Monolayer and thin film behaviour of stereoregular poly(methacrylates)

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Chapter III.

Monolayer crystallization of isotactic PMMA

ABSTRACT. The transition observed at approximately 8 mN/m in pressure area isotherms of isotactic PMMA is attributed to the formation of crystalline double helical structures from the amorphous expanded condition of the monolayer at lower surface pressures. The monolayer crystallization process is suggested to be characterized by a nucleation stage, followed by a onedimensional growth of the monolayer crystallites, and is in many respects analogous to corresponding melt crystallization processes. The crystalline monolayers can be transferred to solid substrates to yield (upon annealing) highly crystalline films with pronounced orientation characteristics: the helical structures are oriented parallel to the substrate and possess a clear preferential orientation in the XY plane. This lateral orientation is shown to be a function of monolayer crystallization conditions and sample molecular weight, and can be explained in terms of the rheology of the monolayer in the flow associated with the transfer process. The fact that a helical orientation can be induced perpendicular to the dipping direction, suggests that the monolayer crystallites behave as the rigid structures in the monolayer, rather than the individual helices.

INTRODUCTION.

Sofar, the behaviour of the poly(methacrylates) at low surface pressures was discussed in terms of the behaviour as a twodimensional solution. The characteristic transition that is observed in the pressure area isotherms of isotactic PMMA (as reported in the previous chapter) at higher surface pressures was not addressed in this context; this chapter will be completely devoted to the interpretation of the nature of this transition.

Clear transitions observed in pressure area isotherms have been attributed to a range of causes: a very characteristic transition is that from the expanded to the condensed state in monolayers of amphiphilic molecules with long hydrocarbon tails (1). This transition in fact corresponds to a crystallization process, with the hydrocarbon chains assuming some type of hexagonal packing in the monolayer; in the 'flat' region of the isotherms, the expanded phase and the condensed phase coexist. Other phenomena that can be associated with a clear transitions in the pressure area isotherms, include
monolayer to bilayer transitions (e.g. observed for some helical substances (2, 3)), or collapse processes, with the monolayer material being pushed into the subphase or into an overlayer no longer in contact with the interface; in the latter case the monolayers no longer stabilize beyond the transition.

In order to elucidate the nature of the transition discussed in this chapter, surface pressure and surface potential measurements of the monolayers at the air water interface are used; an important role will also be played by infrared measurements on transferred monolayers. As discussed in the chapter 1, FT-IR is a versatile technique, capable of giving more than compositional information: the spectra may contain conformational signatures, and if an appropriate experimental setup is chosen, they may also carry orientational information (4). In the characterization of multilayers of isotactic PMMA, we will encounter both of these aspects of the IR technique.

EXPERIMENTAL.

A description of LB apparatus and procedures can be found in appendix 1, which also contains the characteristics of the materials used. FT-IR experimental information can also be found in this appendix, whereas the calculational procedures for the simulation of IR spectra are elaborated on in appendix 2.

RESULTS AND DISCUSSION.

A. Monolayer behaviour.

**Compression isotherms.** The transition observed at about 8 mN/m in the pressure area isotherms of monolayers of isotactic PMMA (figure 2.1 of chapter 2) is characteristic for this material: monolayers of syndiotactic (or atactic) PMMA exhibit no such phenomenon. The isotherm of isotactic PMMA shows another inflection point at about 20 mN/m; above this surface pressure, the monolayer no longer becomes stable so that this must probably be attributed to a collapse phenomenon. Monolayers of isotactic PMMA become stable in the expanded regime, up to surface pressures of 5 mN/m, as well as at 12 mN/m, before and beyond the monolayer transition respectively. At low pressures the monolayer is instantaneously stable when compression is paused; in the latter case the time required for complete stabilization is about 30-40 minutes.
In figure 2.7 of chapter 2, the isotherms of isotactic PMMA are reported as a function of temperature. The aforementioned transition can be seen to shift to higher surface pressures upon raising the temperature, suggesting a negative entropy change to be associated with the transition process involved.

A pronounced effect of the compression speed on the shape of the pressure area isotherms can be observed (figure 3.1). As the compression rate is lowered, the pressure where the transition becomes evident in the isotherm drops significantly. At the same time, a 'dip' (a drop in the surface pressure as compression proceeds just past the onset of the transition) remains observable even at very low compression rates. The strong compression speed dependence clearly indicates that the monolayer transition is associated with a relatively slow process, with the conversion speed dependent on the surface pressure. The 'dip' observed in the isotherms is a more puzzling phenomenon. If a simple phase transition was to take place between two phases, with the transformation speed only dependent on the surface pressure, one would anticipate the pressure to remain constant or in fact rise slowly during the transition process. An interpretation of the pressure dip in terms of an 'overshoot' mechanism cannot explain the fact that it remains clearly observable even at low compression speeds, down to 0.2 Å²/monomeric unit.minute.
Hysteresis. From hysteresis experiments we learn that the monolayer compression is perfectly and instantaneously reversible as long as the monolayer is compressed up to an area corresponding to a point in the isotherm before the transition, up to pressures of 5 mN/m. When the monolayer is compressed beyond this transition (figure 3.2), the decompression isotherm does not follow the compression isotherm: the surface pressure drops sharply at the start of the decompression, and approaches the compression isotherm only at relatively large areas: the monolayer compression is not instantaneously reversible beyond the transition. Upon recompressing the same monolayer (starting from 40 Å²/monomeric unit), the surface pressure perfectly follows the same isotherm as in the first compression run; evidently, no irreversible changes have occurred in the monolayer during the first compression run: upon decompression, a condition is eventually reached identical to that before compression.

Figure 3.2. Hysteresis experiments for i-PMMA (#m8, T=22°C, compression and decompression speed 2 Å²/monomeric unit.minute).

Molecular weight effects. Although in several publications (1, 5, 6) it is argued that the molecular weight is not important in determining the pressure area isotherms of polymeric substances, varying the molecular weight of isotactic PMMA yields interesting results (figure 3.3). Whereas the expanded regime appears to be unaffected by changes in the molecular weight, a striking observation is the fact that, at 22°C and using a compression speed of 2 Å²/monomeric unit.minute, starting from molecular weights of approximately 25.10⁴, the transition phenomenon in the compression isotherms becomes less and less pronounced with decreasing molecular weight.
weights; in the isotherms of samples #m20 and #m21 (\(\bar{M}_n 4.10^3\) and 2.8.10^3 respectively), the transition is no longer detectable and the monolayers appear to remain in the expanded condition until they collapse. The fact that the stereoregularity of the lowest molecular weight samples is somewhat less perfect than that of the higher molecular weight samples, cannot be held responsible for the complete suppression of the transition, since for higher molecular weight fractions of similar tacticities, the transition can still clearly be observed. The lower stereoregularity may be an additional cause for the suppression of the transition in these samples, though, since upon further lowering the tacticity of higher molecular weight samples (down to 66% isotactic triads), the transition in the isotherm is observed to become less pronounced.

Figure 3.3. Compression isotherms of i-PMMA of various narrow molecular weight fractions (22°C). \(\bar{M}_n (.10^3)\) indicated in figure; isotherms are cut off at 20 mN/m.
The extent of the transition observed in isotherms of materials with 'borderline' molecular weights (5.10^2-25.10^3) is very sensitive to variations in compression speed and temperature. Under conditions that are more critical for the monolayer transition to be observed (higher temperatures, less perfect tacticities, higher compression speeds), the critical molecular weight regime can be observed to extend up to even higher molecular weights. For samples with molecular weights above 25.10^3, up to more than one million, the pressure area isotherms are effectively identical.

Table I. Typical transfer ratios for i-PMMA.

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>5 mN/m down</th>
<th>5 mN/m up</th>
<th>12 mN/m down</th>
<th>12 mN/m up</th>
</tr>
</thead>
<tbody>
<tr>
<td>low (&lt;20.10^3)</td>
<td>0.2 -0.3</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>intermediate</td>
<td>0 - 0.3</td>
<td>1.0</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>high (&gt;200.10^3)</td>
<td>0.4</td>
<td>1.0 - 0.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The nature of the transition: an IR study. In order to elucidate the nature of the transition in the isotherm of isotactic PMMA, multilayers built by transfer of isotactic PMMA monolayers at surface pressures below (5 mN/m) and above (12 mN/m) the transition pressure, were studied with FT-IR techniques. Transfer ratios, characteristic for transfer to gold substrates, are listed in table I.

Grazing incidence reflection infrared spectra of Langmuir Blodgett layers of isotactic PMMA, transferred to gold substrates at surface pressures of 5 mN/m, are shown in figure 3.4c, together with an isotropic bulk transmission spectrum (figure 3.4a), a calculated GIR spectrum based on optical constants derived for isotropic amorphous isotactic PMMA (figure 3.4b, the calculation procedure is described in appendix 2), and the GIR spectrum of a thin layer of i-PMMA that was heated to above 170 °C (above Tg and Tm) in order to remove all possibly remaining order and orientation (figure 3.4d). Because of the high absorption coefficients of PMMA, the GIR spectra are severely distorted with respect to the normal bulk transmission spectra (as is evident from a comparison of figure 3.4a and 3.4b), which makes it necessary to calculate the reflection spectrum of a film of isotropic amorphous i-PMMA so as to have a reference spectrum to compare with the experimental spectra. Comparing the experimental GIR spectrum of the multilayer transferred at 5 mN/m, with the
simulated spectrum for an amorphous isotropic sample, we observe that these spectra are almost identical. We can conclude that there are no indications that the structure of the multilayer deviates significantly from the amorphous bulk structure in terms of orientation or conformation. A thin film of isotactic PMMA, heated to above 170°C and assumed to be completely amorphous and isotropic, also yields a GIR spectrum practically identical to the 5 mN/m as-deposited multilayer and the calculated amorphous spectrum. Probably, during transfer at low surface pressures, the monolayers are deposited in a more or less random segmental conformation, the polymer chains being rather flexible in the expanded condition of the monolayer.

Figure 3.4. IR spectra of isotactic PMMA: (A) Bulk transmission spectrum of amorphous i-PMMA; (B) calculated GIR spectrum of amorphous i-PMMA on gold; (C) GIR spectrum of an as-deposited multilayer of i-PMMA, transfer pressure 5 mN/m; (D) GIR spectrum of a thin film of i-PMMA on gold after heating to 170°C.
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The GIR spectrum recorded from a multilayer transferred at 12 mN/m, on the other hand, deviates significantly from the spectrum calculated for isotropic amorphous i-PMMA (figure 3.5a). The features that distinguish this spectrum from the calculated amorphous spectrum include in the first place a strong difference in the intensities of the partially overlapping bands at 1265 and 1255 cm⁻¹, which have been reported to be conformation sensitive (7, 8, 9, 10). Other deviations include a shoulder emerging at 1296 cm⁻¹, a narrowing (and a shift) of the broad band at 1154 cm⁻¹, some changes in the C-H bending vibrations around 1440 cm⁻¹ and in the α-methyl and methylene C-H rocking vibrations around 950 and 840 cm⁻¹, respectively. The C-H stretching region (2800–3100 cm⁻¹, not shown in figure 3.5) also exhibits some differences. For a list of assignments of the absorption bands in the spectrum of isotactic PMMA, we refer to table I of appendix 3.

Figure 3.5. (a) GIR spectrum of an as-deposited multilayer of i-PMMA, transfer pressure 12 mN/m (solid line); calculated GIR spectrum for a thin film of amorphous i-PMMA on gold (dashed line); (b) calculated GIR spectrum for an isotropic thin film of crystalline i-PMMA on gold.
For all the observed deviations indicated in the previous paragraph, similar discrepancies can be observed when comparing a bulk spectrum of amorphous isotactic PMMA with a spectrum of crystalline i-PMMA. This is illustrated by figure 3.5, in which simulated GIR spectra based on optical constants derived from amorphous and crystalline i-PMMA are shown. When using (partially) deuterated samples of isotactic PMMA (α-methyl CD₃, ester methyl CD₃, backbone CD₂ and perdeuterated MMA-CD₃), it can be seen that the grazing incidence reflection spectra of multilayers transferred at 12 mN/m also deviate from the calculated amorphous spectra, and again the differences can be traced back to similar differences between the bulk transmission spectra of amorphous and crystalline samples of these materials. For the α-CD₃ and the ester methyl CD₃ materials, this is illustrated in figure 3.6 and 3.7, respectively. On the basis of these data, it can be concluded that the structure of isotactic PMMA in these multilayers must have definite crystalline characteristics.

![Figure 3.6](image)

**Figure 3.6.** GIR spectrum of a multilayer of i-PMMA-CD₃, transfer pressure 12 mN/m (solid line), and a calculated GIR spectrum for an amorphous thin film of this material (dashed line).

The crystal structure of isotactic PMMA has been subject of some debate, but is now generally accepted to be a 10, double helix (11, 12). The similarity between the infrared characteristics of the multilayers transferred at 12 mN/m and the crystalline bulk samples strongly suggests that during the transition, analogous double helical structures are formed in the monolayer at the air water interface upon compression.
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![Absorbance vs. Wavenumbers](image)

**Figure 3.7.**  *GIR spectrum of a multilayer of i-PMMA-α-CD, transfer pressure 12 mN/m (solid line), and a calculated GIR spectrum for an amorphous thin film of this material (dashed line).*

When recording the surface potential of the monolayers upon compression, we see a very clear discontinuity in the trend of a rising potential upon compression, exactly at the onset of this phase transition (chapter 2, figure 2.11): the average dipole moment per segment starts to fall rapidly. This is in agreement with the idea of helical structures being formed, implying that all segments can no longer be in amphiphilic contact with the interface (and thus contribute fully to the surface potential), since the conformation of the chains is fixed in the helical structure.

The interpretation of the monolayer transition in terms of a double helix formation process will prove to be adequate in explaining the observed monolayer and multilayer behaviour discussed in the rest of this chapter.

**Limiting area.** Calculating the area pro monomeric unit that a 10, double helix, lying flat on the water surface, would occupy on the basis of the crystal parameters reported in literature (helix diameter 12.5 Å, pitch 21.1 Å), yields a value of 13.2 Å²/monomeric unit (11, 12). Considering the post transition region of an isotherm that was recorded stepwise, with the film being allowed to stabilize after each pressure step so as to eliminate kinetic effects, we find upon extrapolation to zero surface pressure a limiting area of approximately 14.5 Å²/monomeric unit (figure 3.8), which is not far from the value calculated for the double helical structure. The deviation of the extrapolated value to the high area side can easily be caused by the presence of a small fraction of 'amorphous' material with a high compressibility.
Another helical structure that was originally proposed for crystalline isotactic PMMA (α 5, single helix) (13), was later dismissed, when the concept of the double helix was introduced. A helix structure such as that can easily be seen to occupy a significantly larger area per monomeric unit at the air water interface, as compared to the values calculated for the 10, double helix, and as compared to the experimentally determined limiting areas. Analogous arguments were used to reject the single helix hypothesis for the threedimensional crystal structure: no ways were found to accommodate four of these helices in the unit cell.

In literature, several polymers have been reported to retain a helical conformation, present in the spreading solution, at the air water interface (3, 14, 15, 16, 17), but isotactic PMMA appears to be the first example of a polymer that acquires such a structure as a result of the surface pressure build-up during compression. As far as we know, no other synthetic materials assuming a double helix structure at the air water interface have been reported. In chapter 5, another example of a double helical structure formed at the air water interface will be discussed.

**Monolayer thermodynamics.** Having identified the structural nature of the isotherm transition, we can try and use this (double) helix formation hypothesis to explain the monolayer behaviour of isotactic PMMA. At large areas, isotactic PMMA tends to form an expanded phase, with all segments in contacts with the interface. This conformation will have a lower free energy than a helical structure of the chains, mainly because of the higher entropy of the system. When the monolayer is
compressed, the entropy is lowered. When the entropy difference between the expanded phase and the alternative helical conformation of the chains becomes so small that it no longer compensates for possible differences in internal energy and the gain in free energy as a result of the decrease in occupied area upon transformation to the helical structure (the $\Pi \Delta A$ contribution to the free energy of transition, $\Delta A$ being negative), a transition takes place from the 'amorphous' expanded conformation to the 'crystalline' (double) helical conformation, these helical structures oriented parallel to the water surface. The temperature dependence of the transition also points to a negative transition entropy: at higher temperatures, the transition shifts to higher surface pressures, and at 50°C, it is completely suppressed. Evidently, we are in the regime where the crystallization rate is determined by the free energy gain upon crystallization rather than by transport phenomena, the mobility of the i-PMMA chains in the expanded monolayer being high.

The double helix hypothesis can also successfully be used to explain the remarkable molecular weight effect with respect to this transition. For the lowest molecular weight materials this helix formation was observed to become less favourable (figure 3.3): this effect can be rationalized in terms of a critical chain length phenomenon. The concept of critical chain length phenomena is well known e.g. from studies of polymer-polymer complexes (18, 19). Next to free energy contributions that are proportional to the number of segments involved (and thus to the length of the helical sequences formed), the helix formation can be expected to be associated with an initial entropy loss (e.g. the loss of translational entropy when two chains combine to form a double helical structure), which is not proportional to the length of the helix structure formed:

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

where $N$ represents the number of segments actually in the helix conformation.

Short chains will only be able to form relatively short helical sequences and the free energy gain upon helix formation will consequently be lower for these short chains: the loss in entropy upon complexation or crystallization is relatively higher than for the higher molecular weight samples. For the lowest molecular weight fractions, the second term may not be large enough to overcome the initial entropy loss. At higher surface pressures, the critical chain length can be expected to become smaller since the second term of the expression for the thermodynamic driving force will be larger; a shift of the transition pressure to higher values can be expected, and is observed for these low molecular weight materials.

In melt crystallization experiments (reported in chapter 4), a similar suppression of the crystallization of low molecular weight samples of i-PMMA was observed, a phenomenon that can be explained using similar arguments as given above.

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Transition kinetics. The fact that the pressure area isotherm of isotactic PMMA shows a drop in surface pressure upon compression during the suggested helix formation process, may seem puzzling at first sight. Apparently, at the onset of the helix formation (at surface pressures just over 5 mN/m), the rate is slow and the area generated by this transition from the expanded conformation to the helical conformation cannot compensate for the decrease in area due to the mechanical compression, so that the surface pressure keeps rising, which in turn causes the transition process to accelerate. When the area created per time unit by the transition process equals the (constant) area consumed by the compression, the slope of the isotherm will be zero: the 'top' of the isotherm. After this point, the helix formation rate evidently increases even further, instead of remaining constant, leading to an actual increase of the relative area available for the non-helix phase and thus to a drop in the surface pressure. If the conversion rate would only be determined by the surface pressure, it can be anticipated that the isotherm will bend to an almost zero slope at a surface pressure, where compression speed and transition rate are matched. In reality, the transition to the helix conformation must have an autotaccelerating character to be able to produce the observed pressure drop. This autotaccelerating character of the process is clearly demonstrated by isobaric stabilization experiments at surface pressures close to the transition pressure, as shown in figure 3.9. The decrease of the area as a function of time is directly correlated to the conversion of the crystallization process in the monolayer.

Figure 3.9. Isobaric stabilization experiments of monolayers of i-PMMA (#m8, T=22°C). Surface pressure a: 6.8 mN/m; b: 6.5 mN/m; c: 6.1 mN/m.
We can explain the observed phenomena, if we consider the helix formation process as an actual twodimensional crystallization process analogous to the normal three-dimensional crystallization of isotactic PMMA. If we consider the helix formation as the result of an activated nucleation mechanism, followed by a lamellar type growth of the stable nuclei formed, an autoaccelerating effect can be anticipated.

Polymer crystallization kinetics in normal three dimensional systems can be studied using Avrami-analyses of the conversion-time plots. Gabrielli (20) already reported using an Avrami type approach to describe the kinetics of the collapse of PMMA monolayers at high surface pressures; in this case, the use of the Avrami analysis was probably not correct, since the fall of the surface pressure was monitored at constant areas; in doing so, the thermodynamic driving force was not constant during the experiment. The well known expression that Avrami proposed to describe the time dependence of the crystalline fraction during isothermal crystallization is (21):

\[ 1 - \alpha = \exp(-Kt^n) \]

where \( \alpha \) represents the fraction of crystalline material, \( K \) is a constant, \( t \) represents time and \( n \) is the so called Avrami exponent. Using isobaric and isothermal monolayer crystallization conditions (to ensure a constant thermodynamic driving force), this equation may be expected to apply also to the helix formation process in monolayers of isotactic PMMA at the air water interface. The conversion can be estimated from the area lost referenced to the beginning of the process, divided by the area loss associated with the completed process, when the monolayer has become stable. The results of the Avrami analyses are shown in figure 3.10. The conversion of the crystallization processes is characterized by straight lines in the Avrami plots for all surface pressures studied, up to conversions of about 75%. The Avrami exponents that can be calculated from the slope of these lines, range from 1.8 to 2.0, indicating that the twodimensional monolayer crystallization of i-PMMA may be described either by an instantaneous non-activated nucleation stage followed by a twodimensional growth of the crystallites, or by an activated nucleation mechanism followed by a onedimensional growth. This latter possibility is the most likely when we consider the fact that we are dealing with helical structures being formed.

An isolated helix will lack stabilization due to lateral contacts with neighbouring helices in the monolayer. During the crystallization process, the helices will probably line up next to each other so as to optimize these lateral contacts, lowering the free energy per helix: the lateral cohesive interactions in the monolayer can be expected to be significantly stronger for the helical structures than for the segments in the expanded monolayer. It is likely that there will be a critical nucleus size required to render the nucleus stable; growth of the nucleus can then be expected to occur principally in the direction perpendicular to the helix direction, the newly formed
helices being lined up parallel to the existing helices in the monolayer crystallite, analogous to a lamellar growth mechanism; this is illustrated by figure 3.11. This model is in agreement with the value found for the Avrami exponent, and is supported by experimental results presented later in this chapter.

Figure 3.10. Results of Avrami analyses of isobaric stabilization experiments. Surface pressure 6.1 (O), 6.3 (□), 6.5 (△), 6.8 (○) and 7.1 (*) mN/m.

Figure 3.11. Schematic representation of the suggested crystallization process in monolayers of i-PMMA.
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Stability of the crystalline monolayer structure. Now that we have established that the monolayer exhibits an actual crystallization process, in many respects analogous to a regular melt crystallization, we may try and interpret the hysteresis curves from this point of view. Upon decompression, the surface pressure falls and the crystallites become unstable with respect to 'melting', returning to the expanded conformation. The decompression curve does not follow the compression curve in the transition region, the crystallites melting at lower pressures than those at which they were formed (figure 3.2). This phenomenon is completely analogous to that of regular melt crystallized samples, exhibiting melting points higher than the crystallization temperature. Following this analogy, the decompression curve is comparable to a DSC temperature scan. The decompression isotherm is not strongly dependent on the decompression speed, indicating that it is mainly determined by the thermodynamic stability of the crystallites.

Bearing this in mind, we can attempt to interpret the differences in the decompression runs shown in figure 3.12. The experiments reported in this figure differ in speed of compression, and thus in the surface pressure during the monolayer crystallization process. In both cases, the monolayer crystallization has been completed to a large extent, the difference being that for the fast experiment the crystallization has effectively taken place under conditions of a high thermodynamic driving force (high surface pressure), whereas for the slow experiment only a mild thermodynamic driving force was operative. In the first situation, the critical nucleus size (and lamellar thickness) are expected to be small, resulting in smaller crystallites than in the monolayer crystallized at low surface pressures. Upon decompression, the crystallites will 'melt' when the surface pressure is so low that they are no longer thermodynamically stable. Figure 3.12 indicates that the decompression isotherm of the monolayer crystallized at high surface pressures follows a higher path than the monolayer crystallized at low surface pressures, and returns to the expanded conformation at higher surface pressures (3.5 mN/m vs. 2 mN/m). The stability of the monolayer crystallites is clearly determined by the crystallization conditions, an effect which is completely analogous to the effect of the crystallization temperature in regular melt crystallization experiments: samples crystallized at higher degrees of undercooling (a higher thermodynamic driving force) are less stable than crystallites formed at lower degrees of undercooling.

The results presented so far clearly indicate that there is a strong analogy between the monolayer crystallization process and regular melt crystallization processes. An important difference is the fact that the monolayer process can be completed in a matter of minutes, whereas the melt crystallization process of i-PMMA is extremely slow and usually requires annealing periods of weeks (22). The cause for this difference probably lies in the higher mobility of the polymer chains in the monolayer condition, relative to the viscous polymer melt.
High molecular weights do not seem to impose any significant restrictions on the monolayer crystallization process: the isotherms of all samples with molecular weights of $25.10^9$ up to over one million are effectively identical. Here the analogy with the regular melt crystallization process of i-PMMA definitely does not apply any longer: as discussed in chapter 4, the melt crystallization becomes strongly suppressed when using higher molecular weight samples, the viscosity being a severe limiting factor, almost inhibiting crystallization of the highest molecular weight fractions. In the monolayer, high molecular weight samples crystallize with similar rates as samples of lower molecular weights, indicating that the crystallization rate is mainly determined by the local segmental mobility. The reason for this intriguing observation is probably that because of the twodimensional nature of the monolayer the chains do not form extensive entanglement networks, as in the threedimensional melt situation (23).
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B. Multilayer behaviour.

**GIR experiments.** In figure 3.5, it was shown that the spectra obtained from multilayers built at 12 mN/m clearly exhibit crystalline characteristics. Still, the reflection spectrum of the 12 mN/m multilayer is not identical to a calculated reflection spectrum based on optical constants derived from isotropic crystalline i-PMMA (figure 3.5b). Partly, this is caused by the fact that the Langmuir Blodgett structures are oriented with respect to the substrate, which causes dichroic effects to become evident in the GIR spectra because of the anisotropic orientation of the electrical field probing the film in this set-up (appendix 3); we will elaborate on this subject later in this chapter. Apart from dichroic effects, the crystalline features are also less pronounced in the as-deposited multilayer spectrum compared to the spectrum of bulk crystalline material. This may be caused not only by a significant fraction of amorphous material present (the area occupied by the monolayer suggests that the monolayer crystallization has reached a high conversion, but there is no guarantee that upon transfer the degree of crystallinity is completely retained), but also by the absence of a threedimensional crystalline packing of the helical subunits. A crystalline packing will be very difficult to achieve directly, depositing rigid structures from the water surface onto the substrate, especially since these monolayers do not exhibit a perfect X, Y or Z type transfer. The 'loose' structure anticipated (experimental indications are discussed later on) may well have less pronounced crystalline IR characteristics compared to a real crystalline packing.

**Annealing above Tg.** When the high surface pressure multilayers are heated to above the glass transition temperature of i-PMMA (approximately 50°C), the anomalous crystalline-like features do not disappear from the GIR spectra: the deviating conformation evidently does not relax by heating it to above the normal Tg, which is another strong indication that we are dealing with crystalline structures. What we do see upon annealing above Tg, is a decrease in the absorption intensity of the film over the whole spectrum, equally affecting all absorption bands: this is illustrated in figure 3.13. This decrease in absorption intensity may be related to variations in the density of the as-deposited film upon annealing (as discussed in appendix 2), and can be rationalized as the result of a significant densification of the film upon annealing above Tg: the loose structure of the as-deposited multilayer starts to collapse due to the enhanced mobility in the film. Ellipsometry experiments yield anomalously low values for the refractive index of the films, also indicating a low density of the as-deposited films relative to the normal bulk density.
Post-crystallization. When we anneal the multilayers, as-deposited at 12 mN/m, at 120°C, we observe a rapid change in the GIR spectra: the crystalline features become more and more pronounced, to a similar extent (or even stronger) as in bulk spectra of crystalline i-PMMA (figure 3.14); the pseudo-crystalline structure of the Langmuir Blodgett multilayer is converted into a real threedimensionally packed crystalline structure. The relative band ratios in the GIR spectrum of the crystallized multilayers are still not identical to those in the GIR spectrum calculated from the optical constants of an isotropic crystalline sample; in fact, the deviations are quite strong (figure 3.15). The intensities of e.g. the C=O stretching vibration (1740 cm$^{-1}$), the $\alpha$-methyl symmetric bending vibrations at 1390 cm$^{-1}$, and the absorption bands at 2958 and 1255 cm$^{-1}$ are too high relative to the simulated spectrum, whereas e.g. the bands at 3000 and 1265 cm$^{-1}$ are too low. The dichroic effects are qualitatively similar to those observed in the spectra of the as-deposited films, only much more pronounced. The dichroism exhibited by the films is in agreement with helical structures oriented parallel to the substrate. Such an orientation is to be expected, considering the fact that the helices are transferred layer by layer from a horizontal orientation at the air water interface. Appendix 3 gives a short discussion of the dichroic effects that can be calculated for this situation. Assuming a $\phi$ (the angle between the transition dipole

Figure 3.13. GIR spectra for an as-deposited multilayer of i-PMMA (transfer pressure 12 mN/m) (...), after heating to 50°C for 14 h (---), and after heating to 70°C for 2h (solid line). The spectra are shown on the same scale.
moment and the helix axis) larger than 55° for the C=O stretching vibration and the α-CH\textsubscript{3} symmetric bending vibration, as is indicated by the structure proposed by Bosscher et al. (12), a relative increase of the absorption bands associated with these vibrations can indeed be anticipated. The rotation position of the ester groups within the helical structure has not been completely elucidated beyond doubt so far, based on X-ray results and energy minimalization studies; there are e.g. differences between the structures as proposed by Kusanaga (11) and Bosscher (12). A more elaborate comparison between these proposed structures and the infrared dichroic results is discussed in appendix 3.

The enhancement of the dichroic features of the crystallized i-PMMA films upon post-crystallization may be caused by an increase of the helix content of the film, or by an enhanced orientation of the helices present in the film along the common average direction of the helices in order to attain an efficient packing, but also by the fact that a threedimensional packing of the helices, which is probably not attained until the annealing process at 120°C, may force the side groups into a fixed position and orientation with respect to the helix. If the absence of a crystalline packing of the helices were to allow a higher side group mobility, this would tend to diminish the dichroic effects observable in the GIR spectra.
Figure 3.15. GIR spectrum of a crystallized multilayer (solid line), and a calculated GIR spectrum for an isotropic thin film of crystalline i-PMMA of the same thickness (--). Spectra are shown on the same scale.

Figure 3.16. Intensity of the C=O stretch absorbance as for a multilayer of i-PMMA as a function of annealing time at 120°C. m: value after melting at 170°C.
The post-crystallization of the multilayer is a relatively rapid process, compared to the bulk crystallization kinetics of isotactic PMMA. Already after 5 minutes of annealing at 120 °C, significant changes toward the real crystalline structure are observable in the GIR spectrum. The processes in the film upon annealing at this temperature can be monitored e.g. using the absorption intensity of the C=O stretching vibration (figure 3.16). The t=0 value corresponds to the as-deposited multilayer. Upon annealing, the absorption intensity first drops sharply (approximately 25%) due to the collapse of the loose, as-deposited structure into a more dense packing, as discussed before. Subsequently, the intensity of the 1740 cm⁻¹ band starts to increase rapidly, and levels off in a few hours’ time. When the film is heated to 170 °C, the GIR spectrum loses its crystalline features and the film attains an amorphous isotropic structure with a corresponding significantly lower value for the C=O stretching absorption.

The observation that isotactic PMMA, deposited at these high surface pressures, easily attains a highly crystalline structure, is especially striking when it is compared to the normal melt crystallization characteristics of this material. As mentioned before, i-PMMA crystallizes notoriously slowly in the melt, even at 120 °C, which is considered to be the optimal crystallization temperature. Even for the most favourable molecular weight fractions, it may take days for any crystallization to be observed by IR or DSC. The ease of crystallization of isotactic PMMA films prepared by the LB technique becomes even more remarkable, when it is compared to the behaviour of amorphous thin films with similar thicknesses up to several hundreds of Ångstroms. Because of the restricted geometry of the thin film, crystallization will be severely suppressed with respect to infinitely large bulk samples (as elaborated on by Billon (24)), resulting in the observation that thin films of amorphous i-PMMA (transferred at low surface pressures, or heated to above 170 °C) do not show any sign of crystallization even after one month at 120 °C. With increasing molecular weights of the i-PMMA, the melt crystallization rate is even suppressed further rapidly, and the crystallization of these samples is extremely time-consuming (25). In contrast, LB layers of high molecular weight samples of isotactic PMMA (up to one million), deposited at surface pressures of 12 mN/m to form a multilayer, easily crystallize. The spectrum of as-deposited films of i-PMMA transferred in the crystalline monolayer conformation, does not vary with the molecular weight of the sample: multilayers of the materials with very high molecular weights yield identical spectra as those prepared from materials with molecular weights of approximately 20.10⁴. Upon annealing, there are no strong differences in the rate of the post-crystallization process, although the highest molecular weight fractions can be observed to yield slightly lower limiting crystallinity levels than the lower molecular weight samples.

As expected, the lowest molecular weight i-PMMA samples, which did not exhibit a
crystallization process in the monolayer, also did not exhibit crystalline features upon transfer at 12 mN/m, and transferred multilayers built from this material could not be crystallized.

**Melting behaviour.** The melting behaviour of the crystallized multilayers was studied by alternately heating the film up to a certain temperature and subsequently recording the GIR spectrum in order to evaluate the level of crystallinity. In order to compare the melting behaviour with that of a normal melt crystallized sample, IR transmission spectra were recorded of a 2 μm thick film of melt crystallized i-PMMA on KBr after simultaneous heat treatments. The melting region of the 'bulk' film was thus found to extend somewhere from 155 up to 164°C, in good agreement with DSC results. The crystallized LB multilayer starts to lose its crystalline features at much lower temperatures, the melting region extending from under 140°C up to 155°C, varying somewhat with the layer thickness. For the thicknesses studied (up to 300Å) the melting region was significantly lower than that of the corresponding melt crystallized control samples. The cause for the relatively lower melting points may be found in the first place in the fact that in the multilayers, crystallites are formed starting from a situation which is totally different from an amorphous melt. The extremely high 'nucleation' density, which can be expected for the crystallized multilayer due to the high number of potential 'nuclei' (the helix structures as transferred from the water surface), may initially lead to small crystallites in the layer, smaller than the more extensive, lamellar structures which result from a regular melt crystallization process (26). On the other hand, the lateral dimensions of the crystallites may also be restricted by the film thickness. An indication that this latter restriction may be important is illustrated by the observation that extremely thin films (thickness less than approximately 60Å, assuming a normal density), transferred at 12 mN/m, do not attain a crystalline packing upon annealing at 120°C, but instead lose the pseudo-crystalline features present in the as-deposited layer (figure 3.17). Evidently, these films are too thin for crystallites to be formed with lateral dimensions large enough to be stable at the crystallization temperature. When studying the melting region of thin films of varying thicknesses (above the apparent crystallization threshold), the melting range was observed to shift somewhat to higher temperatures upon increasing the film thickness. The monolayer history of the crystallized monolayers is not very significant in determining the melting region: films built from monolayers crystallized at low surface pressures (suggested to be characterized by more extensive lamellar structures in the monolayer) did not exhibit a significant shift in the melting region with respect to films based on monolayers that were crystallized at higher surface pressures, indicating that extensive reorganization processes are probably operative during the annealing process (25).
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Figure 3.17. GIR spectrum of a 50Å multilayer of i-PMMA (#m8, transfer pressure 12 mN/m): as-deposited (a), after annealing at 120°C for 2h (b).

Lateral orientation. Apart from the GIR experiments reported earlier in this chapter, we also performed transmission experiments on multilayers transferred to IR transparent substrates like ZnS and hydrophobized silicon. This allows the film to be probed by an electrical field parallel to the substrate, with the possibility of distinguishing the dipping (transfer) direction from the direction perpendicular to it, by using polarized radiation. The polarization parallel to the dipping direction will be referred to as 0°, and the polarization perpendicular to this dipping direction as 90°.

When transmission spectra are recorded from a 300 Å thick multilayer of isotactic PMMA (Mn 36.10^3) on a ZnS substrate, transferred at 12 mN/m, the transmission spectra, recorded using non-polarized IR radiation, confirm the dichroic effects deduced from the GIR spectra, the relative band ratios being oppositely affected. Performing these experiments with polarized IR radiation, we observe that the spectrum obtained using 0° polarization is different from that obtained using 90° polarization (figure 3.18). Dichroic effects are observed, qualitatively similar to those in the GIR spectra: the same bands are consistently affected, e.g. the 1732 cm⁻¹ C=O stretching absorption is e.g. stronger in the 0° spectrum than in the 90° spectrum.

For the GIR spectra we argued that the relatively high intensity of the carbonyl band was caused by the fact that the angle of the C=O stretching vibration dipole transition moment with the helix axis is larger than 55° in crystalline i-PMMA, resulting in a higher absorption value for IR radiation polarized in a direction perpendicular to the helix axis than for a polarization parallel to this axis (appendix 3). The observation that light polarized perpendicular to the dipping direction is absorbed more strongly by the carbonyl dipoles than radiation polarized parallel to the transfer direction, indicates that the helices must be oriented preferentially in the
dipping direction. A similar orientation of helical structures in the transfer direction has been reported by various authors (3, 14, 17, 27). The lateral orientation of the isotactic PMMA helical structures must be caused by the flow that occurs at the meniscus between the substrate and the water surface as the monolayer is transferred onto this substrate, and the shear forces accompanying this process. A 90° rotation of the substrate with respect to the movement direction of the moving barrier yields the same results, indicating that the lateral orientation observed in the multilayers is caused by the transfer process itself, and not by a preferential orientation of the helices in the monolayer on the water surface due to the direction of the moving barrier during compression. In chapter 4, we will address this latter possibility.

Figure 3.18. Polarized transmission spectra of an as-deposited multilayer of i-PMMA (Mn 36.10, transfer pressure 12 mN/m), and the difference spectrum. Polarization direction is indicated. All spectra are shown on the same scale.

In order to quantitatively discuss this lateral orientation effect, we introduce a lateral orientation parameter \( L \) defined as:

\[
L_x = \frac{I_{90} - I_0}{I_{90} + I_0}
\]

in which \( I_{90} \) and \( I_0 \) represent the absorption intensities of band \( x \) using radiation polarized perpendicular and parallel to the transfer direction, respectively. For the
situation that all helices are oriented parallel to the substrate, in the XY plane, this value can vary between -1 and +1, these values only being able to be reached in the case of perfect orientation by absorption bands associated with dipole transition moments with \( \phi = 0^\circ \) or \( \phi = 90^\circ \), intermediate values of \( \phi \) leading to smaller absolute asymptotic values (appendix 3). For the \( \text{C}=\text{O} \) stretching vibration, with \( \phi > 55^\circ \), positive values for this parameter indicate a preferential orientation of the helical structures parallel to the transfer direction, negative values a preference for the direction perpendicular to the transfer direction. For the spectra of figure 3.18, a value of 0.07 can be calculated for \( \text{L}_{C-O} \).

When the as-deposited multilayer is heated to 70°C, above \( T_g \), we observe, as in the GIR experiments, that the anomalous crystalline features are retained. The \( \text{L}_{C-O} \) value increases slightly (from 0.07 to 0.09). Upon annealing at 120°C, the effect of the (post-)crystallization process can also be followed in the transmission spectra (figure 3.19). The crystalline features in the spectrum become much more pronounced than in the as-deposited spectrum, and, as in the GIR spectra, the dichroic effects are strongly enhanced upon annealing at 120°C. The \( \text{L}_{C-O} \) value for the crystallized film is 0.26, already indicating a fairly strong preferential orientation of the helices in the original dipping direction. The spectrum obtained by digitally subtracting the 90° and the 0° spectra illustrates the dichroic effects observed; the

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**Figure 3.19.** Polarized transmission spectra of the film from figure 18, after annealing for 3 days at 120°C, and the difference spectrum. All spectra are shown on the same scale.
agreement with the dichroic effects observed in the GIR spectrum can easily be verified. When the crystallized multilayers are heated to 170°C, all crystalline features and all dichroic effects in the transmission spectra vanish.

An increase of the dipping speed from 4 to 16 mm/min did not significantly affect the lateral orientation in the transferred multilayers: both the as-deposited as well as the crystallized films yield similar $L_{c=0}$ values for both dipping speeds. When a multilayer is built by transferring low molecular weight i-PMMA ($\bar{M}_n$ 2.8.10$^3$, not being able to crystallize at the water surface) at the same surface pressure, neither the as-deposited multilayers, nor these films after annealing at 120°C, exhibit any lateral orientation effects. For all molecular weights, Langmuir Blodgett layers transferred from the water surface at low surface pressures from the expanded amorphous conformation also did not show any significant differences between the 0° and the 90° transmission spectra.

![Figure 3.20](image)

**Figure 3.20.** $L_{c=0}$ values as a function of molecular weight ($\bar{M}_n$). (v) as-deposited, stabilization at 12 mN/m; (A) same films following post-crystallization; (o) as-deposited, stabilization at 6.5 mN/m; (o) same films following post-crystallization. Transfer pressure 12 mN/m.
Variation of the lateral orientation. The lateral orientation observed in the multilayers transferred at 12 mN/m exhibits remarkable variations with the monolayer crystallization conditions and the molecular weight characteristics of the isotactic PMMA samples used. Figure 3.20 summarizes experimental data for both as-deposited, as well as post-crystallized thin films.

The first observation we can extract from this figure is that in all cases the lateral orientation is strongly enhanced by the post-crystallization process. With increasing molecular weights, the value for the lateral orientation parameter $L_{c-o}$ increases consistently, both for the as-deposited as well as for the annealed films. The use of the highest molecular weight samples results in multilayers in which the preference for the dipping direction becomes very strong, especially following after post-crystallization at 120°C. For the crystallized films of the highest molecular weight samples, this results in values for $L_{c-o}$ close to 0.45; the spectra for this film are shown in figure 3.21. The dichroic effects observed in the 90° spectrum are of a similar magnitude as those observed in the GIR spectrum indicating that the preference for an orientation parallel to the dipping direction is similarly strong as the preference of the helices for the plane parallel to the substrate. The dichroic effects in these spectra appear to be even stronger than those observed in the polarized IR spectra of isotactic PMMA, uniaxially crystallized after being stretched up to draw ratios of 10-
15, as reported by Dybal and Krimm (28).
Lowering the molecular weight of the i-PMMA results in a decrease of the $L_{c-o}$ value, which becomes zero at molecular weights of about $15.10^3$. For these materials there appears to be no overall preference for either direction within the $XY$ plane. Lowering the molecular weight even further (clearly into the critical regime, without entering it so far that the helix formation is completely suppressed), we observe negative values for the orientation parameter, indicating a preference of the helices for an orientation perpendicular to the transfer direction. A similar reversal of the preferred helix orientation is observed when a monolayer of i-PMMA with an intermediate molecular weight ($\overline{M_n} 36.10^3$) was stabilized at the water surface at a relatively low surface pressure (6.5 mN/m), allowing the helix formation to take place slowly under mild conditions, with a low thermodynamic driving force relative to the original procedure, which featured a compression of the monolayer with a compression speed of approximately 5 Å²/repeating unit.minute, the crystallization taking place at surface pressures of 9 mN/m and higher. Upon completion of the monolayer crystallization process at 6.5 mN/m, the monolayer was further compressed to a surface pressure of 12 mN/m, and subsequently transferred to the substrate; the resulting multilayers also yield a negative value for the $L_{c-o}$, again indicating a preferential helix orientation perpendicular to the transfer direction.

The observation that monolayers of i-PMMA can be transferred in such a way as to give rise to an orientation of the helices perpendicular to the dipping direction cannot be explained if we consider the monolayer as a collection of individual helices being oriented in the direction of the flow, and is also unique in the sense that such a flow induced perpendicular orientation was never reported for other helical substances at the air water interface. Isotactic PMMA differs from these other substances by the fact that the helical structures are formed in a monolayer crystallization process, rather than being spread at the air water interface as helical structures. In this respect, i-PMMA was suggested to be organized in monolayer crystallites, as a result of a lamellar growth process. If we assume that the lateral coherence between the helices within the crystallites is very strong, we can imagine that the rigid structures, behaving as the rheological entities and being oriented in the flow direction, are not the individual helices, but rather the crystallites that the helices are part of.

Accepting the idea of the crystallites being oriented rather than the helices themselves, it may be clear that an orientation of these crystallites parallel to the dipping direction may imply a preferential orientation of the helices perpendicular to the transfer direction, if the aspect ratio of the crystallites is such that the longest axis of the crystallites is oriented perpendicular to the helix axes within the crystallite. This possibility is illustrated by figure 3.22. Following this argumentation, the aspect ratio of the crystallites will be a very important parameter in determining the lateral orientation.
The aspect ratio will be determined by the crystallization process, which was suggested to feature a onedimensional crystallite growth. If the crystallites have the opportunity to grow extensively before running into another growing crystallite (i.e. a low nucleation density), broader crystallites can be imagined to result compared to a situation in which crystallite growth is limited by a high nucleation density. The experimental results also suggest a correlation between the monolayer nucleation density (and indirectly the crystallite aspect ratio) and the observed lateral orientation. If the monolayer crystallization is to occur at low surface pressures (e.g. 6.5 mN/m), the critical nucleus size will be relatively large because of the low thermodynamic driving force for helix formation. Therefore the nucleation density will be low, leading to large crystallites to be formed: because of the onedimensional character of the growth, this will correspond to broad crystallites, broader than the crystallites formed during crystallization at higher surface pressures. These arguments can be used to explain the difference in lateral orientation between the 6.5 mN/m stabilized monolayers of the Mn 36.10\(^9\) material, and the monolayers of the same material that were rapidly compressed to 12 mN/m.

For the materials with lower molecular weights, in the critical regime, the nucleation process can be expected to be suppressed relative to the high molecular weight samples, since these samples approach the critical chain length for helix formation under these conditions: the gain in free energy upon helix formation will be lower than that of higher molecular weight samples under identical conditions, leading to a
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larger critical nucleus size, and consequently to a lower nucleation density. Again, the lower nucleation density may eventually lead to broader crystallites and a helix orientation perpendicular to the transfer direction, as is experimentally observed. Mixing of i-PMMA fractions of intermediate molecular weights (e.g. $\bar{M}_n 36.10^6$) with a oligomeric fraction ($\bar{M}_n 2.8.10^3$, not being able to crystallize itself) also yields deviating values for $L_{c-o}$: using mixtures with 26 and 45% oligomeric material, multilayers can be built in which the preference of the helices for the dipping direction has disappeared, and even small negative values are observed. Probably, in these mixtures, we are also dealing with a suppressed nucleation rate (as will be elaborated on in chapter 6) due to the presence of the low molecular weight component, lowering the thermodynamic driving force for crystallization through the demixing process that has to take place upon crystallization.

The correlation of the lateral orientation with the anticipated aspect ratio of the crystallites works quite well for the effects discussed above, although it should be emphasized that considering the crystallites as isolated units being oriented in the flow direction may still present a somewhat oversimplified model, neglecting e.g. possible effects due to tie molecules connecting different crystallites, which may considerably complicate the picture. Especially when using high molecular weight samples, these tie molecules may play an important role in determining the rheological behaviour. The consistent increase of the lateral orientation observed with increasing molecular weights up to one million, can no longer be correlated with differences in the aspect ratio of the crystallites, but must be caused by the increased viscosity, related to the presence of such tie molecules. In this respect it is interesting to note that when a high molecular weight sample ($\bar{M}_n 250.10^6$) is transferred following a monolayer crystallization process at 6.5 mN/m, a preferential helix orientation parallel to the transfer direction is observed (although less strong than for the monolayer crystallized at higher surface pressures (figure 3.20)), in contrast to the $\bar{M}_n 36.10^6$ material, which exhibited an inverson of the preferential orientation. This difference may be caused by complications due to a stronger contribution of tie molecules for the higher molecular weight sample.

Summarizing, we see that the lateral orientation of the crystalline structure in the multilayers can be controlled by the molecular weight composition as well as by the monolayer crystallization surface pressure. An important conclusion is that, unlike other helical substances, the (double) helices of isotactic PMMA are not oriented individually, but as organized crystallites. The reason for this difference must be the lateral coherence of the helices within the crystallites, probably enhanced by their (speculative) lamellar nature, maybe with tight folds inhibiting their mobility. The alignment of the helices in the crystallites is clearly of another nature than a simple alignment of the helices with a local nematic type ordering, which may be expected
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for other types of helical substances (29). In this last case, during flow, the helices may still be oriented individually due to the lack of lateral coherence. The typical behaviour of isotactic PMMA may have an analogy in the rheological behaviour of liquid crystalline materials: for mesogens exhibiting a nematic ordering (without strong specific lateral interactions), an orientation in the flow direction is usually observed, whereas for layer-like smectic phases (with the mesogens laterally organized), an orientation of these smectic layers in the flow direction is observed, the mesogens oriented perpendicular to it (30, 31).

CONCLUSIONS.

In this chapter we demonstrated that monolayers of isotactic PMMA exhibit a crystallization process upon compression, analogous to the melt crystallization process. The process was described in terms of an activated nucleation stage with a subsequent onedimensional (lamellar type) growth of the crystallites, these crystallites consisting of one monolayer of double helices parallel to the air water interface. Remarkable differences with the melt crystallization process include the time scale associated with the crystallization process and the insensitivity of the monolayer process for high molecular weights; this latter aspect was rationalized in terms of the absence of entanglements in the monolayer.

These crystallized monolayers can be transferred to solid substrates to give highly crystalline films following a short annealing procedure. Without this LB technique, the preparation of very thin films of crystalline i-PMMA would be extremely time consuming. The crystalline thin films formed were shown to have distinct orientational characteristics, the crystalline helices oriented parallel to the substrate, but also with a clear preferential orientation within the XY plane. The crystallization conditions and the sample characteristics provide good handles to control these lateral orientational characteristics, which can be changed from parallel to, to perpendicular to the transfer direction. The almost uniaxially oriented thin films that can be prepared this way, may be interesting because of the easily controllable anisotropy of various properties.

The indications for the suggested crystallization process are fairly consistent, although admittedly indirect: more direct evidence may be obtained using high resolution imaging techniques as AFM or STM, which may be able to prove the existence of the speculative monolayer crystallites, and to yield quantitative information about their dimensions.
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