Monolayer and thin film behaviour of stereoregular poly(methacrylates)
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Chapter II.

Influence of the tacticity on the monolayer behaviour of poly(methacrylates)

ABSTRACT. In this chapter, the monolayer behaviour of some poly(methacrylates) with short ester side chains (methyl, ethyl and isobutyl) is studied as a function of the tacticity. In all cases, the isotactic polymers are observed to form expanded monolayers, whereas the syndiotactic materials yield more condensed monolayers. These observations were attributed to differences in the lateral cohesive interactions of the segments in the monolayer, which again can be correlated to the difference in spatial orientation of the ester groups with respect to the backbone and the air water interface. The anomalous temperature dependence of the isotactic polymers (a contraction of the monolayers at higher temperatures) can be interpreted in terms of an enhancement of these lateral cohesive interactions. Surface potential measurements yield results which appear to be in agreement with the interpretation of the monolayer isotherm data. Isotactic poly(methacrylic acid) is observed to form stable monolayers on a pure water subphase, in contrast to syndiotactic PMAA.

INTRODUCTION.

The monolayer behaviour of poly(methacrylates) has been extensively studied in the last 50 years. This standard class of polymers can easily be spread on the water surface to give well defined monolayers, due to the amphiphilic character of the materials, the polar parts of the ester groups representing the hydrophilic part, and the backbone, the $\alpha$-methyl groups and the ester alkyl side chains composing the hydrophobic part. Crisp already reviewed the behaviour of these materials in 1946 (1). Since then, a lot of effort has been dedicated to the investigation of the monolayer behaviour of all kinds of poly(methacrylates), with the ester side chains ranging from methyl up to octadecyl groups (2, 3, 4, 5), including aromatic (6, 7) and branched (8, 9) substituents, and incorporated dye functionalities (10).

With all this work on these poly(methacrylates), the matter of the tacticity of the polymers has hardly been addressed. Beredjick and Ries (11, 12, 13) published isotherms of isotactic, syndiotactic, and atactic and PMMA 30 years ago: the
pressure-area isotherms of the isotactic polymer proved to be quite different from those of the atactic and the syndiotactic samples. No adequate explanation was given at that time. Sutherland and Miller (14) also reported isotherms for isotactic PMMA, but since then monolayers of isotactic PMMA have not received much attention in the literature. Very recently, Henderson and Richards also published isotherms of isotactic PMMA (15). Sutherland and Miller also reported isotherms of several polymeric tert-butyl esters of varying tacticity: the observed differences were explained in terms of a different packing efficiency of the segments in the monolayer (14). Schouten (16) recently reported on the monolayer behaviour of atactic and isotactic poly(octadecylmethacrylate) (PODMA): no significant effects of the stereoregularity were observed.

In this chapter, we will discuss the monolayer behaviour of some stereoregular poly(methacrylates) with rather short ester side chains: poly(methylmethacrylate), poly(ethylmethacrylate) and poly(isobutylmethacrylate). The short side chains can be expected to result in a clearly observable effect of the backbone stereoregularity, without this effect being overshadowed by the behaviour of long hydrocarbon tails (as is the case for PODMA). For these materials, we hope to be able to interpret a stereoregularity effect in terms of the conformational structure of these materials at the air water interface. The results and discussion section first deals with the isotherm data obtained from these monolayers, subsequently with surface potential measurements on these monolayers, and finally with infrared data collected from transferred LB layers. At the end of this chapter, we will shortly address the effects of the tacticity on the monolayer behaviour of poly(methacrylic acid).

**EXPERIMENTAL.**

The LB troughs used to monitor the monolayer behaviour, are described in appendix 1. All materials were spread from approximately 0.3 g/l chloroform solutions, except for the poly(methacrylic acid) samples (insoluble in pure chloroform), which were spread from DMF/CHCl₃ (35:65 v/v) mixtures. A description of the characteristics of the samples used can also be found in appendix 1, as well as a description of the apparatus and procedures used to acquire infrared data on the transferred monolayers. Surface potential measurements were carried out at the Max Planck Institut für Biophysikalische Chemie in Göttingen, BRD, in collaboration with Prof. D. Möbius. Experiments were performed using the vibrating plate technique (17), with simultaneous recording of the surface pressure using a Wilhelmy plate.
RESULTS AND DISCUSSION.

Figure 2.1. Pressure area isotherms of syndiotactic (s), atactic (dashed line) and isotactic (i) poly(methylmethacrylate) (m8) at 22°C.

A. Monolayer isotherms.

Figure 2.1 shows pressure area isotherms of syndiotactic, atactic and isotactic PMMA, recorded at room temperature. It can easily be seen that the isotactic polymer has a distinctly different monolayer behaviour as compared to the atactic and the syndiotactic samples. As mentioned in the introduction, the first authors to report pressure area isotherms of isotactic PMMA were Beredjick and Ries (11, 12, 13). Beredjick interpreted the isotherm as consisting of at least three distinct parts (0-8 mN/m, 8-18 mN/m, and the region of even higher surface pressures) and determined characteristic limiting areas for all these regions by extrapolation to zero surface pressure. The structural nature of the deviating monolayer behaviour of isotactic PMMA was not addressed in detail. The linear extrapolation of the low pressure part of the isotherm is quite arbitrary, since there appears to be no actually linear part in the isotherm in this region. Instead, the isotherm is very similar to those of expanded type monolayers as poly(vinylacetate) (18, 19) and poly(methylacrylate) (20), exhibiting a surface pressure build up even at large areas because of the geometric constraints (which limit the number of available conformations and thus the entropy) imposed on the twodimensional coils formed by these polymers at the air water interface. A comparison of the monolayer behaviour of stereoregular poly(ethyl-
Tactility effects

methacrylate) and poly(isobutylmethacrylate) (figure 2.2 and 2.3, respectively) indicates similar trends as observed for poly(methylmethacrylate): in all cases the isotherms of the isotactic polymers are characterized by a long tail extending to large areas, indicating an expanded condition of the monolayer, whereas for the syndiotactic polymers pressure area isotherms suggest a more 'condensed' monolayer, characterized by a contracted chain conformation and a high segment density.

The transition at approximately 20 Å²/monomeric unit observed in the compression isotherm of i-PMMA will be discussed in chapter 3.

Figure 2.2. Pressure area isotherms of syndiotactic (solid line, s), atactic (dashed line), and isotactic (i) poly(ethylmethacrylate) at 22°C.

Figure 2.3. Pressure area isotherms of syndiotactic (#b6, solid line, s), atactic (#b3, dashed line), and isotactic (i) poly(isobutylmethacrylate) (#b1) at 22°C.
Monolayer thermodynamics: isotherm fitting. The thermodynamics of monolayers of polymeric substances have been described by various authors. For the evaluation of the monolayer behaviour of the stereoregular poly(methacrylates), we have chosen to use the equation of state theory as formulated by Matuura and Motomura (21). They used a twodimensional lattice model for polymeric monolayers similar to Singer’s original approach (22), but in their calculation of the equation of state they explicitly took into account both the entropic constraints due to the limited available area, as well as the enthalpic effects due to the area dependent number of intersegmental contacts on the lattice. Enthalpic effects due to cohesive lateral interactions are not accounted for in Singer’s original theory. Gabrielli and Huggins (23) later developed and used a more elaborate thermodynamic model, in which more parameters are used to describe relevant physical quantities. We have chosen to use the approach of Matuura and Motomura because of the low number of parameters that have to be fitted.

In the treatment of Matuura and Motomura, the surface pressure of a polymer monolayer (Π) is described in terms of the actual ('hard') area occupied by a segment (A₀), the fraction of lattice sites occupied, the lattice coordination number Z, the number of segments per chain r, the temperature, and the contact enthalpy for two segments on adjacent lattice sites W.

\[
Π = \frac{kT}{A_0} \left[ \ln \left( \frac{r}{q^v (\frac{r}{q} - 1)} \right) - \frac{Z}{2} \ln \left( \frac{r}{q} - 1 \right) - \frac{Z}{2} \ln \frac{\beta + 2v - 1}{\nu(\beta + 1)} \right]
\]

with:

\[
q = \left[ 1 - \frac{2}{Z} (1 - \frac{1}{r}) \right] r
\]

\[
\beta = \left[ 4\nu\nu(\eta^2 - 1) + 1 \right]^{\frac{1}{2}}
\]

\[
\eta = \exp \left( \frac{W}{kT} \right)
\]

with v and u as the fraction of empty and occupied sites on the lattice, respectively. Favourable enthalpic interactions are represented by a positive value for W. In contrast to Singer’s original theory, the exact value of Z is not essential for a good fit to be obtained. In examples discussed by Matuura and Motomura, a coordination number of 4 was used, which appears to be a realistic value for a twodimensional...
system. In Singer's treatment, for condensed monolayers, very low $Z$ values close to 2 must be used (so as to lower the contribution of the conformational entropy), which do not seem to have a direct physical meaning. In the calculations we performed, a standard value of 4 was used; with this value, the effect of the molecular weight is small for reasonable values for $r$. In our fits we substituted the experimentally determined degree of polymerization $\overline{P_n}$ for $r$. The area pro monomeric unit $A_0$ and the interaction parameter $W$ were varied so as to produce the best fit with the experimental data from the isotherms.

![Figure 2.4. Fit of experimental isotherm data (22°C): a: i-PMMA; b: a-PMMA.](image)

The model proves to give satisfying results in fitting the surface pressures up to about 6 mN/m: the values obtained from the fit procedures appear to be useful at least for mutual relative comparisons. In figure 2.4a, the pressure area isotherm of isotactic PMMA, as calculated by the procedure described above, is drawn together with the experimental data. The fit parameters $A_0$ and $W/kT$ can be varied only over a rather narrow range to produce acceptable fits: for $A_0$, the fit uncertainty is only some tenths of $\AA^2$/monomeric unit, with an accompanying variation in the value for $W/kT$ of several hundredths.

If we compare the values obtained for isotactic PMMA with those derived from the isotherms of a predominantly syndiotactic PMMA (figure 2.4b), we see that the value for the intersegmental cohesion energy $W$ is much higher for the latter materials (table I); the value for $A_0$ is somewhat lower. The fact that the simulated curve for syndiotactic PMMA drops to give negative values for the surface pressure, whereas the experimental curve does not, is a consequence of the fact that the pressure is calculated for a 'homogeneous' system, whereas in the real monolayer, phase separation can occur. The concentrated phase should then correspond to the point
where the calculated curve crosses the zero pressure line, that is, where the free energy of the system has a minimum ($\Pi = \delta F/\delta A = 0$). Experimental indications for such macroscopic phase separation phenomena include patchy structures observed with dark field illumination microscopy (1), ellipsometry (24) and surface potential measurements as discussed later in this chapter. Poupinet (25) reported negative second virial coefficients for atactic PMMA monolayers, illustrative of attractive interactions between the twodimensional PMMA monolayers.

### Table I. Fit results.

<table>
<thead>
<tr>
<th>sample #</th>
<th>tacticity</th>
<th>$W/kT$</th>
<th>$A_0$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m8</td>
<td>&gt;97</td>
<td>0.29</td>
<td>13.7</td>
</tr>
<tr>
<td>m25</td>
<td>90 8 2</td>
<td>0.37</td>
<td>13.6</td>
</tr>
<tr>
<td>m26</td>
<td>81 15 4</td>
<td>0.43</td>
<td>13.2</td>
</tr>
<tr>
<td>m28</td>
<td>66 28 6</td>
<td>0.62</td>
<td>13.0</td>
</tr>
<tr>
<td>m31</td>
<td>3 34 63</td>
<td>1.35</td>
<td>12.2</td>
</tr>
<tr>
<td>m45</td>
<td>1 14 85</td>
<td>1.38</td>
<td>12.1</td>
</tr>
</tbody>
</table>

The isotherms of a series of PMMA samples of varying tacticities were analyzed using this approach: the results are reported in table I. The calculated cohesive energy parameter ($W/kT$) is plotted as a function of the diad tacticity in figure 2.5. Starting from the highly isotactic material, the value extracted for $W/kT$ increases rapidly as the meso diad content decreases.

![Figure 2.5. Interaction parameter $W/kT$ as a function of meso diad fraction of PMMA.](image-url)
It should be emphasized that the absolute significance of the fit parameters is obviously subject to the limitations of the lattice model; e.g. possible pressure induced changes in the lateral cohesive interactions related to varying orientations of the segments cannot be accounted for, possible effects of variations of the persistence length of the polymers are not considered, details of local segmental correlations are neglected because of the mean field nature of the approach, and the exact nature of the segment-segment interactions cannot be taken into consideration. Especially for the condensed monolayers, a lattice model with one value for the interaction enthalpy will be gross oversimplification, and the experimental isotherms will strongly depend on the details of the segments that are in so intimate contact. Vilanove and Rondelez (26) derived scaling exponents for monolayers of atactic PMMA, suggesting that the polymeric monolayers are best characterized as being in a surface (sub)-theta state. Since they also used the steep part of the isotherm to calculate the scaling exponent, without taking into account the monomer-monomer interactions, this result is subject to similar criticism; in a later publication, the scaling exponent was determined from the low surface concentration regime, yielding similar values (25).

Structural interpretation. The cohesive interactions between the segments at the air water interface may contain several contributions. Apart from forces associated with the non-polar parts of the segments, there may be significant contributions from the dipolar interactions originating from the polar parts of the ester groups, if the chains can approach each other closely enough (i.e. unless they are held far apart by steric interactions of bulky side groups). These latter interactions of the polar moieties will be strongly affected by their interaction with the water subphase. To explain the apparently strong differences in cohesive interactions in the monolayer, it is important to discuss the conformational characteristics of isotactic and syndiotactic PMMA. Calculations on the various possible conformations of isotactic and syndiotactic PMMA have been carried out by Vacatello and Flory (27), and by Sundararajan (28, 29). For isotactic PMMA, the dominant backbone conformation corresponds to (slightly twisted) trans-trans conformations of successive C-C bonds; other conformations may contribute significantly, since the energy differences are not very large: the backbone of isotactic PMMA is quite flexible. Syndiotactic PMMA has a much stronger preference for an all-trans backbone conformation: the energy of deviating backbone conformations is much higher, resulting in a strong domination of all trans backbone sequences. At the air water interface, the energy of these macromolecules will of course be strongly affected by their asymmetric environment, but the intrinsic energy of the polymer itself can be expected to provide extra boundary conditions for the conformational characteristics. For isotactic PMMA in this favourable nearly all trans conformation, the ester groups are all more or less on the same side of the polymer backbone: the polymer has a
clear overall amphiphilic character (figure 2.6). This may allow this part of the chain by a simple rotation to orient itself favourably with respect to the water subphase similar to a low molecular weight amphiphile, with the hydrophilic part (the ester groups) oriented toward the water phase, and the more hydrophobic part (the main chain and the α-methyl groups) more or less on the air side. Furthermore, the flexibility of the isotactic PMMA backbone easily allows for small conformational adjustments so as to optimize this amphiphilic orientation, which may well extend over a large number of segments. Such sequences of oriented segments can be argued to stabilize the orientation of the individual segments, since a segment cannot rotate completely independently from its neighbouring segments, suggesting that some kind of cooperative effect may be responsible for maintaining such an amphiphilic segment orientation. In contrast, for syndiotactic PMMA, a complete alignment of its ester groups on the water side would require very strong deviations from the all-trans backbone conformation, which will be impeded by the low backbone flexibility.

Figure 2.6. Schematic drawing of isotactic (i) and syndiotactic (s) PMMA in an all-trans conformation; carbon atoms coloured dark, oxygen atoms light. Note the amphiphilic architecture of the isotactic chain.

These suggested differences in ester group orientation in isotactic and syndiotactic PMMA may affect the lateral cohesive interactions between the segments in the monolayer. In isotactic PMMA the ester groups will tend to point downward toward the water phase, instead of inevitably more or less sideways as in syndiotactic PMMA (figure 2.6). The dipolar interactions between the ester groups can be screened by the water phase more effectively in the case of isotactic PMMA, whereas in syndiotactic PMMA these dipolar interactions may contribute significantly stronger to the lateral cohesive forces in the monolayer, since a selective submersion of its hydrophilic parts is not efficiently possible: submersion of the ester groups would be accompanied by a submersion of more hydrophobic parts of the molecule, which, if it were to occur,
would cause strong hydrophobic interactions to contribute to the lateral cohesive interactions. The cohesive forces due to the polar ester group interactions may even have a self-enhancing character: the proximity of other segments may induce orientation and conformation changes so as to optimize their mutual interaction.

The stereoregularity of the backbone has a similar effect on the monolayer behaviour of PEMA and PiBMA, which can be explained through analogous orientational differences as discussed for PMMA. In the case of PiBMA, the importance of the large ester side chain may be higher relative to the backbone in terms of determining the interactions with neighbouring segments. For this material we can observe significant differences between the conventional atactic and the highly syndiotactic polymer, more than for PMMA and PEMA: the isotherm of the atactic polymer shows a pressure onset at significantly higher areas than that of the syndiotactic material, and a higher compressibility in the low pressure regime. In this case it is conceivable that, next to the cohesive interactions, the packing efficiency of the large side groups plays a role, this efficiency being higher for the more stereoregular polymer. In general, with increasing dimensions of the ester alkyl groups, the effect of the stereoregularity of the backbone becomes smaller, the behaviour being dominated more and more by these side groups, the backbones (and ester moieties) being held further apart. In the case of poly(octadecylmethacrylate), no significant effect of the stereoregularity was observed, as reported by Schouten (16), the side chains completely dominating the monolayer behaviour.

**Temperature dependence.** Figure 2.7 shows the isotherms of isotactic PMMA as a function of temperature. The low pressure part of the isotherms reflecting the behaviour of the monolayer in the expanded state exhibits a rather surprising temperature dependence: the surface pressure associated with constant area pro monomeric unit decreases with increasing temperature, opposite to what can be expected for an entropy associated surface pressure. A negative value for the $\delta \Pi / \delta T$ is seldom found, and other expanded type polymeric monolayers like e.g. poly(methylacrylate) (20) and poly(vinylacetate) (19) exhibit an expansion with increasing temperatures. Isotactic PEMA and (to a less extent) isotactic PiBMA exhibit the same temperature dependence as isotactic PMMA: at higher temperatures the monolayers become less expanded (figures 2.8 and 2.9).

The unexpected temperature dependence of the surface pressure of the monolayers of isotactic poly(methacrylates) in the expanded condition can be explained by assuming temperature dependent lateral cohesive interaction energies. In poly(methacrylate) and poly(vinylacetate), the low level of the cohesive forces leading to an expanded monolayer for the atactic polymers may be caused by a higher degree of submersion in the subphase due to the absence of an extra hydrophobic methyl
Figure 2.7. Pressure area isotherms of i-PMMA. a: 10°C; b: 22°C; c: 32°C; d: 41°C.

Monolayers of poly(ethylene oxide) exhibit a temperature dependence similar to that of isotactic PMMA, although the effect is somewhat less pronounced (30). PEO is a water soluble polymer, that, at higher surface concentrations, adsorbs at the interface in a loop-tail structure, extending far into the subphase, up to distances comparable to the radius of gyration of the polymer in solution (31); at lower surface concentrations, the behaviour is probably more monolayer like (32). The monolayer behaviour of isotactic PMMA cannot be described following a similar model, since this polymer is not water soluble like PEO (an argument which is even...
Table II. W vs. T for i-PMMA.

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>W (10^{-3}J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.7</td>
</tr>
<tr>
<td>22</td>
<td>1.2</td>
</tr>
<tr>
<td>32</td>
<td>1.8</td>
</tr>
<tr>
<td>41</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Figure 2.8. Pressure area isotherms of i-PEMA. a: 10°C; b: 22°C; c: 32°C; d: 41°C.

Figure 2.9. Pressure area isotherms of i-PiBMA. a: 10°C; b: 22°C; c: 32°C; d: 41°C.
stronger for isotactic PEMA and PiBMA). Still, the negative value of $\delta\Pi/\delta T$ observed for PEO may have a similar origin as for the isotactic poly(methacrylates): it is known that upon raising the temperature, the solvent quality of water with respect to the PEO segments is lowered (33), leading to an effectively stronger cohesion between the PEO segments adsorbed at the interface.

The temperature dependence of the syndiotactic materials is different from that of the isotactic materials (figure 2.10): upon raising the temperature the main effects observed are a higher compressibility of the monolayer and a slightly higher limiting area, especially for PiBMA. These effects are probably related to the temperature dependent segment packing characteristics in the highly condensed monolayers.

![Graphs showing pressure area isotherms](image-url)

**Figure 2.10.** Pressure area isotherms for s-PMMA (a), s-PEMA (b) and s-PiBMA (c) at 10°C (solid lines) and 41°C (dashed lines).
B. Surface potential measurements.

More information about the conformation of the poly(methacrylates) at the air water interface can be inferred from surface potential measurements. Crisp (1) already reported surface potential measurements for a series of (atactic) poly(methacrylates). Although exploited for a long time, the measurement of the surface potential of a monolayer still suffers from difficulties in the quantitative interpretation of the data. This is due to the fact that the monolayer is not easily captured in an adequate model, and that the contribution of phenomena like e.g. the reorientation of the subphase molecules due to the presence of the monolayer is not well understood (17). The dipole moments deduced from the surface potential measurements are invariably too low compared to values known from bulk or solution measurements. Still, the values obtained appear to be very useful for mutual comparisons. Alexander (34, 35) tried to interpret the surface potential data in a more quantitative way, extracting rather detailed orientations of functional groups at the air water interface, using more or less empirically determined group contributions for this purpose. M"obius more recently applied a similar approach, distinguishing contributions from the monolayer water interface and the monolayer air interface (36). It is clear that such detailed analyses should be used with caution, especially in cases (such as the poly(methacrylates)) where there is probably not one single orientation, but where the surface potential is simply an average of a great variety of conformations present.

The best way to discuss the surface potential measurements is in terms of the $\mu_\perp$, the projection of the dipole moment of the repeating unit along the axis perpendicular to the interface. This value can be calculated from the surface potential data by the relation (17):

$$\mu_\perp = \frac{A \Delta V}{12\pi}$$

with: $\mu_\perp$: the surface dipole moment per segment (in mD),

$A$: the molecular area in Å² per repeating unit,

$\Delta V$: the surface potential in millivolts,

Since upon pressure build up, the monolayers yield a decreasing value for the dipole moment due to deformations that may occur, the most useful quantity to discuss in terms of the undisturbed monolayer is the value for $\mu_\perp$ extrapolated to zero surface pressure.

A typical example of a surface potential measurement is given in figure 2.11: the surface potential is measured simultaneously with the surface pressure. The gradual increase of the surface potential upon compression is the direct consequence of the
increasing surface concentration of monomer units; at low surface concentrations, the surface dipole moment per segment falls slowly upon compression. The results for the values of $\mu_{\perp, n=0}$ are summarized in table III.

Table III. $\mu_{\perp, n=0}$ (in D).

<table>
<thead>
<tr>
<th>Material</th>
<th>10°C</th>
<th>21°C</th>
<th>32°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>isotactic</td>
<td>0.385</td>
<td>0.35</td>
<td>0.315</td>
</tr>
<tr>
<td>atactic</td>
<td>0.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>syndiotactic</td>
<td>0.225</td>
<td>0.225</td>
<td>0.22</td>
</tr>
<tr>
<td>PEMA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>isotactic</td>
<td>0.455</td>
<td>0.425</td>
<td>0.395</td>
</tr>
<tr>
<td>atactic</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>syndiotactic</td>
<td>0.335</td>
<td>0.335</td>
<td>0.335</td>
</tr>
<tr>
<td>PiBMA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>isotactic</td>
<td>0.52</td>
<td>0.505</td>
<td>0.485</td>
</tr>
<tr>
<td>atactic</td>
<td>0.46</td>
<td>0.455</td>
<td>0.46</td>
</tr>
<tr>
<td>syndiotactic</td>
<td>0.42</td>
<td>0.42</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Recording the surface potential of monolayers of syndiotactic (and atactic) PMMA and PiBMA yields non-reproducible, fluctuating results up to close to the onset of the pressure build up, probably due to the fact that these monolayers do not cover the surface homogeneously, but tend to form large patchy structures, unlike the expanded monolayers of the isotactic materials. Still, in all cases the dipole moments could be determined with an accuracy of a few percent. From the results listed in table III, we can see that for PMMA as well as for PEMA and PiBMA, the values for the isotactic polymers are significantly higher than for the syndiotactic materials, with values for the atactic material close to those of the syndiotactic polymers. At the same time, the values for the dipole moments increase with larger ester alkyl substituents (as was observed already by Crisp (1)), not only for the syndiotactic samples, but also for the
isotactic polymers. Remarkable is the temperature dependence of the $\mu_{\perp, \text{ad}}$; for the syndiotactic polymers, there appear to be no significant variations in the temperature range studied, whereas for the isotactic polymers a consistent trend is observed of decreasing $\mu_{\perp}$ values with increasing temperature.

For the interpretation of these results, it is important to discuss the dipole characteristics of the poly(methacrylates). The dipole moment of these materials is mainly associated with the ester side group (37), and the value found for $\mu_{\perp}$ will be largely determined by the spatial orientation and the conformation of this ester group. Relevant variables include:

- the angle of the C(backbone)-C(=O) bond with respect to the water surface: this angle is subject to restrictions imposed by the tacticity of the backbone as discussed in the previous section.
- the angle of rotation over this bond: the dipole moment of the ester group makes an angle with this bond, being close to parallel to the C=O bond.
- the position of the ester alkyl group with respect to the C(backbone)-C(=O) bond; for a trans conformation, the absolute value of the dipole moment is lower than for a cis conformation. The direction of the dipole moment vector within the ester group is also different for these two conformations: in the cis conformation this vector makes a larger angle ($\sim 15^\circ$) with the C=O bond than in the trans conformation.

The segments at the air water interface will tend to orient themselves as favourably as possible, trying to accommodate their polar parts toward the water phase. Simultaneously, a conformation is favoured such that the dipole moment perpendicular to

**Figure 2.11.** Surface potential (solid line), $\mu_{\perp}$ (dashed line) and surface pressure for a monolayer of i-PMMA at 10°C.
Chapter 2

the interface is high (1). At the same time, the monolayer itself will influence the force field that the segments experience, this effect being especially strong in the case of high (local) surface concentrations. For isotactic PMMA, at low surface concentrations, the segments have a large degree of freedom so as to attain a favourable conformation of their ester groups: the backbone will not impose important restrictions, as discussed in the previous section. Also, because of the expanded nature of the monolayer, cohesive forces will be low, so that the optimal orientation of the ester groups is determined mainly by the water subphase, and not by interactions with neighbouring segments (apart from those to which they are covalently connected). The syndiotactic polymers, on the other hand, will experience strong lateral cohesive interactions, which will compete with the air-water interface in determining the spatial orientation and conformation of the ester groups. As suggested before, the backbone of the syndiotactic polymer will probably force the ester groups to point more or less sideways; still, this is not a direct inhibition for the ester groups to orient their dipole moment toward the interface, since this is oriented more along the C=O bond than parallel to the C(backbone)-C(=O) bond. An efficient orientation of the dipole moment is still possible by a suitable rotation over this latter bond, leading to interface structures as proposed by Crisp (1). The projection of the dipole moment along the z-axis will be very sensitive to variations in this rotation angle though. The strong cohesive forces in the s-PMMA monolayer are very likely to affect this orientation: the orientation that is optimal for the segment's interaction with the interface, will not be the most favourable with respect to the interaction with the neighbouring segments which are very close: e.g. a high value of the parallel dipole moments of two neighbouring segments may give rise to an unfavourable contribution to their interaction energy. Apart from this, the orienting influence of the water subphase on the s-PMMA segments may have been less pronounced to begin with because of the unfavourable (less amphiphilic) chain architecture. The overall orientational and conformational characteristics of the s-PMMA monolayer will therefore be the result of the competing forces exerted by the interface and the surrounding segments in the monolayer. It can easily be seen that this may lead to deviations in the rotation position of the ester group, in the position of the methoxy group (a significant amount of trans conformers present (strongly dominating in bulk PMMA (38))), and maybe also in the orientation of the ester group with respect to the backbone. Evidently, the average \( \mu_\perp \) will be lowered due to these cohesive interactions. This effect is comparable to the lowering of the \( \mu_\perp \) due to pressure effects: the strong cohesion induces analogous deformation effects.

For the materials with longer ester alkyl chains, higher values for \( \mu_\perp \) are observed. These large alkyl groups can be expected to cause several effects. In the first place, the growing unfavourable interaction between the water and this hydrophobic side chain will restrict the structural variation, since the rotational energy profile will have
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a more pronounced minimum. This is probably the reason for the increase in the dipole moment for the isotactic series. For the syndiotactic materials an extra effect will be steric hindrance caused by the large side groups. This causes the backbones (and the polar parts of the ester groups) to be further apart in the condensed state, leading to smaller influences of the cohesive interactions on the ester group orientation and conformation. The $\mu_{\perp}$ of the syndiotactic materials exhibits a stronger dependence on the length of the alkyl group than the isotactic materials, which may be due to this additional effect. The values found for the s-PiBMA samples are comparable to values that can be calculated based on Alexander's functional group contributions and monolayer structures as those suggested by Crisp (1), with dominating cis ester conformations.

The $\mu_{\perp}$ temperature dependence observed provides useful clues for the interpretation of the monolayer behaviour. For the syndiotactic materials, in the condensed state, no significant variations are observed. For the isotactic polymers in the expanded low cohesion condition, we do observe variations of the dipole moment with temperature, indicating variations in the orientation or conformation of the polymer segments. Higher temperatures probably lead to higher mobilities and more structure variations: the decrease in amphiphilic orientational order may thus be responsible for the lower dipole moments observed. These data correlate well with the observed increase in cohesive interactions in the monolayers of the isotactic materials.

C. Infrared experiments.

All polymers described in this chapter can be transferred to substrates to build multilayers, which can be studied by IR techniques in order to gain some insight in their orientational or conformational characteristics. Figures 2.12 and 2.13 show reflection-absorption IR spectra of gold supported multilayers of syndiotactic PMMA and syndiotactic PiBMA, respectively. These spectra may contain information on the orientation of the functional groups because of the fact that when using parallel polarized radiation, only vibrations associated with dipole transition moments with a component perpendicular to the substrate can absorb IR-radiation. We can see that the spectra of the as-deposited multilayers deviate somewhat from the spectra of the same films after a heat treatment above their Tg. The most significant differences are found in the ester vibrations in the 1000-1300 cm$^{-1}$ region, especially for the PiBMA films. Transmission spectra of multilayers on ZnS show opposite deviations, indicating that the observed differences are indeed orientation effects.

For these films, surface potential measurements indicate that the carbonyl group has to point more or less downward towards the water phase. If this orientation were to be retained upon transfer, we would expect to find a relatively strong C=O ab-
absorption peak in the reflection spectrum of the as-deposited multilayer compared to the isotropic film. This is not observed in the infrared spectra: on the contrary, the carbonyl band appears to be even slightly lower relative to the rest of the spectrum in the as-deposited film. Naito (9) already reported similar phenomena in transferred layers of atactic PiBMA, an observation which lead him to propose a structure with the ester groups located more or less at the air side of the backbone, with the carbonyl groups lying almost parallel to the water surface. It is clear that such a structure is contradicted by the surface potential results, which demand a more perpendicular orientation of the carbonyl groups, as e.g. suggested by Crisp (1).

![Absorbance vs Wavenumbers](image)

**Figure 2.12.** Grazing incidence reflection IR spectra of s-PMMA transferred to a gold substrate (transfer pressure 7 mN/m), before (a) and after (b) annealing at 140°C.

The apparent contradiction of the infrared results and the surface potential measurements suggests that the structure of the multilayers may not be identical to that of the monolayer on the water surface. This is not surprising: upon transfer, the monolayer loses its contact with the water surface and thus the driving force for the alignment of the carbonyl groups perpendicular to the interface. Since the monolayer is not fixed in any kind of crystalline order, we can expect that the monolayer structure is subject to relaxation processes. All syndiotactic materials studied have glass transition temperatures far above room temperature, so that extensive backbone motions are unlikely. In contrast, rotation of the ester group around the bond with which it is connected to the backbone, is feasible: this rotational motion is usually
associated with the $\beta$-relaxation observed in mechanical and dielectric measurements of these materials. At deformation frequencies of 1 c/s, this (broad) relaxation band has its maximum at 30°C (39) for PMMA. The $\beta$-relaxation process is rather insensitive to changes in the alkyl side group, and mobilities can be expected for PEMA and PiBMA (39). Since upon transfer, the monolayer will no longer feel the forces exerted by the subphase, the original monolayer structure will become unstable (due to the unfavourable parallel alignment of the ester dipoles), and will relax by rotation of the ester group. The result will be that the average angle of the carbonyl group with respect to the substrate is altered. This relaxation process will not lead to an isotropic structure, since it does not involve the polymer main chain: the average angle of the link between the backbone and the ester group may largely be retained. The anisotropic orientation of the ester group can still be inferred from the orientation effects in the ester vibrations in the 1000-1300 cm$^{-1}$ region; unfortunately, these absorption bands are all associated with coupled or delocalized vibrations, and the direction of their dipole transition moments with respect to the ester group is not clear (40), prohibiting detailed structural interpretation.

The spectra of syndiotactic PMMA show smaller deviations between the as-deposited and the isotropic films, since the structure of the monolayer will already be deformed by the high cohesive forces, as argued earlier on, and as can be deduced from the surface potential measurements. It is interesting to see that multilayers transferred at higher surface pressures yield spectra which are closer to the isotropic spectra.
indicating a higher degree of deformation in the monolayer, with the structure being less and less determined by the water subphase (figure 2.14).

**Figure 2.14.** GIR spectra of s-PMMA transferred at 2.5 mN/m (dotted), 12 mN/m (dashed), and after annealing at 140°C (solid line).

IR spectra of isotactic PMMA are reported in chapter 3: it is observed that upon transfer from the expanded condition, multilayers are formed yielding spectra which do not deviate significantly from isotropic spectra (41). In this case, we can imagine that backbone relaxation is possible upon transfer, since in the expanded state the segments can be expected to possess a high degree of mobility.

**Poly(methacrylic acid).**

Poly(methacrylic acid) (PMAA) can be spread from DMF/chloroform mixtures onto the water surface. In the case of syndiotactic (or conventional) PMAA, spreading on a pure water subphase does not result in a stable surface film: the polymer is dissolved in the subphase, and no pressure is detected upon compression. Isotactic PMAA on the other hand, forms well-behaved monolayers, instantaneously stable upon compression, with a collapse pressure of approximately 12 mN/m (figure 2.15); the tacticity evidently has a very strong effect on the stability of the molecules at the air water interface.

As for the poly(methacrylates), the differences in the monolayer behaviour of the stereoregular PMAA's can be traced back to the structural differences of the backbone. The acidity of the carboxyl groups in isotactic PMAA is somewhat less than
that of s-PMAA (42, 43), but this effect is small (several tenths of a pK, unit), and cannot be responsible for the extreme differences observed. More relevant is the fact that, due to the more amphiphilic character of the isotactic material, its interaction with the air water interface will be more favourable, following the same arguments as given for the poly(methacrylates). Parallel to this effect, the water solubility is lower. Isotactic PMAA is known to be sensitive to hydrophobic association processes at low degrees of ionization (for $\alpha<0.35$ (42, 44)). The effects of these hydrophobic association processes are stronger for the isotactic polymers than for the syndiotactic polymers, as can be inferred from the results of Barone (42) or Nagasawa (43), a phenomenon that is probably also directly correlated with the more amphiphilic architecture of the isotactic chains. In this context, the air water interface can be imagined to act as an infinite, strongly hydrophobic wall for adsorption of isotactic PMAA from solution, a process for which s-PMAA is less susceptible. Since isotactic PMAA is water soluble, it is tempting to compare its monolayer behaviour with that of poly(ethylene oxide), another water soluble material. The sharp collapse transition for both materials marks the surface concentration in equilibrium with the dissolved polymer; further compression simply drives the polymer into solution. As for PEO (30), the collapse pressure increases with increasing temperature, opposite to the behaviour of the poly(methacrylates). This observation for i-PMAA can be understood, if we consider the adsorption process to be caused by hydrophobic association type phenomena. Since hydrophobic association is entropy driven (45), adsorption can be anticipated to be stronger at higher temperatures, leading to higher collapse pressures and higher equilibrium surface coverages.

Figure 2.15. Pressure area isotherms of isotactic poly(methacrylic acid). a: 10°C; b: 21°C; c: 41°C.
CONCLUSIONS.

The monolayer behaviour of the polymethacrylates studied is strongly dependent on the tacticity of the backbone. In all cases, the isotherms of the isotactic polymers are characterized by an expanded tail extending to large areas, whereas monolayers of the syndiotactic polymers exhibit a more condensed character. The latter materials have a smaller dipole moment perpendicular to the water surface. The differences can be explained by the different spatial orientation of the ester and methyl side groups with respect to the backbone and the air water interface, leading to stronger cohesive interactions in the syndiotactic polymers than in the isotactic polymers, the isotactic polymers being able to assume a more natural amphiphilic orientation. The effects of the tacticity of the backbone become less pronounced with increasing length of the ester alkyl side chain.

Infrared measurements of multilayers of the syndiotactic polymers cannot be used to deduce the water surface orientation of the polymers, since relaxation processes with respect to the rotation angle of the ester group appear to be operative. Isotactic poly(methacrylic acid) forms stable monolayers on pure water subphases, in contrast to syndiotactic poly(methacrylic acid).

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