Monolayer Behavior of Some Stereoregular Poly(methacrylates)

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The monolayer behavior 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 are attributed to differences in the lateral cohesive interactions of the segments in the monolayer, which again can be correlated with 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 (a decrease of the solvent quality of the environment). Surface potential measurements yield results which appear to be in agreement with the interpretation of the monolayer isotherm data and also illustrate the monolayer crystallization process proposed for isotactic PMMA in a previous publication. Isotactic poly(methacrylic acid) is observed to form stable monolayers on a pure water subphase, in contrast to syndiotactic poly(methacrylic acid).

Introduction

The monolayer behavior of poly(methacrylates) has been extensively studied over the last 50 years. This standard class of polymers can easily be spread 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 α-methyl groups, and the ester alkyl side chains composing the hydrophobic part. Crisp already reviewed the behavior of these materials in 1946.[1] Since then, much effort has been dedicated to the investigation of the monolayer behavior of all kinds of poly(methacrylates), with the ester side chains ranging from methyl up to octadecyl groups,[2-5] including aromatic[6,7] and branched[8,9] substituents, or 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[11-13] published isotherms of isotactic, syndiotactic, and atactic poly(methyl methacrylate) (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. Jaffé et al. also compared isotactic and atactic samples of poly(methyl methacrylate) and suggested using the mono-layer characteristics as a measure of sample tacticity.[14] Since then monolayers of isotactic PMMA have not received much attention in the literature, until, very recently, Henderson and Richards published isotherms of isotactic PMMA[15] and Brinkhuis and Schouten extensively discussed the monolayer behavior of this material, identifying a pressure-induced crystallization process taking place in these monolayers.[16,17]

Sutherland and Miller 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.[18] Schouten[19] recently reported on the monolayer behavior of atactic and isotactic poly(octadecyl methacrylate) (PODMA); no significant effects of the stereoregularity were observed.

In this article, we will discuss the monolayer behavior of some stereoregular poly(methacrylates) with rather short ester side chains; apart from the poly(methyl methacrylates), poly(ethyl methacrylate) and poly(isobutyl methacrylate) (PiBMA) will be addressed. These short side chains can be expected to result in a clearly observable effect of the backbone stereoregularity, without this effect being overshadowed by the behavior 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 isotherms obtained from these monolayers and subsequently with surface potential measurements on these monolayers and infrared data collected from transferred LB layers. Finally, we will briefly address the effects of the tacticity on the monolayer behavior of poly(methacrylic acid).

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Table I

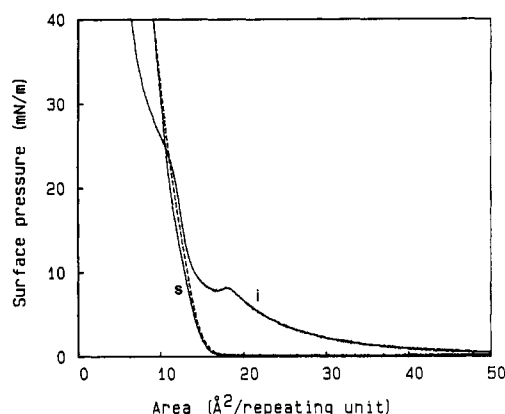| material	tacticity			$\bar{M}_n \times 10^{-3}$	D
	i	h	s		
PMMA					
isotactic	>97			36	1.17
atactic	5	31	64	33	1.14
syndiotactic	1	14	85	46	1.20
PEMA					
isotactic	95	5		115[a]	
atactic	6	28	66	n.d.	
syndiotactic	3	9	88	93[a]	
PiBMA					
isotactic	95	5		3.2	4.8
atactic	6	28	66	30	1.31
syndiotactic			3	97	16	1.09
PMAA					
parent					
isotactic PMMA	>97			36	1.18

[a] $\bar{M}_v$, determined in butanone.

Figure 1. Pressure–area isotherms of syndiotactic (solid line, s), atactic (dashed line), and isotactic (i) poly(methylmethacrylate) at 22 °C.

Figure 2. Pressure–area isotherms of syndiotactic (solid line, s), atactic (dashed line), and isotactic (i) poly(ethyl methacrylate) at 22 °C.

Figure 3. Pressure–area isotherms of syndiotactic (solid line, s), atactic (dashed line), and isotactic (i) poly(isobutyl methacrylate) at 22 °C.

Experimental Section

Characteristics of the samples used are listed in Table I. The poly(methacrylates) were synthesized according to procedures as described in ref 16. Syndiotactic PiBMA was synthesized according to the tBuLi–Al(n-octyl)$_3$ route suggested by Hatada.[20] Isotactic PMAA was the hydrolysis product of i-PMMA (i = isotactic);[21] from NMR spectra, the remaining ester group content was estimated to be 2.5%. 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/CHCl$_3$ (35:65 (v/v)) mixtures. The LB troughs used to monitor the monolayer behavior are described in ref 16, as is the apparatus used for the acquisition of the IR spectra. Surface potential measurements were performed at the Max Planck Institut für Biophysikalische Chemie, Göttingen, BRD, using the vibrating plate technique,[22,23] with simultaneous recording of the surface pressure using a Wilhelmy plate.

Results and Discussion

A. Monolayer Isotherms. Figure 1 shows pressure–area isotherms of syndiotactic, atactic, and isotactic PMMA, recorded at room temperature, and clearly illustrates the strongly deviating monolayer behavior of isotactic PMMA, as we discussed in a previous publication.[16] A comparison of the monolayer behavior of poly(ethyl methacrylate) and poly(isobutyl methacrylate)
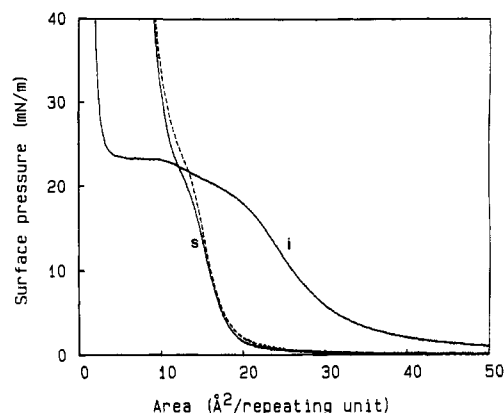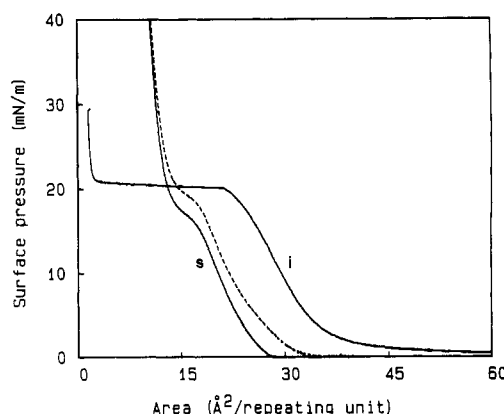
samples of different stereoregularities (Figure 2 and 3, respectively) shows similar trends as observed for poly(methyl methacrylate); in all cases the isotherms of the isotactic polymers are characterized by a long tail extending to large areas, indicating an expanded condition of the monolayer, whereas for the syndiotactic polymers, pressure–area isotherms suggest a more "condensed" monolayer, characterized by a contracted chain conformation and a high local segment density.

When considering the poly(methacrylate) monolayers as a two-dimensional solution, the differences in the monolayer behavior can be described in terms of strongly different levels of the lateral cohesive interactions between the segments in the monolayer, these interactions being much weaker for the isotactic polymers, leading to "good solvent conditions" experienced in the monolayer, in contrast to the syndiotactic materials.[16]

Structural Interpretation. The cohesive interactions between the segments at the air–water interface may contain several contributions. Apart from forces associated with the nonpolar parts of the segments, there may be significant contributions from the dipolar interactions originating from the polar parts of the ester groups. These latter interactions of the polar moieties will be strongly affected by their interactions with the water subphase.

For isotactic PMMA in the most favorable nearly all trans backbone conformation,[16,24] the ester groups are all more or less on the same side of the polymer; the polymer has a clear overall amphiphilic character (Figure 4). As we have argued in a previous publication,[16] this may allow

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Figure 4. Schematic drawing of isotactic (i) and syndiotactic (s) PMMA in an all-trans conformation. Carbon atoms are colored dark; oxygen atoms are light. Note the amphiphilic architecture of the isotactic chain.

this part of the chain by a simple rotation to orient itself favorably with respect to the water subphase similar to a low molecular weight amphiphilic molecule, with the hydrophilic part (the polar parts of the ester groups) oriented toward the water phase and the more hydrophobic parts (the main chain and the α-methyl groups) more or less on the air side. Furthermore, the flexibility of the isotactic PMMA backbone may easily allow small conformational adjustments so as to optimize this amphiphilic orientation, which may well extend over a large number of segments. In contrast, for syndiotactic PMMA, a complete alignment of its ester groups on the water side would require very strong deviations from the dominating all-trans backbone conformation, something which will be impeded by the low backbone flexibility of this material.[24] These suggested differences in ester group orientation in isotactic and syndiotactic PMMA can be argued to affect the lateral cohesive interactions between the segments in the monolayer. In isotactic PMMA the ester groups will tend to point downward the water phase, instead of inevitably more or less sideways as in syndiotactic PMMA (Figure 4). The selective submersion of the ester groups of the isotactic polymer causes the dipolar interactions between the ester groups to be screened effectively by the water phase. The structure of syndiotactic PMMA does not allow for such a selective submersion of the hydrophilic parts of the chains: 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 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 behavior of PEMA and PiBMA, which can be explained through analogous orientational differences of the segments as discussed above for PMMA. In the case of PiBMA, the importance of the large ester side groups may be higher relative to the backbone in terms of determining the interactions with neighboring segments. For this material we also 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 an additional role, this efficiency being higher for the more stereoregular polymer.

In general, with increasingly large ester alkyl groups, the effect of the stereoregularity of the backbone becomes smaller, the behavior being dominated more and more by these side groups, the backbones (and ester moieties) being held further apart. In the case of poly(octadecyl methacrylate), no significant effect of the stereoregularity was
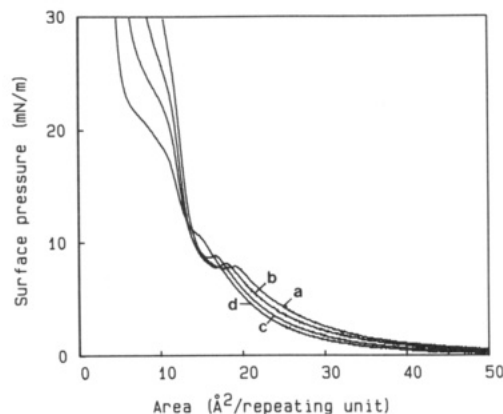

Figure 5. Pressure–area isotherms of isotactic PMMA: a, 10 °C; b, 22 °C; c, 32 °C; d, 41 °C.
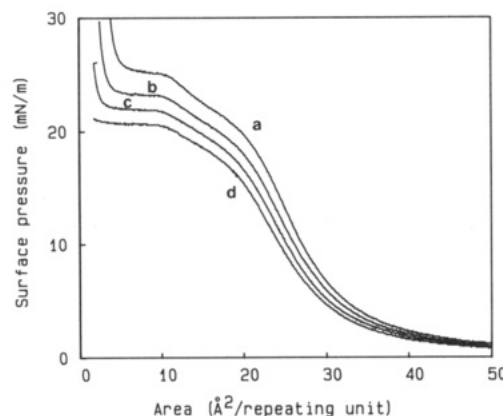

Figure 6. Pressure–area isotherms of isotactic poly(ethyl methacrylate): a, 10 °C; b, 22 °C; c, 32 °C; d, 41 °C.

observed, as reported by Schouten,[19] the side chains completely dominating the monolayer behavior.

Temperature Dependence. Figure 5 shows the isotherms of isotactic PMMA as a function of temperature. The low pressure part of the isotherms reflecting the behavior of the monolayer in the expanded state exhibits a rather surprising temperature dependence; the surface pressure associated with constant area per monomeric unit decreases with increasing temperature, opposite to what can be expected for an entropy associated surface pressure.[25] A negative value for the $\delta II/\delta T$ is seldom found, and other expanded type polymeric monolayers like e.g. poly(methyl acrylate)[26] and poly(vinyl acetate)[27] exhibit an expansion with increasing temperatures. Isotactic PEMA and (to a less extent) isotactic PiBMA qualitatively exhibit the same temperature dependence as isotactic PMMA; at higher temperatures the monolayers become less expanded (Figures 6 and 7).

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 interactions. In poly(methyl acrylate) and poly(vinyl acetate), 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 group, leading to a more effective solvation. For these polymers, we find that the monolayers expand at elevated temperatures, which is to be expected if the pressure is mainly entropy

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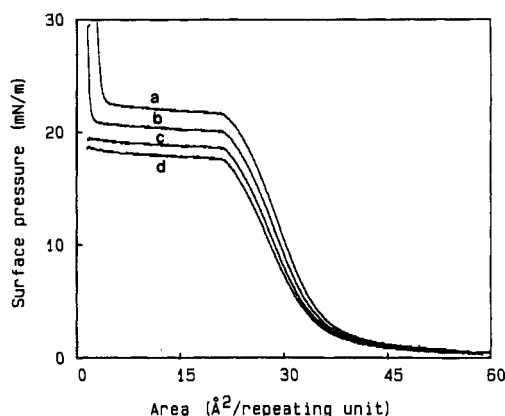(27) Yoo, K. H.; Yu, H. *Macromolecules* **1989**, *22*, 4019.

Figure 7. Pressure–area isotherms of isotactic poly(isobutyl methacrylate): a, 10 °C; b, 22 °C; c, 32 °C; d, 41 °C.

determined,[25] without a strong variation in the segment contact enthalpy.

In contrast, we suggest that the low level of lateral interactions in isotactic PMMA is strongly related to the *orientational* effects described above. The order required to align the ester groups of isotactic PMMA (or PEMA or PiBMA) toward the water phase (and to minimize the lateral interactions) is likely to be disturbed by the thermal motions of the polymer chain as the temperature is raised, leading to stronger cohesive forces, overcompensating a first–order entropy effect. Surface potential measurements, discussed later on in this paper, provide additional indications for variations of the segmental orientation characteristics with temperature.

Monolayers of poly(ethylene oxide) exhibit a temperature dependence similar to that of isotactic PMMA, although the effect is somewhat less pronounced.[28] 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, as discussed by Rennie et al.;[29] at lower surface concentrations, the behavior is probably more monolayer like.[30] The monolayer behavior of isotactic PMMA cannot be described following a similar model, since this polymer is not water soluble like PEO (an argument which applies even stronger to 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,[31] 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 8); 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.

B. Surface Potential Measurements. More information about the conformation of the poly(methacrylates) at the air–water interface can be inferred from surface

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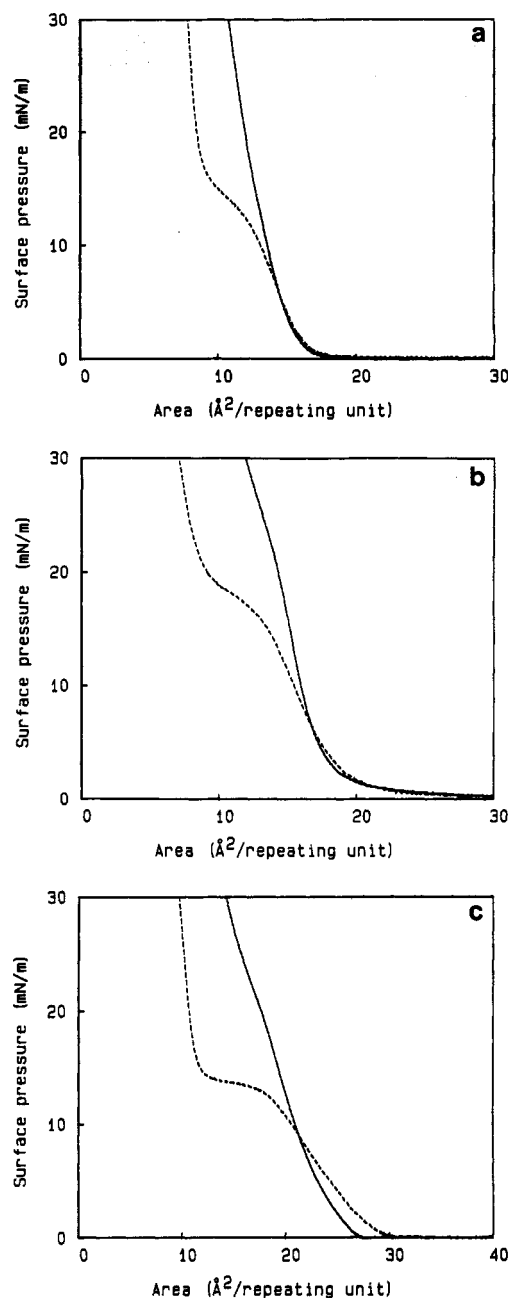(31) Gregory, P.; Huglin, M. B. *Makromol. Chem.* **1986**, *187*, 1745.

Figure 8. Pressure–area isotherms for s-PMMA (a), s-PEMA (b), and s-PiBMA (c) at 10 °C (solid lines) and 41 °C (dashed lines).

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 the fact 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.[22] The dipole moments deduced from the surface potential measurements are invariably too low compared to values known for these dipole moments from bulk or solution measurements. Still, the values obtained appear to be very useful for mutual comparisons. Alexander[32,33] tried to interpret

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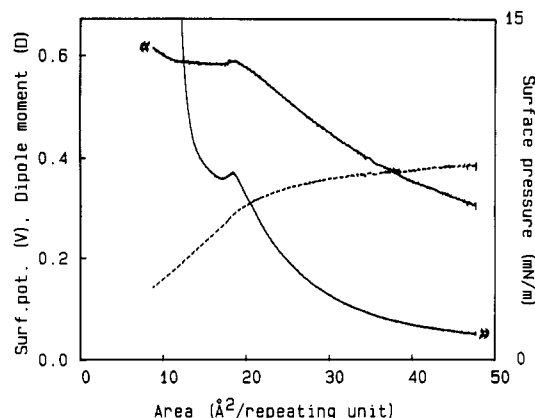(33) Alexander, A. E. *Proc. R. Soc. London* **1942**, *A179*, 776.

Figure 9. Surface potential (solid line), $\mu_\perp$ (dashed line) and surface pressure for a monolayer of i-PMMA at 10 °C.

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. Möbius more recently applied a similar approach, distinguishing contributions from the monolayer–water interface and the monolayer–air interface.[23] 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 that may be 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[22]

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

with $\mu_\perp$ the surface dipole moment (in mD), A the molecular area (in Å^2/repeating unit, and ΔV the surface potential in millivolts.

Since upon pressure buildup, the monolayers of the poly(methacrylates) yield a gradually 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 9; the surface potential of an i-PMMA monolayer is measured simultaneously with the surface pressure. The corresponding values for $\mu_\perp$ are also shown. 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 falls slowly upon compression. Isotactic PMMA exhibits a pressure-induced monolayer crystallization process,[16] which is visible in the isotherm as the transition observed at approximately 8 mN/m. It can be seen that the onset of this process is associated with a sudden stop in the rise of the surface potential of the monolayer, which marks the beginning of a sharp fall of the average dipole moment. This observation is in agreement with the proposed nature of the monolayer crystallization process; the amphiphilic orientation of the i-PMMA segments is exchanged for a *double helical* conformation,[16] which can easily be argued to contribute less to the surface potential.

The results for the values of $\mu_{\perp,\Pi\rightarrow0}$ are summarized in Table II. The surface potential measurements of the syn-

Table II. $\mu_{\perp,\Pi\rightarrow0}$ **(D)**

material	10 °C	21 °C	32 °C
PMMA			
isotactic	0.385	0.35	0.315
atactic		0.24	
syndiotactic	0.225	0.225	0.22
PEMA			
isotactic	0.455	0.425	0.395
atactic		0.35	
syndiotactic	0.335	0.335	0.335
PiBMA			
isotactic	0.52	0.505	0.485
atactic	0.46	0.455	0.46
syndiotactic	0.42	0.42	0.42

diotactic (and atactic) PMMA and PiBMA all yield fluctuating results up to close to the onset of pressure buildup, 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.[1,34] Still, in all cases the dipole moments could be determined with an accuracy of a few percent. From the results listed in Table II, 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 $\mu_{\perp,\Pi\rightarrow0}$: 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,[35] and the value found for the $\mu_\perp$ will be determined by the spatial orientation and the conformation of this ester group. Relevant variables include the following:

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 case of a cis conformation this vector makes a larger angle ($\sim$15°) with the C=O bond than in the case of a trans conformation.

The segments at the air–water interface will tend to orient themselves as favorably as possible, trying to accommodate their polar parts toward the water phase. A conformation is favored such that the dipole moment perpendicular to the interface is high.[1] Simultaneously, the monolayer itself will influence the force field that the segments experience, particularly at high (local) surface concentrations.

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For the isotactic poly(methacrylates), at low surface concentrations, the segments have a large degree of freedom so as to attain a favorable conformation of their ester groups; the backbone will not impose important restrictions. Also, because of the expanded nature of the monolayer, cohesive interactions will be low, so that the optimal orientation of the ester groups is determined mainly by the water subphase, and not by interactions with neighboring 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 favorable with respect to the interaction with the neighboring segments which are very close; e.g. a high value of the parallel dipole moments of two neighboring segments may give rise to an unfavorable contribution to their interaction energy. Apart from this, the orienting influence of the water subphase on the s-PMMA (s = syndiotactic) segments may have been less pronounced in the first place, because of the unfavorable (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[36])), 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 $\mu_{\perp,\Pi\to0}$ are observed. These large alkyl groups can be expected to cause several effects. In the first place, the growing unfavorable interaction between the water and this hydrophobic side chain will restrict the structural variation due to thermal motions, since the rotational energy profile will have a more pronounced minimum. 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
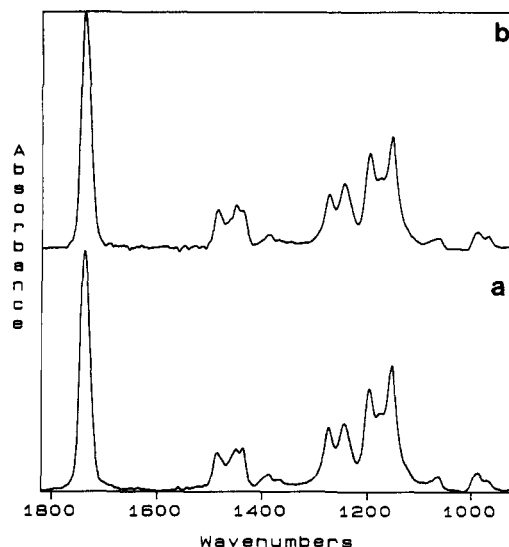
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Figure 10. Grazing incidence reflection IR spectra of s-PMMA transferred to a gold substrate (transfer pressure 7 mN/m), before (a) and after (b) annealing at 140 °C.

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 behavior. 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 at higher temperatures.

C. Infrared Experiments. All polymers discussed in this paper 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 10 and 11 show reflection–absorption infrared 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 parallel to the substrate will 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 to above T_g, in order to remove all orientation. 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 be pointing more or less downward toward the water phase. If this orientation were to be retained upon transfer, we would expect to find a relatively strong C=O 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
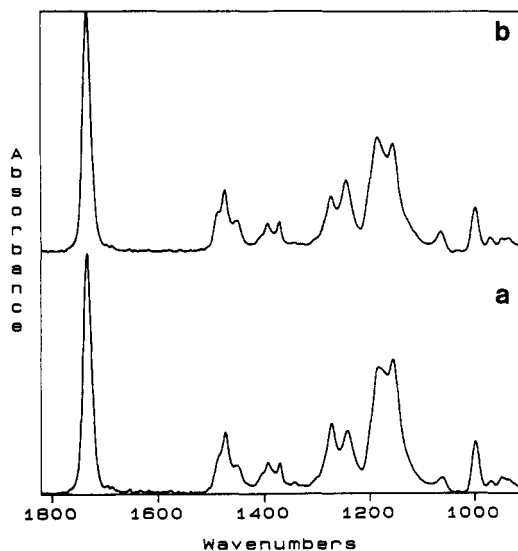
Figure 11. GIR spectra of s-PiBMA transferred to a gold substrate (transfer pressure 7 mN/m), before (a) and after (b) annealing at 100 °C.

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

slightly lower compared 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 led 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 measurements, which demand a more perpendicular orientation of the carbonyl groups, as, e.g., suggested by Crisp.[1]

This 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 the 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 β-relaxation observed in mechanical and dielectric measurements of these materials.[37,38] At deformation frequencies of 1 c/s, this (broad) relaxation band has its maximum at 30 °C[39,40] for PMMA. The β-relaxation process is rather insensitive to changes in the alkyl side group, so that similar mobilities can be expected for PEMA and PiBMA.[39] Since upon transfer from the water surface the monolayer will no longer feel the forces exerted by the subphase, the original surface structure will become unstable (due to the unfavorable 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
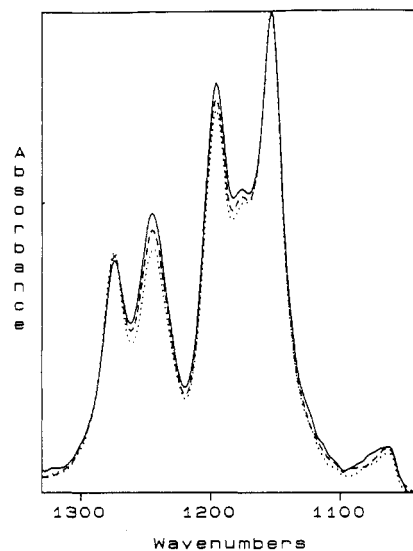
isotropic structure, since it does not involve the polymer main chain: the average angle of the link between the backbone and the ester group may largely be retained. The anisotropic orientation of the ester group can still be inferred from the orientation effects in the carbonyl band and in the ester vibrations in the 1000–1300-cm^{-1} region; unfortunately, these latter absorption bands are probably all associated with coupled or delocalized vibrations, and the direction of their dipole transition moments with respect to the ester group is not clear,[41] prohibiting detailed structural interpretation.

The spectra of syndiotactic PMMA show smaller deviations between the as deposited and the isotropic layers, since the structure of the monolayer will already be deformed by the high cohesive forces, as we have 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 (Figure 12).

IR spectra of isotactic PMMA were reported in ref 17; it was observed that upon transfer from the expanded condition, multilayers were formed yielding spectra which did not deviate significantly from isotropic spectra.[17] 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 13). For these materials, 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 behavior of the stereoregular PMAA's can be traced back to the structural differences of the backbone.

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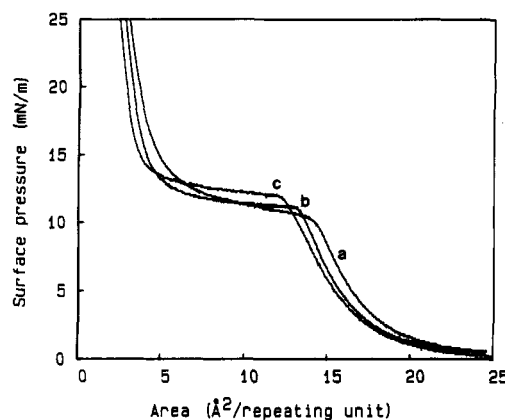(41) Lipschitz, I. *Polym. Plast. Technol. Eng.* **1982**, *19* (1), 53.

Figure 13. Pressure–area isotherms of isotactic poly(methacrylic acid): a, 10 °C; b, 21 °C; c, 41 °C.

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_a 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 favorable, 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 polymer 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 behavior 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,[28] the collapse pressure increases with increasing temperature, opposite to the behavior 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.

Conclusions

The monolayer behavior of the poly(methacrylates) studied is strongly dependent on the tacticity of the backbone. In all cases studied, 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 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 effect of the tacticity of the backbone becomes less pronounced with increasing length of the ester alkyl side chain.

The isotactic polymers exhibit an anomalous temperature dependence, the monolayers becoming less expanded at higher temperatures. This effect can be rationalized in terms of an increasing disturbance of the perfect amphiphilic orientation of the segments, which was responsible for the low level of cohesive interactions. This explanation was found to correlate well with surface potential measurements.

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 will be operative.

Isotactic poly(methacrylic acid) forms stable monolayers on pure water subphases, in contrast to syndiotactic poly(methacrylic acid).

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