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RESEARCH ARTICLE

SYNTHESIS, CHARACTERIZATION, AND SURFACE BEHAVIOR OF POLY(PHTHALIMIDOALKYL ACRYLATE)S

Ligia Gargallo¹, Mathias Schmidt², Jorge Herrera², Angel Leiva² and Deodato Radić^{2*}

¹Facultad de Ciencias, Universidad de Tarapacá, General Velásquez 1775, Arica, Chile

²Laboratorio de Química Física de Macromoléculas, Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 302, Correo 22, 7820436, Santiago Chile

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ABSTRACT

Two phthalimidoalkylacrylates (PhAA)s, phthalimidoethyl acrylate (PhEA) and phthalimidopropyl acrylate (PhPA), and the corresponding poly(acrylate)s (PPhEA, PPhPA) were synthesized by radical polymerization using α, α' -azobisisobutyronitrile (AIBN) as the initiator. Polymers were characterized by proton nuclear magnetic resonance (¹H-NMR) and Fourier transform infrared spectroscopy (FT-IR). Thermal analysis was performed by thermogravimetry (TGA) and differential scanning calorimetry (DSC). Using the Langmuir Blodgett (LB) technique, the surface-area (A) isotherms at the air-water interface were determined for both polymers. Polymers show stable monolayers, which were characterized, and the surface parameters were determined. From contact angle measurements using the Owens, Wendt, and Kaelble (OWK) method, the surface free energies (SE) were estimated for both polymers. The behavior of poly(phthalimidoalkyl acrylate)s (PPhAA)s and poly(phthalimidoalkyl methacrylate)s (PPhAMA) was compared to corroborate the effect of the chemical structure on the surface behavior. The effect of the side chain structure on the surface behavior shows that as the length of the substituent increases the zero surface pressure A_0 and the collapse pressure σ_c diminishes.

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INTRODUCTION

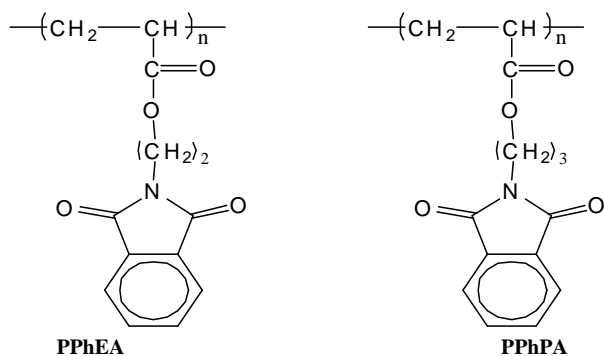
The effect of the side chain structure on different properties of polymeric materials is a matter of current interest [1-12] because depending on the nature of the substituents, it is possible to obtain polymers with different characteristics and applications. The nature of the side chain plays an important role in the physicochemical behavior of polymers. In this way, it is possible to obtain polymers with appropriate functionalities and, therefore, materials for specific utilities. The study of polymers at interfaces is another topic that encompasses the potential applications of these materials. Studies that investigate interfaces are of great importance for basic science as well as from a technological point of view. In the majority of industrial processes that involve polymers, surface characterization is necessary. Extensive studies have been performed to elucidate the structures and intermolecular forces of two-dimensional arrays of molecules at the air-water interface [13-16]. These works have been performed on small amphiphilic molecules, such as surfactants and lipids, at both gas-liquid and liquid-liquid interfaces. The orientation, specific interactions, conformational changes, and organization of quasi

two-dimensional layers of long polymer chains at interfaces have also been investigated [17, 18]. Therefore, the study of polymeric monolayers in different surfaces is of relevant importance, particularly the study of monolayers at the air-water interface. Polymers containing hydrophilic and hydrophobic moieties in the side chain, i.e., amphiphilic polymers, are of interest due to the effect of the balance between hydrophobic and hydrophilic regarding the general surface behavior. The most common hydrophilic groups are carboxylic acids, amines, and alcohols, etc., which are attracted by polar media, such as water, and the forces involved are of the Coulombic ($1/r^2$) type. Hydrophobic groups, such as hydrocarbon chains, are less soluble in water, and the forces involved are primarily of the van der Waals type. Amphiphilic molecules are trapped at the interface because they have two different types of bonds within the molecular structure. When these types of molecules are dissolved in a volatile non-aqueous solvent and are inserted in the surface of a polar liquid, the solvent evaporates, and the molecules remain oriented in the gas-liquid interface. Hydrophilic groups are oriented primarily to the water, and the hydrophobic groups are oriented to the air. Another aspect to take into account in the analysis of

*Corresponding author: Deodato Radi

Laboratorio de Química Física de Macromoléculas, Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 302, Correo 22, 7820436, Santiago Chile

the surface behavior of polymers is the case of polymers that contain the same side chain but with a different backbone, which is primarily the case of polymers with amphiphilic groups.



Scheme 1 Chemical structures of poly(N-phthalimidoethyl acrylate) (PPhEA) and poly(N-phthalimidopropylacrylate) (PPhPA).

Poly(acrylate)s and poly(methacrylate)s are two families of polymers that can be modified by inserting different side functional groups and, therefore, changing the structure of the backbone, where the *α*-methyl group of poly(methacrylate) plays an important role on the strength of the hydrophobicity of the material relative to similar structures in poly(acrylate)s.

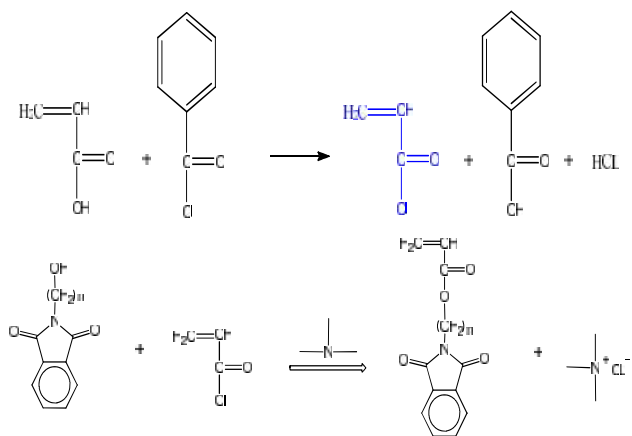
The goal of the present work is to study the surface of a family of poly(acrylate)s and poly(methacrylate)s containing N-phthalimidoalkyl groups in the side chain (see scheme 1) and to analyze the effect of the spacer side groups on the general behavior of both families of polymers.

Experimental Section

Synthesis of monomers and polymers

Phthalimidoethyl acrylate (PhEA) and phthalimidopropyl acrylate (PhPA) were synthesized by esterification of the corresponding phthalimidoalkyl alcohol with acryloyl chloride following the procedure previously described [19]. Acryloyl chloride was obtained by the classical Burtle and Turek method [20] by the reaction between acrylic acid and benzoyl chloride, as shown in scheme 2.

Monomers were purified using a silica column and eluted with methyl ethyl ketone (MEK). Polymers were obtained at 65 °C



Scheme 2 Synthesis of acryloyl chloride and N-phthalimidoalkyl acrylates, PhEA ($n=2$) and PhPA ($n=3$)

by polymerization of the monomers using AIBN as the thermal initiator, which was previously degassed under vacuum.

Thermal analysis of polymers

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851. The scans were performed at temperatures ranging from 25 °C to 700 °C at a heating rate of 10 °/min under a nitrogen environment. The amounts of the samples used were 5-10 mg in 40 μ L alumina pans. Data were processed using STAR^e software version 8.1 from Mettler-Toledo. The thermal transitions of the polymer were studied by differential scanning calorimetry (DSC) on a Mettler-Toledo DSC 821-700 differential scanning calorimeter under dry nitrogen at a heating rate of 10 °C/min. The second heating was used for analysis. The obtained data were processed using STAR^e software version 8.1 from Mettler-Toledo.

Surface pressure-area (π -A) isotherms

The Langmuir monolayer film was obtained by spreading solutions of PPhEA and PPhPA in chloroform (1-1.5 mg mL⁻¹) dropwise on the air-water interface. Before compression, the film was allowed to equilibrate for approximately 15 minutes to ensure full evaporation of the spreading solvent and also to allow the molecules to reach equilibrium. The monolayers were compressed and monitored by surface pressure measurements. Measurements from Brewster angle microscopy were conducted at different surface pressures. The surface pressure area (π -A) isotherms at the air-water interface were established using a NIMA-1232D1D instrument equipped with two barriers and a Wilhelmy plate. The entire setup was enclosed in a transparent methacrylate box to prevent environmental pollution.

The polymer monolayer was 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 control of the monolayer was achieved by a thermostated water flow from an external bath, which passed through the jacket at the bottom of the trough. All measurements were performed at 298 K using ionized water purified with a Milli-Q system with a sub-phase resistivity of 18.2 M Ω /cm. The limiting surface area A_0 was determined by extrapolation to zero pressure from π -A isotherms. The stability test of the monolayer was performed by following the variation of surface pressure and area against time.

The surface energies of the polymers were determined by classical contact angle measurements using diiodomethane and 1-bromonaphthalene. Polymer films were cast onto glass slides for optical microscopy. The cast films were dried for 30 minutes at 333 K under vacuum. Measurements were made using a contact angle system OCA by Dataphysics with a conventional goniometer and a high-performance video camera controlled by OCA20 software. A syringe connected to a Teflon capillary with an inner diameter of approximately 2mm was used to supply liquid into the sessile drops from above. A sessile drop with a radius of approximately 0.4-0.5 cm was used. The contact angles were measured carefully from the left and right side of a drop and subsequently averaged. These procedures were repeated for 10 drops of each liquid on six

new surfaces. 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, Gottingen, Germany) was mounted on the trough 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.

RESULTS AND DISCUSSION

Monomers and polymers were obtained as described previously with a yield of 35%, and the spectroscopic results contained absorption bands that agree with the expected chemical structure. Table 1 compiles the FT-IR signals of the monomers and polymers. As can be observed, the absorption bands correspond to the functional groups present in the respective monomers and polymers. The chemical shifts observed in the $^1\text{H-NMR}$ spectra of the monomers and polymers also agree with the expected chemical structures. Table 2 present the compiled observed signals.

Figure 1 shows the $^1\text{H-NMR}$ signals for PhEA and PPhEA as examples of the spectra obtained. The most important change in the polymer spectra is the disappearance of the vinylic protons, which is similar for PPhEA and PPhPA.

Table 1 FT-IR absorption bands (cm^{-1}) for monomers, PhEA and PhPA and polymers PPhEA and PPhPA.

Monomer-Polymer/ functional group	PhEA (cm^{-1})	PhPA (cm^{-1})	PPhEA (cm^{-1})	PPhPA (cm^{-1})
$-\text{C}_6\text{H}_5$	3100.5	3101.7	3100	3102
$\text{H}_2\text{C}-$	2948.5	2947.9	2949	2948
$-\text{C}=\text{O}$ (Cyclamide)	1770.7	1771.6	1771	1772
$-\text{C}=\text{O}$ (Ester)	1710.7	1711.5	1711	1712
$\text{H}_2\text{C}=\text{CH}-$	1637	1636.1	1637	1636
$\text{H}_2\text{C}-\text{N}=\text{}$	1321.2	1296.3	1321	1296

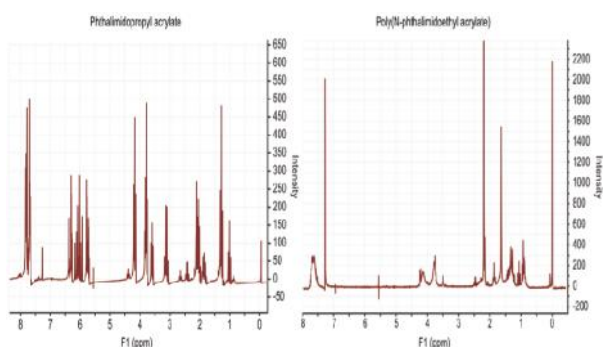


Figure 1 $^1\text{H-NMR}$ spectra for PhEA and PPhEA.

Table 2 $^1\text{H-RMN}$ signals (ppm) for monomers PhEA, PhPA and polymers PPhA, PPhPA.

Monomer-Polymer/ functional groups	PhEA (ppm)	PhPA (ppm)	PPhEA (ppm)	PPhPA (ppm)
$-\text{C}_6\text{H}_5$	7.8-8	7.7-7.9	7.7	7.7
$\text{H}_2\text{C}=\text{CH}-$	6.4-5.8	6.3-5.9	-	-
$\text{CH}-$ (Vinylic)	6.2	6.1	-	-
$\text{H}_2\text{C}-\text{O}$	3.9	3.9	4.2	4.3
$\text{H}_2\text{C}-\text{N}=\text{}$	4.4	4.2	3.8	3.7

To determine the thermal stability of the polymers under study, thermogravimetric analysis of the samples was performed. Figure 2-a and 2-b, show the thermogravimetric profiles for both PPhAs.

The glass transition temperatures for PPhEA and PPhPA are 64.7°C and 54.9°C and the decomposition temperature at 50% degradation ($\text{TD}^{50\%}$) are 409°C and 415°C for PPhEA and PPhPA respectively. As can be observed, the differences in $\text{TD}^{50\%}$ and T_g for both polymers reflect the effect of the side group in the thermal behavior.

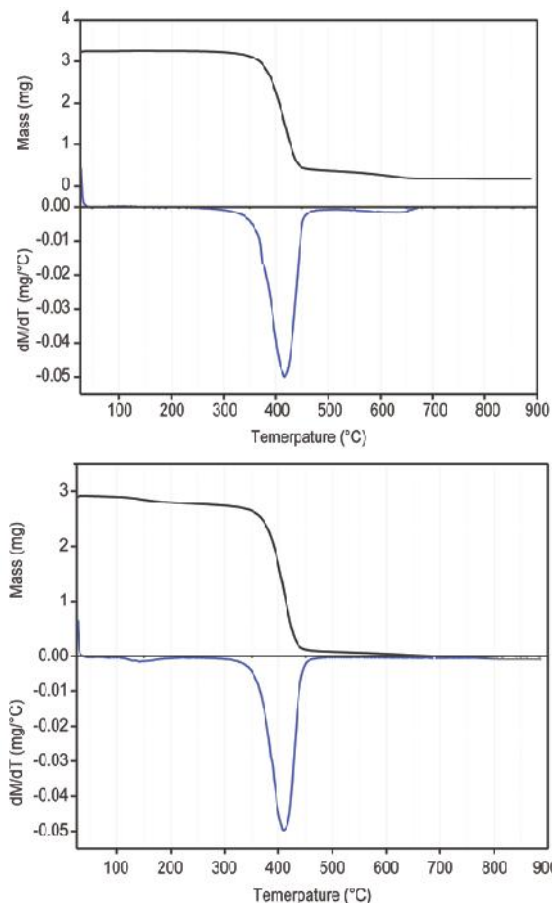


Figure 2 a) Degradation profile or PPhEA represented as TGA (black) and DMTA (blue). b) Degradation profile or PPhPA represented as TGA (black) and DMTA (blue)

On the one hand, the volume of the side group increases the stability, whereas on the other hand, the flexibility of the spacer reduces the T_g value, which agrees well with similar results previously reported [6,8]. The surface behavior of the polymers can be represented by π -A isotherms, such as those shown in Figure 3-a and 3-b for both PPhAs. These isotherms can be

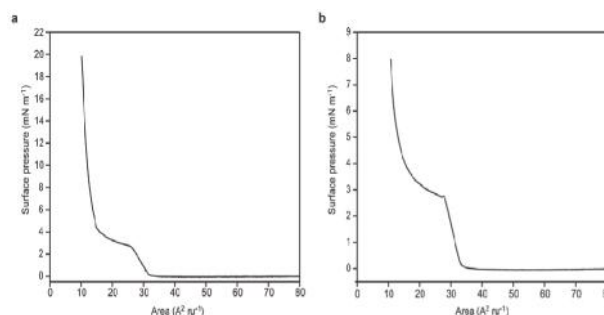


Figure 3 π -A isotherms for: a) PPhEA and b) PPhPA

considered as being of the expanded type, and several irregularities attributed to a pseudo-plateau at low pressures for both polymers can be observed. This pseudo-plateau is found at approximately 2.5 mN/m, which suggests a phase transition between the expanded and condensed liquid.

The collapse pressure, as Crisp noted [21, 22], considers two types of polymeric spread monolayers. This consideration is based primarily on the characteristics of the surface pressure curves as a function of the superficial area, i.e., expanded and condensed liquid monolayers. The isotherms shown in Figure 3 present both behaviors with the transition zone mentioned above.

Table 3 compiles the values of the characteristic surface parameters, such as the area occupied by a molecule extrapolated to zero surface pressure A_0 and collapse pressure π_c for both PPhAs. As can be seen, differences in the values of A_0 for PPhEA and PPhPA are observed where A_0 is larger for PPhEA than for PPhPA. This variation of A_0 with the chemical structure of the polymer can be explained by accounting for the mobility of the side chain, which is affected by the length of the spacer group. [22] In fact, because PPhPA contains only one methylene more than PPhEA, the mobility and flexibility of the side chain affect the orientation of the polymer at the interface. This result is in agreement with the Tg values obtained for both polymers.

Table 3 Values of the limit surface area A_0 , surface pressure at collapse π_c , estimated from the surface pressure-area isotherm (πC) and BAM images (πC^*), and the v exponent of the studied polymers.

Polymer	A_0 ($\text{\AA}^2 \text{ru}^{-1}$)	A_c ($\text{\AA}^2 \text{ru}^{-1}$)	π_c (mN m^{-1})	π_c^* (mN m^{-1})	$v \pm 0.02$
PPhEA	14	10.2	~19.9	~20	0.51
PPhPA	12	10.6	~7.9	~7.5	0.52

From the π -A isotherms shown in Figure 3, information regarding the thermodynamic power of the interface as a solvent of the interface for each polymer was obtained. For this purpose, scaling concepts in the semi-dilute superficial concentration regime were used. [23]

This property is estimated from the values of the v exponent of the excluded volume according to the following relationships:

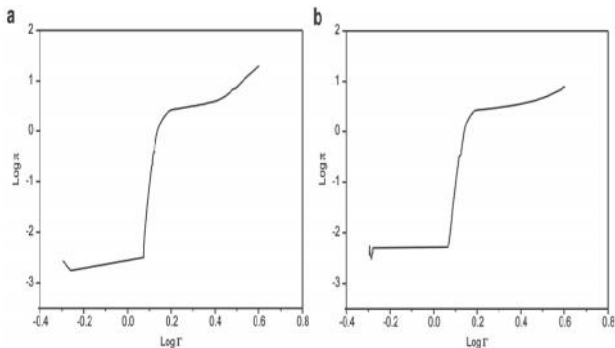


Figure 4 Double logarithmic plots of surface pressure as a function of the surface concentration for a) PPhEA and b) PPhPA at 25°C.

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

$$\log \pi = \frac{2v}{2v-1} \log \Gamma \tag{2}$$

The results were obtained from the double logarithmic plots shown in Figure 4.

The values of the v exponent for PPhEA and PPhPA are 0.51 ± 0.02 and 0.52 ± 0.02 , respectively. These values indicate that the air-water interface behave as a theta solvent for both polymers.

Depending on the thermodynamic conditions, the excluded volume can be avoided by compensation of the long-range interactions. When the long-range interactions are compensated, the systems are in the theta condition (θ); in these conditions, the steric repulsion and the attraction among different units are compensated. In this way, the polymeric chains can be studied in such conditions that their conformation is governed only by short-range interactions, and the macromolecule can reach its unperturbed state. In good solvents ($v = 0.75$), the polymer-solvent interaction is favored; the macromolecule is expanded, and the excluded volume increases; in poor solvents ($v = 0.5$), intramolecular interactions are more favored, the polymer contracts, and the excluded volume diminishes. However, another parameter to take into account in the surface analysis of polymeric systems is the static elasticity of the monolayers, which obtains information regarding the viscoelasticity of the polymeric materials. The static elasticity modulus was calculated from the surface pressure as a function of concentration curves. The surface concentration is obtained assuming that the spreading of the polymers onto the surface occurs without desorption in the sub-phase.

Figure 5 shows the static elasticity as a function of concentration. A maximum corresponding to the semi-dilute region can be observed ($\approx 1.4 \text{ mg/m}^2$), and another maximum appears in the concentrated concentration ($\approx 4.0 \text{ mg/m}^2$). Both polymers show high values of the elasticity and sharp slopes, which is indicative of an extremely elastic monolayer.

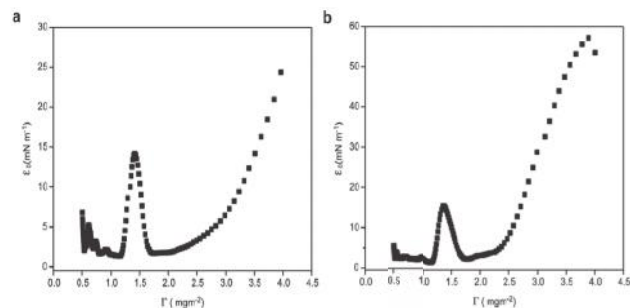


Figure 5 Variation of the static elasticity (E_0) of the monolayer for a) PPhEA and b) PPhPA as a function of the surface concentration at 25°C.

In the semi-dilute regime, polymeric chains behave independently or are in mutual contacts; however, their responses are independent when they are submitted to external tension or deformation. For higher concentrations, the chains overlap, which increases the repulsive strengths of the hydrophobic type. Due to this situation, the system as a whole would lose its response capacity, which would explain the observed decreasing elasticity modulus. Nevertheless, at higher concentrations, it is possible to obtain non-void (null) values of elasticity, as can be observed in Figure 5a-b.

Brewster microscopy (BAM) qualitatively evaluates the morphology of the monolayer, for example, domains formation, presence and coexistence of different phases, and detects the collapse of the monolayer. Figures 6-a to 6-d shows the BAM images obtained for the surface π -A isotherm for PPhEA.

At the beginning of compression, which is when the monolayer exhibits a gas-expanded liquid transition, it is possible to obtain an image that shows an isolated mass of the polymer (bright zones) that is split by the water sub-phase (dark zones). As the pressure increases until the phase transition zone, it is possible to observe brilliant zones in the isotherm, which indicates that the monolayer increases the density, and therefore, the existence of phase coexistence is possible: one expanded and one condensed. Monolayer collapse is observed when the compression is approximately 20mN/m, which is evident due to the formation of brilliant lines. Figure 6-e to 6-h shows the BAM images for PPhPA, which are more or less homogeneous images, which indicates a fast spreading of the polymeric monolayer onto the surface. As the pressure increases in the first transition, bright, obscure zones appear, which indicates that the density of the monolayer increases and suggests the existence of phase coexistence, one expanded and other condensed. The primary two factors that dominate the monolayer characteristics are the attractive interactions between the polar groups of the polymer molecule and the sub-phase and the cohesive interactions between the polymer molecules. The attractive interactions between the polar groups (-C=O) and the sub-phase favor the spreading of the molecules. However, the cohesive van der Waals interactions between hydrophobic chains promote close aggregation of the molecules, which is inclusive in a tri-dimensional structure.

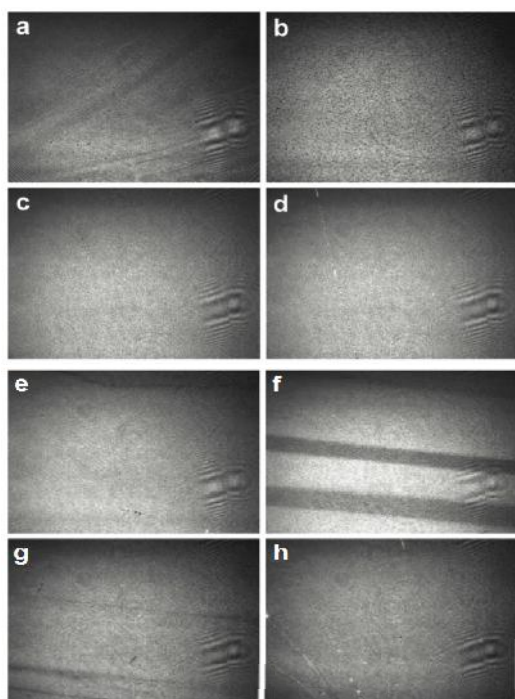


Figure 6 BAM images for PPhEA obtained as: a: $\pi = 0$ mN/m, b: $\pi = 2.7$ mN/m, c: $\pi = 6.5$ mN/m, d: $\pi = 20$ mN/m. and BAM images for PPhPA obtained as: e: $\pi = 0$ mN/m, f: $\pi = 3.1$ mN/m, g: $\pi = 5.4$ mN/m, h: $\pi = 7.5$ mN/m.

These domains appear as brilliant bands and, in the case of

PPhPA at a pressure of 7.5 mN⁻¹, would indicate a collapse of the monolayer at a lower pressure than that shown by PPhEA. This result could be attributed to an effect of the length of the side chain (or spacer group).

To obtain the surface energy of the polymers under study and to estimate its hydrophobic/hydrophilic character, contact angle measurements were performed using polymer films deposited on glass as the solid substrate and water and ethyleneglycol as the solvent with known surface tensions.

By using these data, the free energy of the surface was determined by the Owens, Wendt, and Kaelble method [24, 25] through the systems of equations obtained from two different solvents with known surface tensions. This method can also yield the dispersion and polar contributions to the surface energy.

Table 4 presents the contact angle values (CA) in distinct solvents, the surface energy with its dispersion, and polar components for the polymer under study, and the same values for the corresponding poly(methacrylate)s, i.e., poly(phthalimidoethyl methacrylate) (PPhEMA) and poly(phthalimidopropyl methacrylate), (PPhPMA) taken from previous reported works [12].

Table 4 also summarizes the obtained values for the free surface energy, contact angle, and polar-polar and dispersion contributions for PPhEMA and PPhPMA using water and diiodomethane as solvents with known surface tensions. As in the cases of PPhEA and PPhPA (Table 4), it appears that as the number of methylene groups increases in the side chain, the degree of hydrophobicity increases, and the SE diminishes.

The surface energy values of a polymer provide information on the degree of hydrophobicity, which increases as the surface energy decreases. Therefore, a polymer composed of long alkyl groups present a highly hydrophobic surface, which was experimentally verified due to the low free surface energy values.

Table 4 Values of the contact angles (AC), surface energy (SE), dispersion contribution (γ^d), and polar contribution (γ^p) for PPhEA and PPhPA, and PPhEMA and PPhPMA, (AC*: water; AC**: ethylene glycol)

Polymer	AC*	AC**	SE (mNm ⁻¹)	γ^d (mNm ⁻¹)	γ^p (mNm ⁻¹)
PPhEA	65.7 ± 0.9	53.0 ± 0.9	39.8	4.4	35.5
	66.4 ± 0.8	51.6 ± 0.9	37.4	6.3	31.1
	67.3 ± 0.8	50.5 ± 0.8	35.4	8.8	26.6
PPhPA	69.0 ± 0.9	49.0 ± 0.9	33.6	13.1	20.5
	68.0 ± 0.8	46.4 ± 0.6	34.6	14.8	19.7
	72.0 ± 0.9	52.8 ± 0.9	31.3	13.0	18.3
PPhEMA	47.2 ± 0.9	43.3 ± 0.9	54.8	33.4	21.4
PPhPMA	67.1 ± 0.9	34.9 ± 0.9	46.9	39.6	7.3

Taken from ref. 12.

From the obtained values, it was found that the polar contribution to the free surface energy γ^p for PPhEA is higher than the dispersion contribution, whereas for PPhPA, both contributions have high values.

Figure 7 shows the isotherms for poly (phthalimidoethyl methacrylate) (PPhEMA) and poly(phthalimidopropyl

methacrylate) (PPhMA) previously reported [12]. These isotherms are of the condensed type. In the same figure, the PPhEA and PPhPA isotherms are shown, which are of the expanded type.

The differences in the monolayer behavior of both polymeric families can be described in terms of the different levels of cohesive interactions between the segments located at the air/water interface; one of them involve the strengths associated with the apolar parts of the segments, whereas the other can be attributed to dipolar interactions of the ester groups, which are strongly affected by the interactions with the aqueous sub-phase.

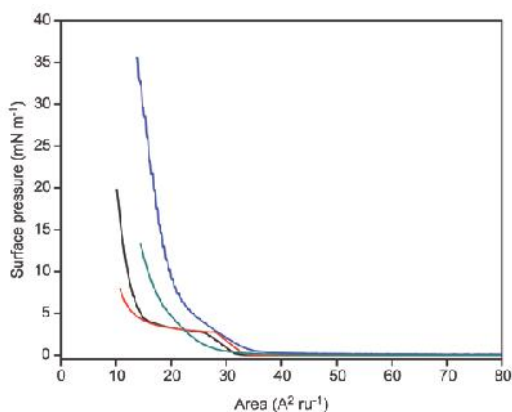


Figure 7 Pressure-area isotherms for PPhEA (black), PPhPA (red), PPhEMA (green), and PPhPMA (blue).

In this case, the behavior of the monolayer for PPhEA and PPhPA is influenced primarily by the polar-type interactions due to the absence of the α methyl group in the main chain, whereas for PPhEMA and PPhPMA, the monolayer behavior is governed by the apolar interactions of the groups of the main chain.

The values of A_0 and the collapse pressures for PPhEA and PPhPA follow the same trend as PPhEMA and PPhPMA. As can be seen in Table 5, the A_0 values diminish as the number of methylene groups in the polymers increases. The values for PPhMAs are higher than those of PPhAAs which is indicative that the surface is better solvent for PPhMAs than for PPhAAs. The values of A_0 and collapse pressures for PPhEA and PPhPA follow the same trend as PPhEMA and PPhPMA (Table 5). As can be seen in Table 5, the A_0 and π_c values diminish as the number of methylene groups in the polymers increases.

Table 5 A_0 , π_c , and π_m component for PPhEA, PPhPA, PPhEMA, and PPhPMA

Polymer	A_0 ($\text{\AA}^2 \text{ru}^{-1}$)	π_c (mN m^{-1})	π_m (mN m^{-1})
PPhEA	14	~19.9	0.51
PPhPA	12	~7.9	0.52
PPhEMA	20	~36	0.57
PPhPMA	17	~13	0.56

One important difference is that for PPhEA and PPhPA, the dispersion contribution to the total free surface energy is higher than the polar contribution. These results can explain the significant influence of the absence of the α -methyl group in the main chain in PPhEA and PPhPA. For this reason, the curves of the surface pressure as a function of surface area differ.

CONCLUSIONS

Monomer and polymers of phthalimidoalkyl acrylates (PPhAAs) were synthesized and the monolayer behavior at the air/water interface were studied. Spectroscopic characterization of the monomers and polymers are in agreement with the expected chemical structure. The surface behavior of PPhAAs were compared with the results previously reported on the corresponding poly (phthalimidoalkyl methacrylate)s (PPhAMAs) i.e. poly(phthalimidoethyl methacrylate) (PPhEMA) and poly(phthalimidoapropyl methacrylate) (PPhPMA). From contact angle measurements using the Owens, Wendt, and Kaelble (OWK) method, the surface free energies (SE) were estimated for both polymers. The behavior of (PPhAA)s and (PPhAMA) was compared to corroborate the effect of the chemical structure on the surface behavior. The effect of the side chain structure on the surface behavior shows that as the length of the substituent increases the zero surface pressure A_0 and the collapse pressure π_c diminishes. The differences in the monolayer behavior of both polymeric families can be described in terms of the different levels of cohesive interactions between the segments located at the air/water interface; one of them involve the strengths associated with the apolar parts of the segments, whereas the other can be attributed to dipolar interactions of the ester groups, which are strongly affected by the interactions with the aqueous sub-phase. In this case, the behavior of the monolayer for PPhEA and PPhPA is influenced primarily by the polar-type interactions due to the absence of the α methyl group in the main chain, whereas for PPhEMA and PPhPMA, the monolayer behavior is governed by the apolar interactions of the groups of the main chain.

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