# Thin-Film Behavior of Poly(methyl methacrylates). 4. Stereocomplexation of Isotactic and Syndiotactic Poly(methyl methacrylate) at the Air–Water Interface

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ABSTRACT: Under the proper conditions, a transition can be observed in compression isotherms of mixed monolayers of isotactic and syndiotactic poly(methyl methacrylate), which is shown to correspond to a pressure-induced stereocomplexation process between the isotactic and syndiotactic components, analogous to similar processes in solution or melt mixtures. The identity of the double-helical stereocomplex structures is confirmed by the distinct 2:1 (s–i) segmental stoichiometry observed, the dependence of the process on the stereoregularity of the components, and the infrared characteristics of transferred multilayers. The monolayer stereocomplex structures can be transferred to solid substrates to yield almost uniaxially oriented thin films. Following annealing treatments, these films were shown to possess melting points close to 190 °C.

## Introduction

In previous publications of this series,[1-3] we extensively discussed the rapid crystallization process that can take place in monolayers of isotactic poly(methyl methacrylate) (i-PMMA) at the air–water interface upon compression and the possibilities to use these crystallized monolayers to build highly oriented crystalline thin films of this material. Bearing in mind that this transition involves the formation of double-helical structures, the question arises whether it is possible to induce an analogous process in monolayers of mixtures of isotactic and syndiotactic (s-PMMA) poly(methyl methacrylate) to form *stereocomplexes* (another example of a double-helix structure) through a similar monolayer compression.

Stereocomplexation is known to take place in mixtures of i- and s-PMMA in the melt and in solution and has been the subject of research for more than 25 years.[4-6] The PMMA stereocomplexes are now believed to consist of double-helical structures, with a syndiotactic strand winding around an isotactic strand, the stoichiometry being 2:1 (s–i) at the monomeric unit level.[7,8] On the basis of the structures proposed for the stereocomplex,[8,9] the stereocomplexes can be anticipated to occupy a smaller area, lying flat on the water surface, than a simple additive mixture of s- and i-PMMA in their "normal" interface conformations, so that a favorable $\Pi\Delta A$ contribution to the free energy of the formation of such a structure can be expected upon surface pressure buildup, as was the case for the crystallization of i-PMMA.

A stereocomplexation process analogous to the i-PMMA monolayer crystallization with the possibility of building thin films of these structures would be interesting for various reasons. The melting range of PMMA stereocomplexes can extend up to temperatures over 200 °C, so that structures with a very high thermal stability could possibly be built. Compared to i-PMMA, the crystalline stereocomplex structures are known to be organized in rather small crystallites,[6,9,10] which would cause less light scattering than the more extensive lamellar structures in crystalline i-PMMA (important with respect to optical applications). The solubility characteristics of the stereocomplexes are also different from those of the individual components, this solubility being relevant with respect to applications of PMMA as a resist material in micro- or nanolithography.[11,12]

Next to these features associated with thin stereocomplex films on solid substrates, the monolayer behavior itself may be very interesting from a more academic point of view: information may be obtained specifically pertaining to the phase behavior in the monolayer, which in this case can be considered as a two-dimensional polymer mixture. The phase behavior of polymer mixtures in two dimensions has received quite a lot of interest in recent years, especially from a theoretical point of view, because of the strong excluded-volume effects, which are, e.g., predicted to result in a segregation of the individual polymer chains in an athermal mixture.[13]

In this paper, we present some results of our quest to prepare PMMA stereocomplex structures at the air–water interface and to use them to prepare an ordered thin film with a high thermal stability.

## Experimental Section

The characteristics of the materials used for the experiments reported in this paper are listed in Table I. Synthesis procedures were described in ref 1; the s-PMMA samples m41 and m42 were prepared through a living anionic polymerization in toluene at −90 °C, using a tBuLi/triethylaluminum initiator system (m41) or a tBuLi/tri-*n*-octylaluminum initiator system (m42).[14] The apparatus and experimental routines used for the recording of the pressure–area isotherms and the thin-film infrared spectra are described elsewhere.[1] Spreading was done from approximately 0.3 g/L solutions of the pure components or their mixtures in chloroform, chloroform being a noncomplexing solvent for i- and s-PMMA mixtures,[5] implying that no preformed stereocomplex structures are present in the spreading solution. Unless stated otherwise, a compression speed of 2 Å$^2$/monomeric unit (mmu)·min was used.

Surface potential measurements were performed at the Max Planck Institut für Biophysikalische Chemie, Göttingen, BRD, in collaboration with Professor D. Möbius, with simultaneous monitoring of the surface pressure using a Wilhelmy plate technique: the apparatus is described elsewhere.[15]

## Results and Discussion

The monolayer behavior of i- and s-PMMA was discussed in a previous publication.[1] i-PMMA experiences "good solvent" conditions and forms an expanded type monolayer, whereas s-PMMA forms a condensed monolayer, a difference that was attributed to the much higher level of the lateral cohesive interactions between the

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Table I

| material | tacticity i | tacticity h | tacticity s | $\bar{M}_n$, $\times 10^{-3}$ | $D$ |
|---|---|---|---|---|---|
| m6 | >97 | | | 63 | 1.30 |
| m13 | >97 | | | 13 | 1.19 |
| m26 | 81 | 15 | 4 | 18 | 1.13 |
| m29 | 66 | 27 | 7 | 21 | 1.26 |
| m33 | 3 | 33 | 64 | 18 | 1.15 |
| m41 | 2 | 8 | 90 | 11 | 1.22 |
| m42 | 1 | 4 | 95 | 9.0 | 1.20 |
| m44 | 2 | 11 | 87 | 270 | 1.20 |
| m48 | 1 | 13 | 86 | 18 | 1.14 |

segments of the syndiotactic polymer. When spread from a mixed solution, the polymers will form a two-dimensional polymer blend. Unless strong favorable interactions between both components are operative, the polymers cannot be expected to be mixed at the monomeric unit level, due to a tendency of the two-dimensional chains to segregate.[13] Especially at low surface concentrations, this effect may be enhanced by the fact that the isotactic component experiences good solvent conditions in contrast to the condensed syndiotactic chains. It is even conceivable that a macroscopic phase separation takes place in the mixed monolayers. A more elaborate discussion of the complications due to the two-dimensional phase behavior of the monolayer mixtures will be postponed for another publication.[16] In order to minimize possible complications due to these effects, low molecular weight fractions were used for the experiments throughout this paper.

**Compression Isotherms of the Mixed Monolayers.** In Figure 1a, the room-temperature pressure–area isotherms are given for s-PMMA, i-PMMA, and a mixture of these two polymers (base mole ratio 2:1 (s:i); $\bar{M}_n$ 9000 and 13 000, respectively). The compression rate was 2 Å²/mm u·min for the s-PMMA and the s–i mixture and 4 Å²/mmu·min for i-PMMA.[17] The monolayer behavior of the mixture clearly deviates from what would be expected for perfect additivity: a transition can be observed, its onset is at significantly lower surface pressures than the crystallization transition observed in the isotherm of pure i-PMMA, and the area pro monomeric unit in the part of the isotherm directly beyond this transition is significantly lower than that of either of the individual components. At the same time, the original i-PMMA crystallization transition has completely disappeared.

The situation is even clearer when we consider the isotherms of the same samples, but now recorded at 45 °C (Figure 1b). For this temperature, the picture is not complicated by the possibility of monolayer crystallization of i-PMMA, since this is thermodynamically prohibited at this temperature.[1] In the isotherm of the s–i mixture, the same transition can be observed as in the isotherm recorded at 22 °C, and even more clearly so. The apparent onset of the transition has shifted to lower surface pressures, and the plateau region is longer, leading to smaller specific areas and a stronger deviation from the additive value, suggesting a higher "conversion" to the newly formed structure. At both temperatures, the isotherms of the mixture reflect an approximately additive behavior at low surface pressures, preceding the transition region, which is to be expected for a mixture in which the number of intimate i–s segment contacts will be low due to a tendency of the chains to segregate.

**Compression Speed Dependence.** The isotherms of the 2:1 mixture of s- and i-PMMA recorded at 45 °C at various compression speeds are shown in Figure 2. The surface pressure associated with the plateau region of the stereocomplexation process is significantly higher for higher compression speeds. This indicates that we are dealing with a rather slow process, with the transformation rate directly correlated with the surface pressure. A similar effect of the compression speed on the transformation rate was observed for the crystallization process in monolayers of pure i-PMMA.[1]

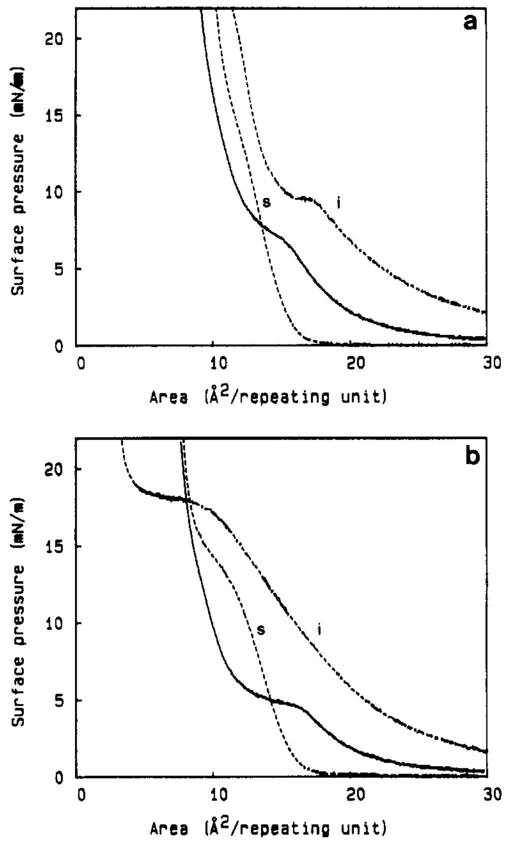

Figure 1. Pressure–area isotherms of i-PMMA (m13, i), s-PMMA (m42, s), and a mixture of the two (s:i = 2:1, solid line): (a) 22 °C; (b) 45 °C.

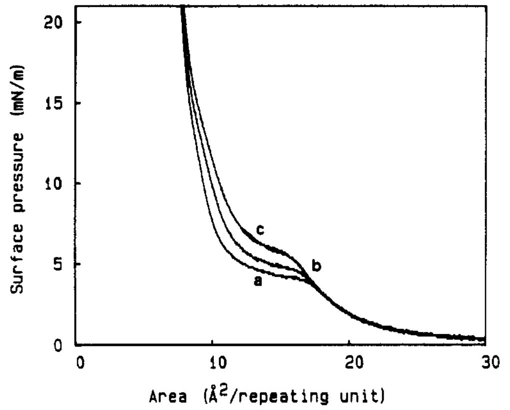

Figure 2. Pressure–area isotherms of a 2:1 mixture of s-PMMA (m42) and i-PMMA (m13). $T$ = 45 °C, compression speed 0.67 (a), 2 (b), 6 (c) Å²/mmu·min.

**Surface Potential Measurements.** Additional information about the monolayer behavior of these mixtures of i- and s-PMMA can be obtained from surface potential measurements. These experiments were performed at 32 °C, because of practical limitations of the apparatus used with respect to operating at higher temperatures. The results are shown in Figure 3. The surface potential at low surface concentrations (corresponding to the regime in the isotherm where the surface pressure exhibits approximately additive behavior) is equal to the value calculated as the weighted average of the individual components, again in agreement with additive behavior due to an absence of a significant amount of s–i segmental

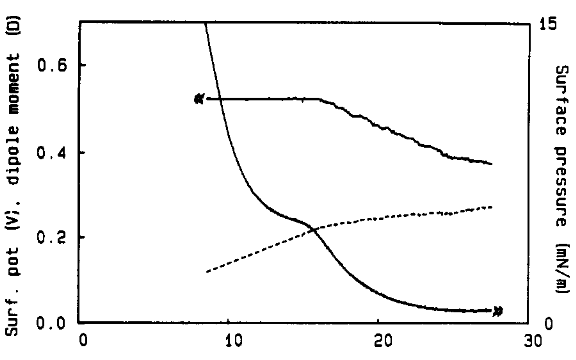

**Figure 3.** Surface potential (solid line), $\mu_\perp$ (dashed line), and surface pressure of a 2:1 mixture of s-PMMA (m42) and i-PMMA (m13). $T$ = 32 °C.

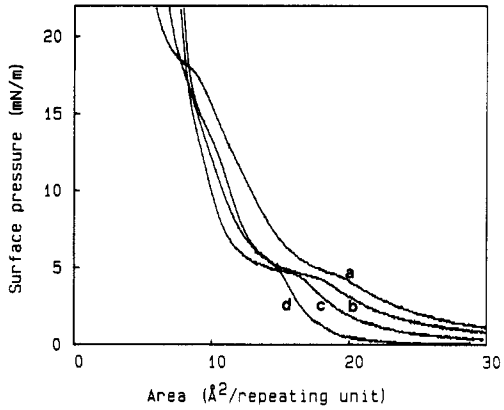

**Figure 4.** Pressure–area isotherms of mixtures of s-PMMA (m42) and i-PMMA (m13). $T$ = 45 °C, compression speed 2 Å$^2$/mmu·min. Fraction of s-PMMA 0.33 (a), 0.5 (b), 0.67 (c), and 0.86 (d).

interactions. The dipole moment projection per monomeric unit $\mu_\perp$, extrapolated to zero surface pressure, is calculated to be 0.26 D, with the values for the individual components being 0.225 and 0.315 D for s- and i-PMMA, respectively.[18]

The surface potential abruptly stops to rise further upon compression, just at the onset of the transition in the isotherm: during the transition, $\mu_\perp$ falls rapidly. This situation is analogous to the rapid fall of the dipole moment observed during the crystallization of i-PMMA, when the initial amphiphilic orientation of the segments is exchanged for a double-helical structure.[1-18] The similarity between the surface potential behavior during the two transition processes suggests that, also for the s–i mixtures, a helix formation (e.g., a stereocomplexation) may be responsible for the monolayer transition observed.

**Stoichiometry.** So far we only discussed the 2:1 (s:i) PMMA mixtures. In Figure 4, isotherms are given for a range of mixing ratios at 45 °C. We can clearly see that the transition, observed before in the 2:1 mixture, is evident for all mixing ratios, except for the pure components. The surface pressure associated with the onset of the transition is independent of the composition; the plateau region appears to be longest for the already discussed 2:1 s–i mixture, which also yields the lowest area pro monomeric unit directly past the transition region. Furthermore, beyond this post-transition region, we no longer see clear indications of the inflection points associated with the collapse of the individual components for this stoichiometry; for other mixing ratios, there is still some evidence of one of these inflection points.

The monolayers can be stabilized in the post transition regime: for a surface pressure of 12 mN/m, approximately 1 h is required for complete stabilization. In Figure 5, the limiting areas upon stabilization at 12 mN/m at 45 °C are plotted as a function of the mixture composition. The specific area exhibits a very distinct minimum at a mixing ratio of s:i = 2:1, and the curve is characterized by two more or less linear regions from the values of the individual components to the value observed for this 2:1 mixture. This behavior is in agreement with a new phase being formed with a stoichiometry of exactly 2:1 (s–i), characterized by a high conversion up to the point where one of the two components is used up.

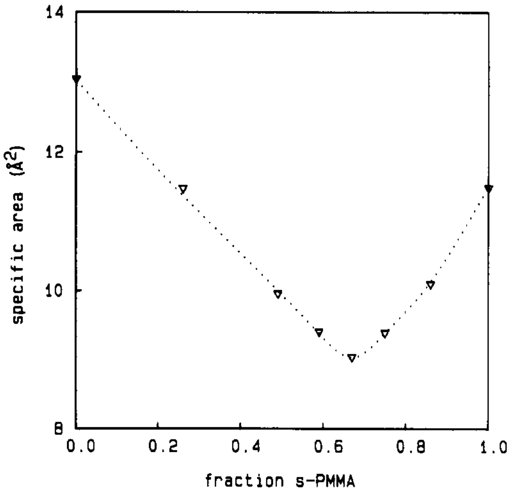

**Figure 5.** Specific area upon stabilization at 12 mN/m for mixtures of s-PMMA (m42) and i-PMMA (m13), as a function of composition. Compression speed 1.5 Å$^2$/mmu·min, $T$ = 45 °C.

The stoichiometry of the PMMA stereocomplex has been the subject of confusion and debate for many years, especially since sometimes maximal effects due to stereocomplexation are observed for mixing ratios not necessarily corresponding to the stoichiometry of the actually complexed sequences, e.g., due to dominating kinetic effects.[6] The structural stoichiometry at the monomeric segment level has been quite convincingly demonstrated to be 2:1 (s–i),[7] which is in perfect agreement with the results shown in Figure 5. The distinct minimum observed very strongly suggests that we are dealing with a pressure-induced stereocomplexation process in the monolayer mixture, with high conversions being reached at 45 °C.

**Limiting Area.** An important consideration in order to tentatively identify the monolayer transition as an actual stereocomplexation process concerns the limiting area on the water surface observed for this "stereocomplex" conformation. In Figure 6, isotherm data are plotted of the 2:1 (s–i) monolayer mixture at 45 °C, the isotherm recorded stepwise, allowing the monolayer to stabilize at each measured surface pressure. From an extrapolation to zero pressure of the linear part (12–18 mN/m) of this isotherm, we can obtain a value of approximately 10.5 Å$^2$/mmu. This value should be considered with some caution, since, if the conversion is not complete, it may be significantly too high. The isotherm data under 12 mN/m, on the other hand, suggest an even higher limiting area, possibly due to an incomplete conversion. The limiting areas are significantly lower than those obtained for crystalline i-PMMA (14.5 Å$^2$/mmu).

Unfortunately, it is not easy to determine exactly which value we should expect for the stereocomplex helices, since the crystal structure of the double-helical units and especially their packing characteristics have not been determined beyond doubt. On the basis of X-ray data and energy minimization calculations, Bosscher[9] proposed a $30_4$ double-helical structure for the stereocomplex,

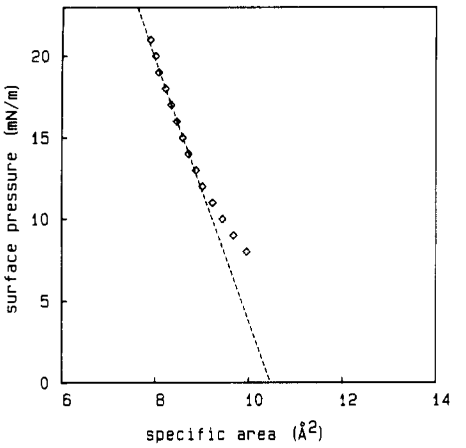

**Figure 6.** Specific area obtained upon stabilization at various surface pressures for a 2:1 mixture of s-PMMA (m42) and i-PMMA (m13). $T = 45$ °C.

without discussing the packing of such helices. The double helix suggested has a diameter of approximately 15 Å and a pitch of 18.4 Å. If we consider the helix as a hard impenetrable cylinder, we can calculate a limiting area of approximately 12 Å$^2$/mmu for this structure lying flat at the air–water interface. On the other hand, the suggested double-helix structure shows clear "grooves" (similar to, e.g., the DNA double helix but unlike the double helix proposed for crystalline i-PMMA[19,20]). Therefore, the assumption of the helix acting as a hard cylinder may not be correct: an efficient packing is likely to involve some kind of "interpenetration" of these grooves, leading to smaller values for the area occupied on the water surface, or at least to a higher value for the compressibility at low surface pressure, a region for which there are no experimental data available.

Using better X-ray diffraction data, Schomaker[8] more recently proposed a $9_1$ double-helical structure for the stereocomplex. This structure is characterized by an even larger diameter (21–22 Å) and an even more pronounced groove structure. The packing of these structures in a unit cell was not addressed. Again, an assumption that the helices pack as impenetrable hard cylinders (which leads to a limiting area of 14–15 Å$^2$/mmu) will not be correct: the density of such a cylinder would only be 0.7 g/cm$^3$, which is evidently far too low to be stable. Also, in order to fit the helices into the suggested unit cell, it is obvious that the helical structures must strongly overlap. The actual limiting area of these structures on the water surface will be determined by this overlapping packing and will be much lower than the 14–15 Å$^2$/mmu suggested above.

An alternative approach to estimate the limiting area of these structures is to use the thickness of a monolayer of these helical structures and to assume that the overall density in the nondeformed condition has a normal value. In this case, it can easily be seen that there will be a relation between the specific volume per segment (assumed to be approximately constant), the area per segment, and the layer thickness $d_{\mathrm{layer}}$ (assumed to be equal to the helix diameter):

$$V_{\mathrm{segm}} \simeq A_{\mathrm{segm}} d_{\mathrm{layer}}$$

For i-PMMA, a helix diameter of 12.5 Å leads to a calculated specific area of 13.2 Å$^2$/mmu. From the stereocomplex structures proposed, we can estimate the diameter to be about 15–20 Å. Assuming a similar density in these monolayers as in the monolayers of crystalline i-PMMA, a limiting area of 8.3–11 Å$^2$/mmu is suggested. This (admittedly very rough) estimate appears to be in good agreement with the experimental results shown in Figure 6.

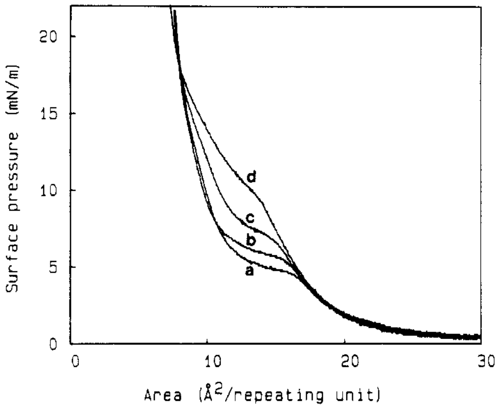

**Figure 7.** Pressure–area isotherms of 1:2 mixtures of i-PMMA (m13) with s-PMMA m42, 95% s (a), m41, 90% s (b), m48, 86% s (c), and m33, 64% s (d). $T = 45$ °C, compression speed 2 Å$^2$/mmu·min.

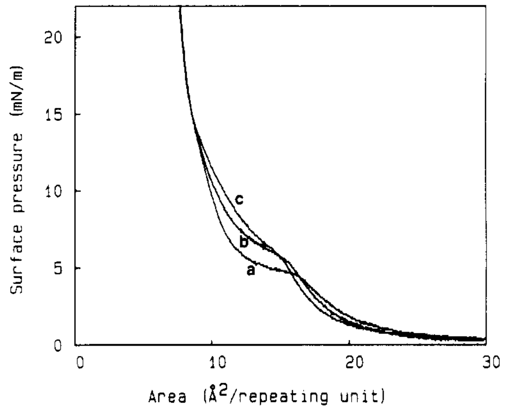

**Figure 8.** Pressure–area isotherms of a 2:1 mixture of s-PMMA (m42) and i-PMMA m13, >97% i (a), m26, 81% i (b), and m29, 66% i (c). $T = 45$ °C, compression speed 2 Å$^2$/mmu·min.

Summarizing, we can state that the observed values for the limiting areas do not contradict the stereocomplex identity of the post transition structure but that the uncertainties are too high to use it as positive conclusive evidence.

**Effect of the Stereoregularity.** For a stereocomplexation process between i- and s-PMMA, a strong influence of the stereoregularity of the components on this process can be expected. In Figure 7, we have plotted the isotherms of mixtures of i-PMMA m13 (>97% isotactic triads) with s-PMMA of varying tacticities; in Figure 8 the isotherms of mixtures of highly s-PMMA m42 with i-PMMA samples of varying tacticities are reported. In all these cases, stereocomplexation between the two components can be observed, and in all cases, the region preceding this transition is characterized by an approximately additive behavior. Lowering the tacticity of the syndiotactic component leads to higher surface pressures associated with the onset of the stereocomplexation: because of the many defects in the syndiotactic helix, the free energy of the stereocomplex will be relatively higher, requiring a higher $\Pi\Delta A$ contribution to the free energy of the transition. Still, stereocomplexation does take place up to rather high conversions, even for a conventional atactic poly(methyl methacrylate) (a-PMMA) sample (m33, 64% syndiotactic triads). In stereocomplexation in melt or solution, the process has been observed to have a high tolerance for defects, and also under these conditions, a-PMMA can form (defect-rich) stereocomplex structures. Schomaker[8] extensively discussed the ability of stereocomplex structures to cope with defects occurring in the double-helical structure. The large grooves in the stereocomplex structure allow for two possible ways of intertwining the two chains, the tolerance for defects being high by the possibility of an easy shift from one position to the other. Also, in the suggested structure, both ester and α-methyl groups of the syndiotactic chain point outward, so that tacticity defects do not strongly disturb the helical sequences.

Lowering the tacticity of the isotactic component also leads to an increase in the surface pressure required to induce stereocomplexation, and also in this case, stereocomplexation is not prohibited. The effect of the stereoregularity of the isotactic component is less than that of the syndiotactic component. The reasons for this may be found in the asymmetric stoichiometry, in the fact that the free energy of the expanded conformation is also affected by the lower tacticity[1] or in another mechanism to deal with defects in the stereocomplex structures. Changes in the ester group of i-PMMA are known to effectively inhibit stereocomplexation (in contrast to changes in the ester group of s-PMMA[21]), the stereocomplex structure being very sensitive to these types of variations. Tacticity defects in the isotactic strand, on the other hand, may well be dealt with efficiently, as was pointed out by Schomaker:[8] in the case of a racemic diad, a torsion of only two backbone bonds of the flexible i-PMMA backbone suffices to retain the overall helix structure.

**Multilayers. An IR Study.** Monolayers of mixtures of i- and s-PMMA can be transferred to solid substrates (gold, ZnS, hydrophobic silicon) in the suggested stereocomplex conformation. Characteristic transfer ratios at 45 °C are 0.3 (downstroke) and 1.0 (upstroke); the incomplete downstroke transfer implies that we cannot expect a well-defined layer structure in the transferred films. The "multilayers" built this way can be studied with standard infrared techniques such as grazing incidence reflection (for gold substrates) and transmission experiments (ZnS substrates) using polarized radiation.

An important characteristic feature of stereocomplex PMMA is the appearance of an 860-cm$^{-1}$ band in the infrared spectra next to the 843-cm$^{-1}$ band observed in amorphous mixtures of s- and i-PMMA. The band appears to be associated with the close to all-trans backbone structure of the syndiotactic chain, which s-PMMA assumes in the stereocomplex and in (probably also double helical) self-aggregates: this phenomenon was extensively studied by Spěváček and Schneider.[5,22,23] Another spectral feature that may be associated with this conformation is a splitting of the carbonyl band, with an extra absorption band emerging a few wavenumbers higher than the normal ("amorphous") band: this feature was only explicitly reported for self-aggregated s-PMMA structures and was attributed to mutual dipolar interactions of the ester groups in the organized aggregates.[23-25]

Figure 9 shows a part of the grazing angle infrared (GIR) spectrum of a 2:1 mixture of i- and s-PMMA, transferred to the gold substrate at 45 °C, using a transfer pressure of 12 mN/m, the monolayer being in the suggested stereocomplex conformation. A clear shoulder at 860 cm$^{-1}$ is visible next to the 843-cm$^{-1}$ band. The reference spectrum given is a simulated GIR spectrum, calculated on the basis of the optical constants derived from an amorphous mixture of the same materials.[2] Figure 9 also gives transmission spectra of a similar as-deposited monolayer, with polarizations of the electrical field parallel to (0°) and perpendicular to (90°) the transfer direction; again, the 860-cm$^{-1}$ band is clearly visible, positively identifying stereocomplex structures in the thin film. Thin films of this same material, heated to 210 °C in order to remove all order present, do not exhibit this band nor is it observed in multilayers of mixtures of s- and i-PMMA, built by transfer of monolayers in the noncomplexes condition (Figure 9e).

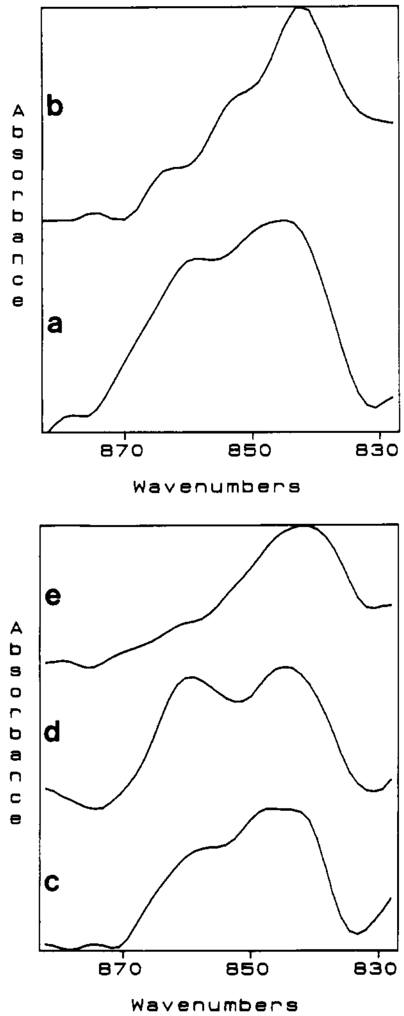

**Figure 9.** Grazing angle infrared (GIR) spectrum of a 250-Å multilayer built from a 2:1 mixture of s-PMMA m42 and i-PMMA m13, in the proposed stereocomplex conformation (a). Calculated GIR spectrum for an amorphous isotropic thin film of this mixture (b). Polarized transmission IR spectrum of a similar as-deposited multilayer on ZnS, polarization: 90°(c), 0° (d). Transmission infrared spectrum of a multilayer of a mixture of s-PMMA m44 and i-PMMA m6, transferred at 5 mN/m at 22 °C (e, no monolayer stereocomplexation).

A shift of the carbonyl band to higher wavenumbers can be observed in the spectra of the as-deposited thin films with respect to an amorphous film (Figure 10): this effect is analogous to the extra band observed for the self-aggregated s-PMMA structures (in which the s-PMMA presumably has a conformation very much like that in the stereocomplex), although it was not explicitly reported for the stereocomplex conformations. When studying thin films of mixtures of s- and i-PMMA annealed at 135 °C for 48 h, starting from an amorphous mixture, a similar shift in the carbonyl band was observed, indicating that it may be characteristic for the stereocomplex structures.

The IR spectra of the as-deposited stereocomplex multilayers also differ from the simulated amorphous spectra in the 1000–1500-cm$^{-1}$ region, and especially in the overlapping bands at 1240–1270 cm$^{-1}$, as can be seen in Figure 11. These differences can be attributed to *dichroic effects*, the GIR setup probing the film with only a significant contribution of the electrical field perpendicular to the substrate. Dichroic effects can also be

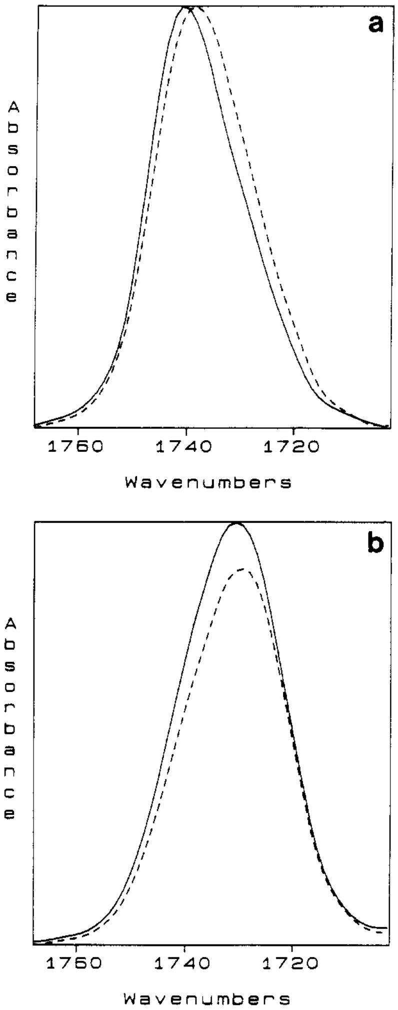

**Figure 10.** (a) GIR spectrum of an as-deposited 250-Å multilayer of a 2:1 mixture of s-PMMA m42 and i-PMMA m13, in the proposed stereocomplex conformation (solid) and after melting at 210 °C (dashed). (b) Polarized transmission spectrum of a similar multilayer on ZnS, polarization 90° (solid), 0° (dashed) (spectra shown on the same scale).

observed in the polarized transmission spectra: the band ratios are significantly different for different directions of the electrical field vector with respect to the transfer direction (Figure 11c,d). The carbonyl band (Figure 10) and the bands in the aforementioned 840–860-cm$^{-1}$ range (Figure 9) also exhibit dichroic effects. In all these cases the dichroic effects are qualitatively similar in the GIR spectra and the 90° transmission spectra, with the opposite effects being observed in the 0° transmission spectra. In the first case, relatively higher absorption intensities are found for the C=O stretching vibration (in particular at the high wavenumber side), the 1073-cm$^{-1}$ band, the 1387-cm$^{-1}$ band, and the 1240-cm$^{-1}$ band; in the latter case, stronger absorption intensities are observed for the 1436-cm$^{-1}$ band, the 1270-cm$^{-1}$ band, the 1150 cm$^{-1}$ band, and the characteristic 860-cm$^{-1}$ vibration.

These observations suggest a more or less uniaxial orientation in the film and are compatible with helical structures with a preferential orientation parallel to the substrate and parallel to the transfer direction, similar to what was observed for multilayers of crystalline i-PMMA under most conditions and similar to results reported for other helical structures.[26-28] The dichoric effects exhibited by a band are directly determined by the angle of the dipole transition moment with the helix axis, as discussed in ref 2. We will not try to give a detailed interpretation of the dichroic effects in terms of the structure suggested for the stereocomplex, because the contributions of the isotactic chain and the syndiotactic chain are difficult to separate and the uncertainty with respect to the details of the proposed structures is too high.

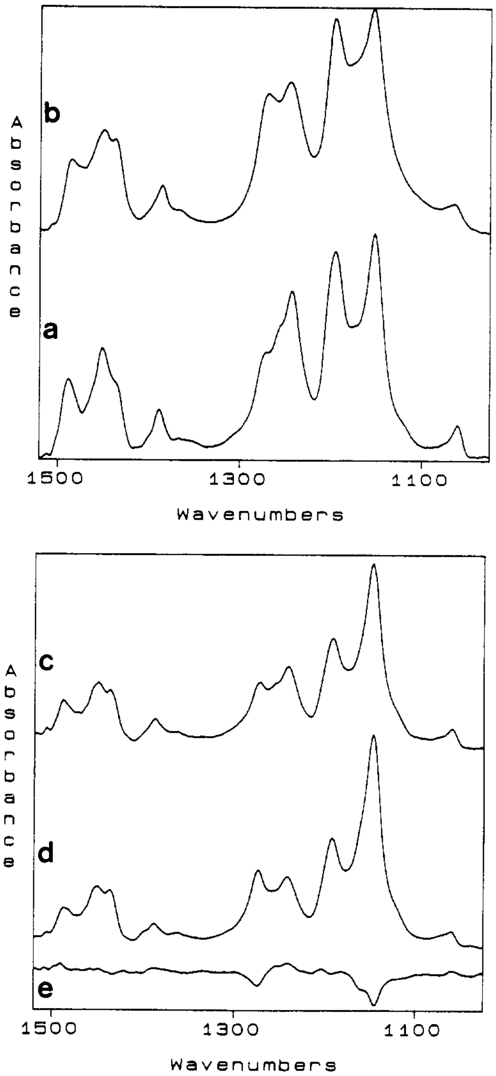

**Figure 11.** GIR spectrum of an as-deposited 250-Å multilayer of a 2:1 mixture of s-PMMA m42 and i-PMMA m13, in the proposed stereocomplex conformation (a). Calculated GIR spectrum for an amorphous, isotropic film of this mixture (b). Polarized transmission spectra of a similar multilayer on ZnS, polarization 90° (c), 0° (d), and the difference spectrum (e).

The orientation of the helical structures in the transfer direction is the direct result of the anisotropy of the rigid helical stereocomplex structures formed and the flow that is caused in the monolayer by the transfer process: the helices are oriented in the dipping direction.[2] A digital subtraction of the two polarized transmission spectra yields a difference spectrum which deviates significantly from similar difference spectra of multilayers of crystalline i-PMMA, confirming that the dichroic effects are not caused by crystalline i-PMMA present in the thin film.

When annealing the as-deposited multilayers at temperatures from 120 to 160 °C (clearly above the $T_g$ of either component), we can see that the multilayers retain the anomalous spectral features indicated above, with the dichroic effects becoming even more pronounced (Figure 12). In the GIR spectra, a small overall drop in the absorption intensity is observed, which can be attributed to a densification of the loose, as-deposited multilayer, as was discussed in ref 2 and as was also observed for multilayers of crystalline i-PMMA.

**Melting Range.** The melting range of the stereocomplex multilayers was estimated by alternatively heating

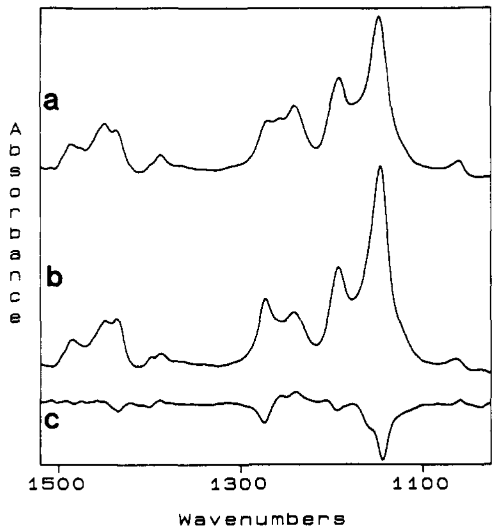

**Figure 12.** Polarized transmission spectra of the film of Figure 11, after annealing at 120 °C for 16 h, polarization 90° (a), 0° (b), and the difference spectrum (c).

the film to various temperatures and subsequently recording an IR spectrum after cooling to room temperature. This procedure permits reorganizations to take place during the annealing process, so that it should be recognized that the results obtained are also determined by the exact thermal history.

When we perform this experiment starting from a 250-Å multilayer (i-PMMA m13, s-PMMA m42, ratio 1:2, initially annealed for 16 h at 120 °C), recording the spectra after annealing the film for a period of 1 h at various temperatures with an interval of 8–10 °C, we observe the disappearance of the stereocomplex features at approximately 165–170 °C, which is a very reasonable value for fringed-micellar type small-scale structures.[29] If the experiment is repeated with an initial annealing period of 24 h at 155 °C and with subsequent annealing periods of 3 h at various temperatures with intervals of 8 °C, we see that the stereocomplex features and the dichroic effects are completely retained up to temperatures of close to 190 °C. Evidently, upon annealing for longer periods at higher temperatures, the stereocomplexed sections reorganize into more stable (lamellar) structures, a phenomenon that was also reported by Schomaker[29] for relatively low molecular weight melt mixtures. During these reorganization processes, the overall orientational features appear to be retained.

Summarizing, we can conclude that, upon using building multilayers from monolayer stereocomplex structures, followed by an appropriate annealing treatment, uniaxially oriented thin films can be prepared with a high thermal stability.

More details about the monolayer stereocomplexation process, especially pertaining to, e.g., the temperature dependence, the kinetics, the monolayer stability of the complexes, and molecular weight effects, will be published in a follow-up paper.[30]

## Conclusions

In this paper, we have demonstrated that it is actually possible to prepare stereocomplex structures between i- and s-PMMA in a monolayer at the air–water interface, this process being driven by the surface pressure buildup upon compression. The process is in many aspects analogous to the monolayer crystallization of i-PMMA, in the first place since it involves the formation of double-helical structures parallel to the air–water interface. The stereocomplexation exhibits a distinct 2:1 (s:i) stoichiometry at the monomeric unit level and is most effectively conducted at elevated temperatures.

Using these stereocomplex monolayers, multilayers can be built on solid substrates. These multilayers exhibit more or less uniaxial orientation characteristics, in agreement with the rigid helical nature of the complexes, these structures being oriented in the dipping direction upon transfer. Following annealing at elevated temperatures, these multilayers can be observed to be stable up to 190 °C; the thermal stability is significantly higher than that of multilayers built from crystalline i-PMMA.

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**Registry No.** s-PMMA/i-PMMA (2:1 mixture), 79616-50-5.