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Poly(Itaconate) Derivatives, at the Air-Water Interface: Case of Poly(Monobenzyl) and Poly(Dibenzyl) Itaconate

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Abstract

The surface behaviors of monolayers of the poly(itaconate) derivatives, poly(dibenzyl itaconate) (PDBzI) and poly(monobenzyl itaconate) (PMBzI), at the air-water interface were investigated at 298 K on an aqueous subphase at pH 5.7 and 3.0. The monolayer characteristics of PDBzI and PMBzI were studied and compared in terms of surface pressure-area (-A) isotherms, surface compressional modulus-surface pressure (Cs-1- π) curves, static elasticity-surface concentration curves (-), hysteresis phenomena and phase images observed with a Brewster angle microscope (BAM.). The results showed that PMBzI and PDBzI gave rise to stable monolayers and that the isotherms presented pseudoplateau regions at different surface pressure values independent of pH. The PMBzI pseudoplateau region may because a change in the lateral packing of the chains. The PDBzI pseudoplateau region is attributed to a phase transition. The morphology of these monolayers was studied by Brewster angle microscopy (BAM). The surface pressure for both studied polymers. The degree of hydrophobicity of the polymers was estimated by determining the surface energy values based on wettability measurements.

Keywords: Poly(benzylitaconate)s; Pressure-area isotherms; Airwater interface; Monolayers; Static elasticity; Anphiphilicity isotherms

Introduction

Polymers derived from itaconic acid are of great interest from both the basic and industrial points of view [1-3]. These polymers, containing saturated rings as side chains, show significant mechanical and dielectric activity when they are affected by force fields [3,4]. This is partly due to the flexibility of the saturated rings which can flip between two conformational states, e.g. chair-to-chair [4]. In contrast, less activity can be expected with aromatic rings because of the planarity of the unsaturated ring. Monoesterification and diesterification of itaconic acid can be carried out to obtain monomers and polymers, with either one or two of the carboxyl groups esterified in each repeat unit [3,5]. In previous articles we have reported the relaxational behavior of poly(monobenzyl itaconate) (PMBzI) [4] and poly(dibenzyl itaconate) (PDBzI) [3] by means of dynamic mechanical and dielectric spectroscopy. From the comparison of the relaxational behavior of the two polymers it was concluded that the small differences in their chemical structures gave rise to significant differences in relaxational behavior. We also studied poly (itaconate)s monolayers at the air-water interface a decade ago [6]. Because of the peculiar relaxational behavior of poly (mono and dibenzyl itaconate)s [3,4] we felt it important to make a comparative study of the surface behavior of this kind of polymer at the air-water interface [6].

The aim of this work was to investigate the changes in surface activity and molecular organization of monolayers of PMBzI and PDBzI and to examine the effect of the chemical structure of these poly(itaconate) derivatives on the surface behavior at the air-water interface. Scheme 1 shows the chemical structures of the studied polymers.

Experimental Section

Synthesis and characterization of monomers and polymers

The monomers were prepared by esterification of itaconic acid with the corresponding benzyl alcohol according to the previously described method [3,7-10]. The polymers were obtained by radical polymerization in bulk at 323 K. using α, α' -azobisisobutyronitrile (AIBN) as catalyst (0.1% mol for PMBzI and 0.2-0.4% mol for PDBzI) [7-9].



The polymers were characterized by light scattering and size exclusion chromatography measurements, as previously reported [8-10]. Samples used in the present work had a weight-average molecular weight of $M_w \approx 3.1 \times 10^4$ for PMBzI and $M_w \approx 3.7 \times 10^4$ for PDBzI corresponding to 141 and 119 repeat unit per molecule, respectively.

Surface pressure-area isotherms

A Langmuir film was obtained by depositing a polymer solution in toluene (1-1.5 mg mL⁻¹) dropwise on the air-water interface. Before compression, the film was allowed to equilibrate for about 15 minutes to ensure full evaporation of the spreading solvent and to allow the molecules to reach equilibrium.

The surface pressure-area (π -A) isotherms at the air-water interface were established in a Teflon Langmuir-Blodgett trough (NIMA-611 M) and a Langmuir film trough (Nima Technology-1232D1D2 and 622D2/ D1, England.) equipped with two barriers and a Wilhelmy plate. The whole setup was enclosed in a transparent poly (methacrylate) box

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to prevent environmental pollution. The polymer monolayers were compressed from 600 to 70 cm² with a compression speed of 5 cm² min⁻ ¹. The isotherms were determined in triplicate to ensure reproducibility. The temperature regulation of the monolayer was obtained by a thermostat-controlled water flow from an external bath, passing through the jacket at the bottom of the trough. All measurements were done at 298 K using ionized water purified with a Milli-Q system to 18.2 M Ω /cm resistivity as a subphase. The limiting surface area, A₀, was determined by extrapolation of the π -A isotherms to zero pressure as shown in Figures 1 and 2. The extrapolation was obtained by a straight line tangent to the isotherm as indicated in the Figure 1. The stability test of the monolayer was performed by following the variation of surface pressure and area against time, as shown in Figure 3. For the hysteresis experiments several compression-expansion cycles at 5 cm² min⁻¹ were performed to approximately 50% compression. The time interval between compression and expansion was 300 s and the temperature was fixed at 298 K (Figure 4).

Contact angle measurements of surface free energy

The surface free energies of the polymers were determined by contact angle measurements using diiodomethane and 1-bromonaphthalene. Polymers films were cast onto glass slides used for optical microscopy. The cast films were dried for 30 min at 60°C under vacuum. The measurements were made using an optical contact angle system (OCA) (Dataphysics, England) with a conventional goniometer and high performance video camera controlled by the OCA20 software. A syringe connected to a Teflon capillary with an inner diameter of approximately 2 mm was used to supply liquid from above to measure the sessile drops, using drops with a radius of 0.4-0.5 cm. The contact angles were measured carefully from left to right of the drop and subsequently averaged. These procedures were repeated for 10 drops of each liquid on all six new surfaces, selected considering the homogeneity of the film and the reproducibility of the results. All readings were then averaged to give an average contact angle. All experiments were performed at room temperature.

Brewster angle microscopy

A Brewster angle microscope (BAM) (Nanofilm Technology GmbH, Germany) was mounted on the Langmuir trough (NIMA-1232D1D2 and 622D2/D1). Both devices were used to check the experimental results, which were in good agreement, in a perpendicular arrangement of the incidence plane with respect to the direction of barrier motion. For viewing and image storage the microscope was combined with a CCD camera and video system (Figures 5 and 6). A NIMA 702 Langmuir balance was used to follow the evolution of the thickness of the monolayer at various surface pressures, with BAM images recorded in several regions of the isotherms.





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Results and Discussion

The surface properties of the two polymers were studied by surface pressure measurements under compression. Figures 1a and 1b present the surface pressure-area (π -A) isotherms for the studied polymers on pure water acidified with HCl (pH: 5.7 and pH 3.0 with HCl at constant

ionic strength) at 298 K. The limiting surface area, A_0 , was determined by extrapolation of the π -A isotherms to zero pressure.

In general, three regions could be distinguished after compression in the surface area (π -A) plot, corresponding to the expanded liquid, condensed liquid and condensed-solid-like states in two dimensions.

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The last state can be identified as the lower area to zero pressure, corresponding to a projected area along axis of a hypothetical long organic chain from molecular models [11].

A pseudoplateau region can be observed in Figure 2 for PMBzI at low surface pressure, 8-20 Å² (ru⁻¹). At high surface pressures, at about 25-35 Å² (ru⁻¹) a pseudoplateau appeared for PDBzI that may represent

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the transition between the condensed solid-like and liquid states at a till low surface pressure of 5 mMm⁻¹ (Figure 2). The reason for this behavior remains unknown, but we are currently running molecular dynamics is simulations (MDS) to clarify if there was a change in the conformation of the polymer chains. A possible explanation is that the plateau is the result of repeated folding of the polymer segments, which are directed outwardly from the interface, forming loops and tails that reduce the scontact points with the water subphase. The formation of these loops, resulting from monolayer compression, decreases the area occupied by the film. Table 1 summarizes the area per repeat unit at zero surface pressure; A0 values for both polymers. The A0 values for PDBzI and SPMBzI are consistent with this explanation given that the area occupied by the hydrophobic film decreased at both pH levels.

The presence of the pseudoplateau in the isotherms implies a change in the surface organization of the polymer systems in this region due to the collapse of the monolayer or phase transitions of the monolayers of both polymers. As compression continued, the surface pressure sharply increased, especially for PDBzI, apparently resulting in heterogeneous films, as shown in the BAM images in Figures 5 and 6. In conclusion, the surface isotherms of both polymers were similar, irrespective of the pH levels. However, they differed in the surface area and resulting surface pressure at which the monolayer presented pseudoplateau regions. The BAM images are in good agreement with the evolution of the shape of the isotherms, as shown in Figures 5 and 6. There is a difference in heterogeneity between PMBzI and PDBzI at pH 5.7, as shown in Figures 5 and 6, which could be attributed to differences in the hydrophobicity of the polymers.

Hysteresis experiments were conducted, consisting of three or four compression and expansion cycles (Figure 4), to evaluate the stability of the monolayers. The monolayers were subjected to four successive

Polymer	рН	A₀(A² r.u¹)	π _c (mNm ⁻¹)
PMBzl	3.0	~30	~31
PMBzI	5.7	~33	~31
PDBzl	3.0	~23	≈45
PDBzI	5.7	~22	≈45

Table 1: Surface properties for PMBzI and PDBzI: Area per repeat unit at zero surface pressure, $A_{_0}$ and collapse pressure, $\pi_{_C}$ values.

cycles of compression-expansion at a rate of 5 cm²/min. The first cycle was carried out by compressing the films up to a pressure of 1 mNm⁻¹ in both Figures 5 and 6, so that the films were in a highly expanded state. Under these conditions the PMBzI decompression curves actually coincided with the compression curve, indicating the reversibility of the process (Figure 4a). The same occurred in the same area when the monolayer was recompressed in the second cycle. Gaines [12] called this behavior "reversible", characterized by the fact that the expansion and subsequent repeated compression curves reproduce the initial compression, although the process reaches higher pressures until 30 mNm⁻¹ (Figure 4a). The results shown in Figure 4b suggested that the PDBzI monolayers adopted a different conformation after the first compression, that is compression up to 10 mNm⁻¹, involved some energy storage during the first expansion. It seems that the duration of the experiment was not sufficient to allow the full relaxation of the monolayer. However, hysteresis was much less pronounced in the subsequent cycles. The maximum surface pressure achieved in all the compressions, as shown in Figures 4a and 4b were constant, showing that no material loss was taking place during the experiments.

All the compression curves in Figure 4b are superposed, while the expansion curves showed changes that can be attributed to hysteresis and all the cycles were less pronounced. This fact may be due to entanglement of the chains during compression or a different arrangement in terms of hydration and conformation of the second cycle from that adopted after spreading. The expansion rate was apparently too rapid to allow the chains to adopt the same conformation they had prior to the compression when they decompress. Table 1 presents the zero pressure limiting areas per repeat units, A0, based on the π -A isotherms (Figures 4a and 4b). The A0 values for PDBzI were lower than those for PMBzI. This may be because in the case of PDBzI, which has two aromatic rings per repeat unit (ru), the area occupied by the aromatic hydrophobic residues per ru, must be smaller than it is for PMBzI; a hydrogen in PMBzI is replaced by a -CH₂- and an aromatic ring per repeat unit (Scheme 1). When the monolayer is compressed on the water surface, it may undergo several phase transformations. It is possible to make an analogy between the intervals of surface concentration and the solution concentrations often used in polymer science. By this analogy, the extrapolated area to zero surface pressure (A_0) and the collapse surface pressure, π_c , correspond to the phenomena that occur in the concentrated region in solution in two dimensions. In the semi-dilute concentration zone, a phase transition, such as expanded liquid, condensed liquids and liquid-solid are observed [13,14]. Comparing surface and bulk concentration regimes commonly used in polymer science allow us to attribute the extrapolated area to zero surface, A₀ and the collapse pressure, π_c , that occur in the concentrated region.

The determination of collapse pressure is not a very clear topic in polymer science. Unlike small molecules, polymeric monolayers do not always collapse abruptly, making it difficult to identify the exact surface pressure at which collapse occurs. Consequently it is necessary to observe more than a single aspect to identify the collapse. A more precise way to determine the collapse surface pressure values (compared to the π -A isotherms) is to plot the compressional modulus (C_s^{-1}) as a function of surface pressure (π) (Figure 7). This parameter, defined by Davies and Rideal [15] as the inverse of two-dimensional compressibility, is given by the relation:

$$C_{S}^{-1} = \varepsilon_{0} = -A(\frac{\partial \pi}{\partial A})_{T} = \Gamma(\frac{\partial \pi}{\partial \Gamma})_{T}$$
(1)

where ε_{o} is the static elasticity and Γ is the surface concentration. C_{s}^{-1} values were obtained by numerical calculation of the first derivative from the isotherm data according to equation 1. By this way, after the determination of C_{s}^{-1} , (Figures 4a and 4b) in order to know the variation of the compressional modulus with surface pressure these values were plotted against surface pressure, as shown in Figure 7. The collapse pressures, $\pi_{c'}$ for PMBzI and PDBzI, i.e., that is ~31 mNm⁻¹ and ~45 mNm⁻¹ respectively (Figure 1 and Table 1), are another difference between the two polymers that probably results from the difference in the degree of the hydrophobicity of the side chains.

Static elasticity, ε_{a} , of the polymer monolayers

The topography of the monolayer partially depends on the strength of the interfacial interactions with substrate molecules and the strength of the intersegmental polymeric interactions. The viscoelastic properties of polymer monolayers may also be dependent on these interactions. From the experimental π -A (Figures 1 and 2) and π - Γ curves (not shown for the sake of clarity), it was possible to calculate the classical static elasticity modulus ε_0 according to equation 1. However, this only accounts for hydrostatic compression.

Figure 8 shows the plot of the compressibility modulus or static elasticity, ε_{o} , calculated from the surface pressure isotherms π versus the surface concentration Γ . The greatest increase in elasticity occurred in the semi-diluted regime. The static elasticity ε_{o} values for the semidilute region represent normal behavior [11,16]. It is known that the maximum ε_{o} values for polymeric systems are found in diluted and semidiluted regions, since the chains are independent or are in contact with each other, but respond more or less individually to deformation. The plot of the compressibility modulus or static elasticity, ε_{o} , in Figure 8 shows that in the case of PDBzI the maximum was located in a more concentrated region where closer contact among chains can be expected, so that the response to deformation is like that of a polymer lattice. According to these results, areas of surface concentration have higher surface static elasticity values, with more sensitivity to changes than dilute regions.

As is generally known [17], the surface concentration of a polymer monolayer spread at the air-water interface can be easily regulated by compressing or expanding the monolayer. It is thus possible to make an analogy between the dilution ranges of superficial and bulk concentrations frequently used in polymer science. By this analogy, the extrapolated area at zero surface pressure, A_0 , and the collapse pressure, π_c , take place in the semidilute region [18,19].

In the semidilute concentration region, surface pressure obeys a power law of surface concentration. Given the results obtained in the concentrated region, we considered it important to estimate the affinity of these systems for the air-water interface. We expected the interface to have different thermodynamic qualities as a solvent for the two polymers. To quantify this property we used the classic equation 2 of De Gennes [13].

$$\pi = \Gamma^{2\nu/2\nu-1} \tag{2}$$

According to this equation, the log π versus log Γ plot (Figure 6)

in the semidilute region shows a linear variation with slope 2v/2v-1. The v exponents for the two polymers (0.53 and 0.52 \pm 0.03 for PMBzI and PDBzI, respectively) were obtained from the slope calculated for these plots. The theoretical prediction is a v value narrowly centered at 0.75 for two-dimensional polymer chains in good solvents [14]. Monte Carlo simulations predict a value of 0.753 [20], while the matrix-transfer method [21] predicts a value of 0.7503. The situation is not clear in the case of a poor solvent and predictions are less precise. Monte Carlo simulations [22] suggest v_o \approx 0.51, while matrix-transfer data suggest v \sim 0.55 [23]. The v values for PMBzI and PDBzI indicate that the two polymers have similar affinities for the interface, which is consistent with values for hydrophobicity (estimated by comparing the chemical structure of PMbzI and PDBzI). The surface free energy value for PDBzI, obtained by contact angle measurements, was lower than the value for PMBzI (27 mNm⁻¹ and 45 mNm⁻¹ respectively).

Because the collapse pressure for PDBzI at pH 5.7 was approximately 45 mNm⁻¹, Brewster angle microscopy experiments helped to clarify the collapsed areas of the isotherms of the studied polymers [24,25] The results obtained by this method were compared to those obtained from the isotherms. As we observed with the Brewster angle microscope (BAM), the images of point D of the isotherm for PDBzI at pH 5.7 reveal areas of local heterogeneity (Figure 5a) that can be attributed to the collapsed area. These results are consistent with other findings indicating that this area corresponds to collapse pressure π_c .

The results observed in Figure 6 are also consistent with previous findings and indicate that the collapse pressure for PMBzI, irrespective of the water subphase pH level, was located \sim 31 mNm⁻¹ (Table 1). At low pressures, BAM images clearly reveal homogeneous morphology at point A, whereas a transition region appears at points B, C and D with areas of local heterogeneity that can be attributed to the collapsed regions.

Conclusions

PMBzI and PDBzI form stable monolayers at the air-water interface. The chemical structures of PDBzI and PMBzI significantly affect the shape of the surface isotherms irrespective of the pH level in the water subphase. The results indicate the existence of pseudoplateau regions at low surface pressures (5 mNm⁻¹ for PDBzI and approximately 30 mNm⁻¹ for PMBzI). This behavior has been interpreted as a phase transition in the first case and a collapse region in the second. The zero pressure limiting area per repeat unit (A0 values based on π -A isotherms) was lower for PDBzI than for PMBzI. In agreement with the concept of polymeric scales in semidilute regions, the air-water interface at 298 K is a bad solvent for these polymers, very close to the theta solvent. PDBzI is less hydrophilic than PMBzI according to level of surface free energy, which is consistent with the chemical structures of the polymers.

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