does not lead to a much higher

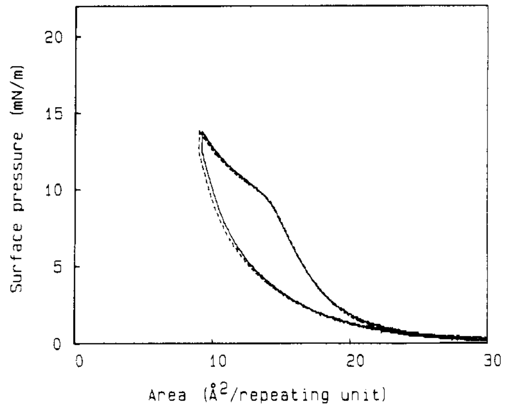

Figure 4. Hysteresis isotherms of a 2:1 mixture of a-PMMA m33 and i-PMMA m13. Compression speed 2 Å²/mmu·min, T = 45 °C: first cycle (solid line); second cycle (dashed line).

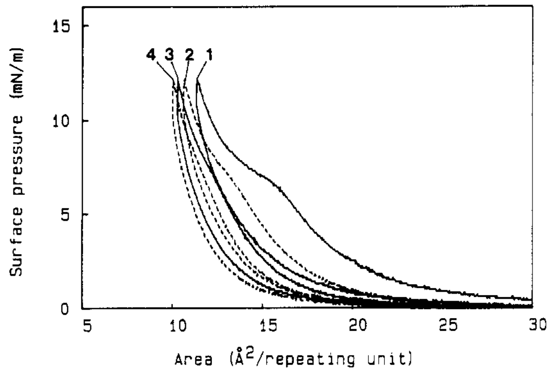

Figure 5. Four subsequent hysteresis isotherms for a 2:1 mixture of s-PMMA m42 and i-PMMA m13. Compression speed 2 Å²/mmu·min, T = 22 °C. Subsequent cycles are alternatingly shown by solid and dashed lines.

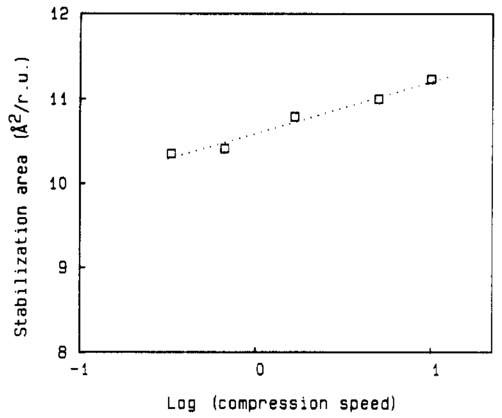

Figure 6. Specific area upon stabilization at 12 mN/m as a function of compression speed (in Å²/mmu·min) for a 2:1 mixture of s-PMMA m42 and i-PMMA m13. T = 22 °C.

conversion. Upon decompression, we see that also, at this lower temperature, the stereocomplex structures do not melt. In the second compression run, the monolayer attains a higher limiting conversion than in the first run. This process can be repeated a number of times, each new cycle leading to a slightly higher conversion. For experiments up to seven cycles, conversions were eventually reached approaching that of a 45 °C compression experiment.

Conversion versus Compression Speed. In Figure 6, the results are shown for stabilization experiments at 22 °C and 12 mN/m, as a function of the initial compression speed. Irrespective of the compression speed, the monolayers completely stabilize at 12 mN/m within 1 h, but the specific area attained is a function of this compression speed: for higher compression speeds a higher limiting area is found, indicating a lower conversion.

For the interpretation of the limited conversions attained when performing the experiments at low temperatures and the variation of this limiting conversion in repetitive hysteresis cycles, or with the applied compression speed, let us first consider the nature of the mixed monolayer.

In ref 2, we discussed the completely different behavior of the two stereoregular forms of PMMA at low surface concentrations (submonolayer coverage). i-PMMA experiences "good solvent conditions" in the monolayer, characterized by only weak cohesive forces between the segments, a phenomenon which we attributed to the spatial orientation of the ester groups with respect to the backbone and the air–water interface.[2] Monolayers of s-PMMA, on the contrary, are characterized by strong intersegment interactions, leading to a two-dimensional sub-Θ or collapsed conformation for the polymer chains.[7] What can we expect for mixtures of these polymers at the air–water interface?

Polymers in monolayers at the air–water interface can be considered as forming a (pseudo-)two-dimensional system, if the interaction of the segments with this interface is so strong as to allow very few defects (as polymer chain crossovers and in general any significant looping either into the water phase or into a "bulk" phase not in contact with the air–water interface). For PMMA, being insoluble in water and having a fairly good amphiphilic interaction with the interface, this assumption probably holds for low surface concentrations (low surface pressures). In athermal two-dimensional polymer systems, de Gennes[8] already predicted that due to dominating excluded-volume effects the individual polymer chains will tend to *segregate*, instead of interpenetrating as in three dimensions. This prediction was later confirmed in several Monte Carlo simulation studies.[9] In two-dimensional mixtures of polymers, similar segregation phenomena can be expected, unless a very favorable χ parameter for mixing is chosen; in this case (in combination with rather low molecular weights), interpenetration is predicted to occur.[10]

For the actual mixture under consideration, i- and s-PMMA, a segregation of the chains should therefore be anticipated, unless the interactions between the isotactic and syndiotactic segment sequences would be very favorable, an assumption for which there is no a priori justification. This tendency for segregation becomes even more probable, if we take into account the fact that, upon spreading the polymers at low surface concentrations, we are in fact dealing with a *ternary* system, with the empty surface sites (not occupied by segments of either component) acting as solvent molecules from a thermodynamic point of view. These surface sites act as a good "solvent" for the two-dimensional i-PMMA chains and as a sub-Θ solvent for s-PMMA (as illustrated by the negative second virial coefficient observed[7]); clearly, under these low surface concentration conditions, the propensity for segregation of the i- and s-PMMA chains may be even stronger: the isotactic and the syndiotactic components cannot be expected to be intimately mixed at the monomeric unit level.

Stereocomplexation obviously requires the proximity of an isotactic strand and a syndiotactic strand: in a chain-segregated monolayer, not all parts of the chains will actually have neighbors of the complementary polymer. For a high conversion to be attained, it is necessary that reorganizations can occur during the stereocomplexation process, so that the parts of the chains initially "hidden" from contact become exposed. At high temperatures, it appears that this can be done effectively: at low temperatures, the monolayer phases appear to be somehow *immobilized* during the stereocomplexation process, and, at some point, extensive reorganizations evidently become prohibited.

Considering the free energy change upon formation of a complexed section

$$\Delta G_{\text{complex}} = \Delta G_{\text{init}} + N(\Delta U_{\text{complex}} - T\Delta S_{\text{complex}} + \Pi \Delta A_{\text{complex}})$$

the first term representing unfavorable contributions from, e.g., an initial loss of conformational or translational entropy and the "surface free energy" associated with the end of the helical sequences, we see that there will be a critical complexation length, involving N segments, with the value for N depending on the complexation conditions. For conditions under which the free energy gain pro length of the complexed sections is high (e.g., at high surface pressures), complexation can be limited to many isolated short sequences. Such a high concentration of short links in a monolayer can be imagined to effectively immobilize the system, much more rapidly than in a situation where a lower concentration of more extensively complexed sections is formed. Complexation at low temperatures takes place at higher surface pressures than complexation at higher temperatures, leading to a higher concentration of shorter sequences and consequently to a stronger immobilizing effect, effectively prohibiting monolayer reorganizations. Similar immobilization effects were also suggested by Schomaker[11] for the stereocomplexation process in melt mixtures of i- and s-PMMA at low complexation temperatures (a situation also characterized by low mobilities combined with a high thermodynamic driving force). Monolayer reorganizations may also be hindered at higher surface pressures by the smaller fraction of free area available.

The enhanced conversion that can be reached when performing multiple hysteresis cycles (as shown in Figure 5) may be explained in terms of parts of the polymer chains being locked in during the first compression run. Upon decompression, the immobilization constraints may be partially lifted: the larger available area allows for some reorganizations, leading to fresh areas of contact between noncomplexed parts of the syndiotactic and isotactic chains that were locked in during the first compression run. Consequently, a higher conversion can be reached during the second compression run, a process that can be repeated several times, leading to high conversions. The effect of the compression speed of the limiting conversion can also be understood: as was illustrated in ref 1, the transition surface pressure associated with the stereocomplexation process strongly depends on the compression speed; in monolayers compressed rapidly, the surface pressure is higher, leading to a higher concentration of short complexed sections and a more rapid immobilization of the chains in the monolayer than in monolayers being compressed slowly, which may reach a higher conversion.

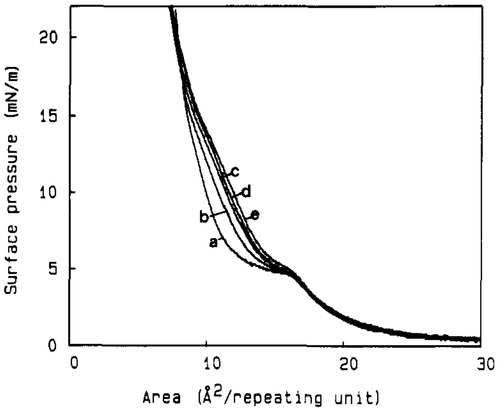

Figure 7. Pressure–area isotherms for 2:1 mixtures of s-PMMA m42 and i-PMMA m13, $\bar{M}_n$ 13K (a), m11, 21K (b), m8, 36K (c), m5, 95K (d), m2, 770K (e). Compression speed 2 Å²/mmu·min, T = 45 °C.

Molecular Weight Effects. High Molecular Weights. In Figure 7, isotherms are reported for a series of 2:1 mixtures of s-PMMA m42 and i-PMMA samples with molecular weights ($\bar{M}_n$) varying from 13K to 770K. The molecular weight has a strong influence on the shape of the isotherms. In all cases the onset of the stereocomplexation can be detected at approximately the same surface pressure, but the efficiency of the transition process following this onset is clearly different: high molecular weights only attain a rather low limiting conversion upon compression, compared to the low molecular weight materials. For these mixtures based on high molecular weight samples, a clear dependence of the conversion on the compression speed is found during stabilization experiments.

At first sight, it may be argued that higher molecular weights lower the overall mobility of the chains and that an increased viscosity is thus responsible for the lower conversion rates. This argument is probably not valid though. In the monolayer crystallization of i-PMMA, we observed that high molecular weights did not significantly limit the crystallization rate, in contrast to the crystallization process in the melt,[2,12] which can be rationalized through the absence of entanglements in the monolayer. The crystallization rate was mainly determined by the local segmental mobility, even though lamellar structures are probably being formed, requiring some kind of "reeling in" process of the chains. Stereocomplexation processes in the melt exhibit an effect of the molecular weight only in the regime where lamellar type crystallites are being formed (i.e., high complexation temperatures); at low temperatures, resulting in only short complexed sections, even in the melt no significant effect of the molecular weight was observed. Schomaker[11] explained this by a "kink-nucleated" mechanism in which two chains can form a double helix (or actually simultaneously two helical structures) without requiring the involvement of a chain end and without requiring extensive chain motions. Such a process is also easily conceivable for the monolayer process. If we consider these facts, it appears unlikely that the molecular weight of i-PMMA would directly influence the segmental mobility in the monolayer, especially since the conditions under which the stereocomplexation takes place as reported in Figure 7 imply fairly short complexed sequences being formed, with these conditions being beyond a possible lamellar growth regime (as will be discussed later on).

A more likely candidate for the actual cause of the conversion limitation in the mixtures with high molecular weight i-PMMA is probably the tendency for *chain segregation* suggested for these monolayer mixtures. For such segregated chains, a higher molecular weight will lead to larger domains, with relatively less contacts between isotactic and syndiotactic strands and less possibilities for extensive reorganizations. This implies that the stereocomplexation process will be less effective and will lead to large parts of the chains locked in upon immobilization of the system. This is in agreement with the pronounced

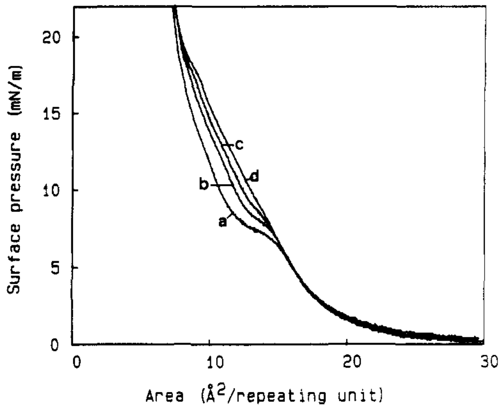

Figure 8. Pressure–area isotherms of 1:2 mixtures of i-PMMA m13 and s-PMMA m48, $\bar{M}_n$ 18K (a), m47, 25K (b), m46, 32K (c), and m45, 46K (d). Compression speed 2 Å²/mmu·min, $T = 45$ °C.

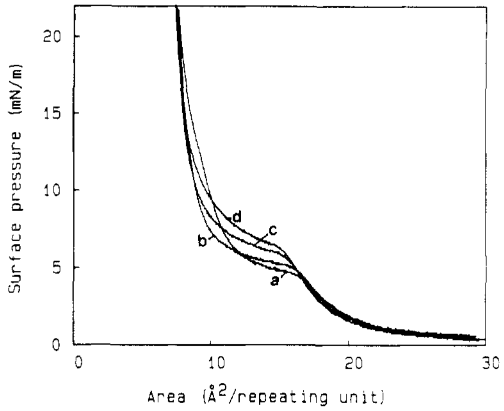

Figure 9. Pressure–area isotherms of a 2:1 mixture of s-PMMA m42 and i-PMMA m13, $\bar{M}_n$ 13K (a), m18, 7K (b), m20, 4K (c), and m21, 2.8K (d). Compression speed 2 Å²/mmu·min, $T = 45$ °C.

effect of the compression speed on the limiting conversion and the observation that repetitive hysteresis cycles can lead to significantly higher conversions. The problem associated with the high molecular weights may not be an intrinsic problem in the formation of the double-helical structures involving a high molecular weight polymer strand but may be related to the *phase behavior* and the chain segregation phenomena in the monolayer.

In Figure 8, isotherms are shown for mixtures of (low molecular weight) i-PMMA with a series of narrow molecular weight fractions of s-PMMA with similar tacticities. Raising the molecular weight of the s-PMMA again leads to a suppression of the rate of stereocomplexation, with the onset pressure of the process remaining approximately invariant, indicating that the thermodynamic driving force is not significantly different. As for high molecular weight i-PMMA samples, the cause for the observed effects may be found in the limited accessibility of the chains in a chain-segregated mixture and the resulting low number of s–i interchain contacts. The effect of the molecular weight of the syndiotactic component is even more dramatic than that of the isotactic component: a molecular weight of 46K results in an almost complete suppression of the stereocomplexation, whereas, for molecular weights for the i-PMMA of up to 1 million, the effects of the onset of stereocomplexation can still clearly be seen in the isotherms. We will discuss these phenomena more extensively in another publication.[13]

Molecular Weight Effects. Low Molecular Weights. Studying monolayers of i-PMMA, we observed that low molecular weight materials exhibited a suppression of the crystallization process, which was attributed to *critical chain length* effects: if a chain can only form short helical sequences, the contribution of the initial loss in free energy upon formation of these structures becomes an important factor. The negative effects were already observable in the isotherms for molecular weights under approximately 25 000, depending on the conditions used. The stereocomplexation process may be subject to similar critical chain length effects.[14,15]

Figure 9 gives the compression isotherms for mixtures of s-PMMA with i-PMMA of various low molecular weights. Indeed, we see that, upon lowering the molecular weight under 10 000, the surface pressure associated with the stereocomplexation increases: apparently, for lower molecular weights, a higher $\Pi\Delta A$ contribution is required to compensate for the relatively higher contribution of the initial entropy loss term. The lowest molecular weight samples used have a somewhat lower stereoregularity (Table I); still, when comparing the effects observed with effects due to a less perfect isotacticity,[1] it is clear that the low molecular weight must play an additional role in raising the transition surface pressure. In all cases, stereocomplexation is observed up to high conversions, indicating that at these higher surface pressures the process is no longer hindered by critical chain length effects, with only very short complexed sequences being formed, short relative to the length of the chains.

The results of these experiments indicate that the critical chain length effects are less pronounced than in the monolayer crystallization of i-PMMA, due to a lower complexation length required to give stable stereocomplex structures.

Monolayer Stereocomplexation Kinetics. In order to obtain information about the growth mechanism of the stereocomplex structures, isobaric stabilization experiments were performed both at 22 °C and at 45 °C.

At 45 °C, attempts to stabilize a mixed monolayer at pressures clearly under the transition pressure observed in the compression isotherms fail: even at low pressure (e.g., 2 mN/m), the monolayer appears to exhibit a very slow stereocomplexation. At these low surface pressures (<3.0 mN/m), the stabilization plot shows some curvature, with the transition rate accelerating somewhat with time (Figure 10a): a similar *autoaccelerating* character (only much clearer) was found for the monolayer crystallization of i-PMMA.[2] For the monolayer stereocomplexation process, we are in the regime of a low thermodynamic driving force, probably requiring a *lamellar type growth*, similar to the melt behavior at high complexation temperatures.[11] These lamellar structures grow only after a nucleation stage, responsible for the induction period: similar induction periods are found in melt stereocomplexation processes under lamellar growth conditions.[11] The autoaccelerating nature is less pronounced than in the monolayer crystallization behavior of i-PMMA; for the stereocomplexation process, there may be a significant contribution of newly formed complexes to the overall conversion rate, instead of a clear dominance of structures growing from a stable nucleus. Moreover, diffusion processes may also be rate determining with respect to the growth of stereocomplex nuclei.

At higher surface pressures, the behavior changes into a linear growth in the initial stages of the process, with only a slowing down observed at higher conversions, as in a simple first-order process. At these higher surface pressures, we are probably no longer dealing with a strong contribution of growing lamellar structures but instead

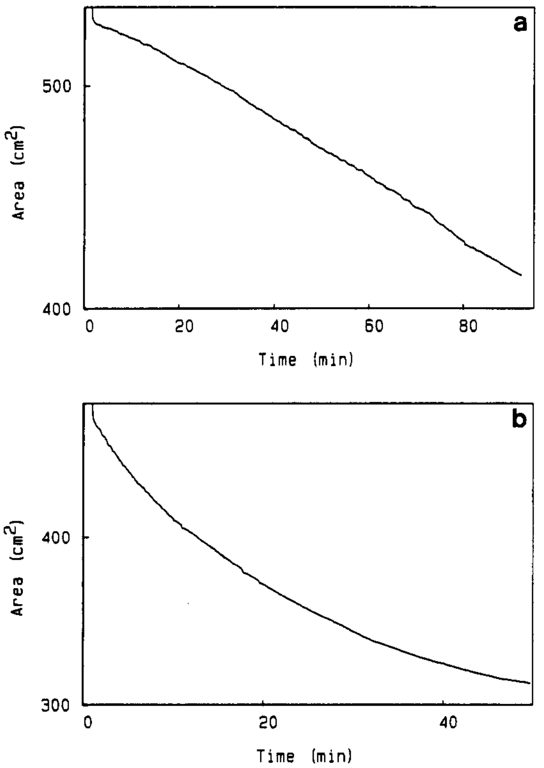

Figure 10. Isobaric stabilization plots for a 2:1 mixture of s-PMMA m42 and i-PMMA m13, T = 45 °C, Π = 2.7 mN/m (a) and 4.0 mN/m (b).

only with isolated short complexed sequences being formed, the rate of formation of these sequences being simply proportional to the amount of noncomplexed material (Figure 10b).

At 22 °C, isobaric stabilization experiments have to be carried out at significantly higher surface pressures in order to observe any stereocomplexation at all. Even at the lowest surface pressures used (and for very slow transition rates, comparable to the lowest studied at 45 °C), only linear conversion plots were found in the initial stages of the process: evidently, we are already operating beyond the regime of the autoaccelerating lamellar growth mechanism. This is another indication that the higher surface pressure required for stereocomplexation at lower temperatures has its origin in a limited segmental mobility rather than being related to a lower free energy of complexation.

The results reported so far indicate that the tendency of the mixed monolayers to form extensive lamellar stereocomplex structures is not as strong as that observed in the monolayer crystallization process of i-PMMA. Multilayers built from monolayers that were complexed at low surface pressure (approximately 3 mN/m) did not exhibit an orientation of the complex helices perpendicular to the dipping direction, as was observed for monolayers of i-PMMA crystallized under analogous conditions.[1,3] In the latter case, this phenomenon was attributed to the presence of extensive rigid lamellar type structures, which are probably not formed to a similar extent in the monolayer stereocomplexation process (even under the conditions used). Also in the corresponding melt processes, the lamellar structures observed for the stereocomplexation are limited to much smaller dimensions than in the crystallization of i-PMMA.[4,16]

Stability of the Monolayer Stereocomplexes. In ref 2, we discussed the effect of the crystallization surface pressure on the stability of crystallites of i-PMMA upon decompression. The results indicated that more stable crystallites were formed when the crystallization process was carried out under more subtle conditions (lower surface pressures). For the stereocomplexation process, similar effects can be expected: structures formed at low surface pressures and consisting of relatively large complexed sections can be anticipated to be more stable than the short complexed sequences formed at higher surface pressures. This effect is demonstrated in Figure 11, which shows isotherms recorded after a stabilization experiment was performed at low pressure (3.0 mN/m) with subsequent compression to 12 mN/m and after a stabilization experiment in which the monolayer was immediately compressed to 12 mN/m. In both cases, following stabilization at 12 mN/m, the monolayers were decompressed: the subsequent compression isotherms are shown. We can see that the complexes formed in the monolayer in which stereocomplexation took place at low surface pressures are more stable than those in the monolayer in which complexation occurred at higher surface pressures: in the latter case, a larger fraction of stereocomplex structures "melted" upon decompression. The limiting conversion in the first case was slightly higher but not enough to account for the difference observed in Figure 11.

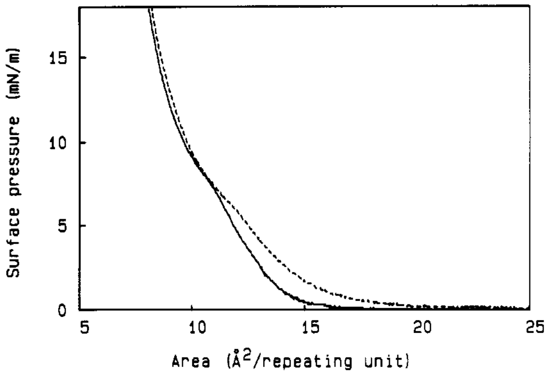

Figure 11. Pressure-area isotherms of a 2:1 mixture of s-PMMA m42 and i-PMMA m13, after complete decompression following stabilization at 3 mN/m (with subsequent compression of 12 mN/m) (solid line) and at 12 mN/m (compression speed 4 Å²/mmu·min) (dashed line). T = 45 °C, compression speed 2 Å²/mmu·min.

The stability of the stereocomplexes upon decompression can also give us information about the thermodynamic stability of the complexes at different temperatures. As already mentioned, the stereocomplexation process itself is probably strongly affected by kinetic factors, and information about the thermodynamic stability cannot easily be extracted directly from the compression isotherms. In order to study the decomplexation behavior, we first compressed the monolayers under identical conditions at 45 °C, so as to ensure an equal formation history of the complexes, and decompressed the monolayer either at 45 °C or after cooling to 22 °C during the 45-min pause time. For this experiment, a mixture of isotactic PMMA and conventional PMMA was used, which completely decomplexates upon decompression. The decompression isotherm exhibits a much steeper fall upon decompression at lower temperatures (Figure 12), suggesting a somewhat higher stability of these stereocomplexes at low temperatures. Still, also at these temperatures, complete decomplexation is attained, as is confirmed by a subsequent compression run.

Spreading from Complexing Solvents. Up to now, we only discussed the monolayer behavior of mixed monolayers of PMMA, spread from solutions in chloroform, a noncomplexing solvent. The observation that stereocomplexes formed in the monolayer can be stable at zero

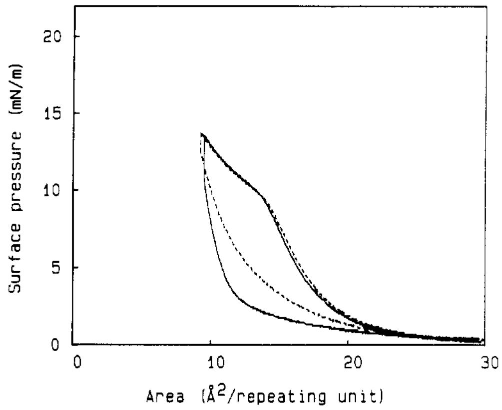

Figure 12. Hysteresis isotherms of a 2:1 mixture of a-PMMA m33 and i-PMMA m17. Compression speed 2 Å²/mmu·min, T = 45 °C. Pause time 45 min. Decompression speed 2 Å²/mmu·min. Dashed line: decompression at 45 °C. Solid line: decompression at 22 °C, after cooling down during pause time.

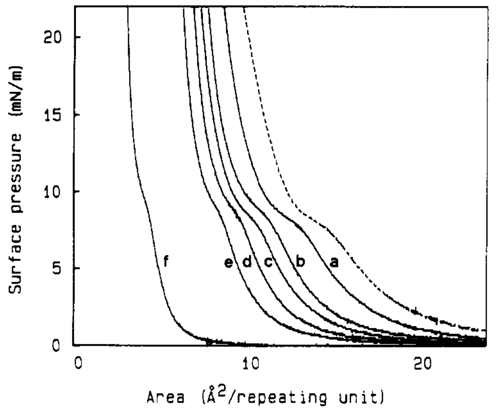

Figure 13. Pressure–area isotherms of a 2:1 mixture of s-PMMA m41 and i-PMMA m13, spread from toluene solution, as a function of the complexation time in solution: (a) 30 min; (b) 14 h; (c) 4 days; (d) 7 days; (e) 20 days; (f) 4 months. The dashed line represents an isotherm of a similar mixture spread from chloroform solution.

surface pressure appears to offer the possibility of spreading preformed stereocomplexes from a complexing solvent. In order to test the feasibility of directly spreading stereocomplex monolayers, we used a solution of i-PMMA m13 and s-PMMA m41 (ratio 1:2) in toluene. Toluene is a solvent that is classified as intermediate between type A and type B, strongly and weakly complexing solvents, respectively.[5] Spreading of the solutions of the individual components in toluene yields isotherms identical to those obtained by spreading from chloroform solutions. In Figure 13, isotherms are shown of monolayers spread from this solution, stored for various times at room temperature after heating to 100 °C (in order to start from a noncomplexed solution). An isotherm of the same components spread from chloroform solution is given for reference. It is evident from the isotherms that the state of aggregation in the solvent strongly affects the monolayer behavior. It is also clear that, upon progress of the stereocomplexation process in solution, incomplete spreading is observed: spreading does not result in well-defined monolayers of stereocomplex structures. Evidently, in toluene solution, three-dimensional aggregates are formed that are stable at the air–water interface and do not spread to form a monolayer. Solutions in benzene exhibit a similar behavior.

Conclusions

The temperature dependence of the monolayer stereocomplexation process (a lowering of the transition pressure at higher temperatures) appears to be attributable to the dominating effects of the segmental mobility in the monolayer. An important and characteristic feature of the stereocomplexation process in the monolayer is the fact that the components are probably not intimately mixed at the monomeric segment level, due to a tendency for chain segregation that can be anticipated based on the (pseudo)-two-dimensional character of the monolayer. This segregation makes the stereocomplexation process very susceptible to immobilization effects, which become effective at higher surface pressures. This latter interpretation can also explain the limiting effect of high molecular weights on the conversion that is attained.

The rate of the stereocomplexation process is strongly dependent on the surface pressure. At relatively high surface pressures, initially linear conversion curves indicate a mechanism of isolated small complexed sections being formed, whereas at low surface pressures at high temperatures, a tendency for autoacceleration appears to suggest a significant contribution of growing lamellar structures. In general, the monolayer stereocomplexation behavior is analogous to that of the mixtures in the melt.

The monolayer stereocomplex process is not reversible: stereocomplex structures formed do not melt upon decompression. Attempts to spread monolayers of preformed stereocomplex structures from complexing solvents failed due to the fact that the three-dimensional aggregates present in the spreading solution evidently did not decompose to form a monolayer.

References and Notes

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Registry No. i-PMMA (homopolymer), 25188-98-1; s-PMMA (homopolymer), 25188-97-0.