

Surface Properties of Monolayers of Amphiphilic Polymethacrylates and Polyitaconates: A Minireview

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Abstract

In this minireview, two types of amphiphilic polymers will be analyzed: Polymethacrylates) and derivatives and polyitaconates) and derivatives. Our focus here is to describe and analyze the peculiar behavior of these polymers at the air-water interface. Their orientation, specific interactions and the most important effects that have a strong influence on the behavior of the Langmuir films of these polymers will be analyzed. This minireview explores the effect of the spreading solvents, the effect of the chemical structure of the polymer, the effect of the presence of other polymers in the water subphase, and the effect of temperature.

Keywords: Surface properties; Polymethacrylates; Polyitaconates

Introduction

The study of the surface behavior of macromolecules is a theoretical and practical theme due to its implication both in the industrial and biomedical science fields. From the studies of the spreading monolayers, they behave as models of biological membranes due to their close structural analogy. They play a special role in understanding the processes that occur there, and why the air-water interface is one of the most studied interfaces. Pockels [1] published for the first time a study about the behavior of polymer monolayers at the air-water interface. Subsequently, intensive work has been carried out on this type of system. The properties of polymers at interfaces have been the subject of many experimental and theoretical studies. For a long time, studies on the surface and interfacial properties of polymers have shown a growing interest. [2-10] Much research has been reported on the formation of monolayers at the air-

water interface and their spreading behavior [11-13]. It is very well known that not all synthetic polymers can form monolayers, for this they must present an adequate hydrophilic-hydrophobic balance [14-16]. This type of polymer, named amphiphilic polymers, is an important class of materials that have found many stimulating applications mainly due to their physicochemical characteristics, including hydrophilicity and stimuli-responsive behavior. They have attracted considerable attention because of their outstanding solution properties, such as self-assembly in the presence of a selective solvent. For all these reasons, the properties of these macromolecules at the interfaces have been the subject of many experimental theoretical studies [11,17-21]. Many surface-active substances, either small surfactants or amphiphilic polymers, tend to adsorb at fluid interfaces. And the same time, they can form either Gibbs monolayers when adsorbed from a bulk solution of the polymer or Langmuir monolayers

when they are insoluble in the adjacent bulk fluid phases. The polymer can be spread and later adsorbed at the interface.

In this review, two types of amphiphilic polymers will be analyzed: Polymethacrylates) and derivatives and polyitaconates) and derivatives. Studies on these polymer monolayers spread at the air-water interface to characterize their surface pressure behavior are abundant [22-26]. Our focus here is to analyze different effects that have a strong influence on the behavior of the Langmuir films of polymethacrylates and derivatives and polyitaconates and derivatives. They are:

- A. Effect of the spreading solvents
- B. Effect of the chemical structure of the polymer.
- C. Effect of the presence of other polymers in the water subphase
- D. Effect of temperature

One of the thermodynamic properties of polymer monolayer spread at the air-water interface, surface pressure-area (π -A) isotherms, has been most widely investigated for a long time. The shapes of the (π -A) isotherms observed in studies of polymer monolayers were classified by Crisp [14] into two groups based on whether they are expanded or condensed. The expanded type monolayers were more compressible than the condensed ones

and showed reversible collapse. Fowkes [27] tried to interpret the difference between the two types molecularly. This led to the conclusion that the polymer segments in the expanded type are miscible with water molecules in the water phase, and some portions are immersed into the water phase as loops and tails; whereas in the condensed type, the polymer segments aggregate preferentially by themselves, and water molecules are substantially excluded.

From the (π -A) isotherm, it can deduce some important properties such as the limiting surface area determined A_0 , extrapolating the steepest portion of the (π -A) isotherm curve to zero surface pressure, and the collapse surface pressure π_c where a polymer monolayer begins multilayer formation or precipitation of some parts of the spread polymer chains with further compression. It is important to emphasize that the determination of the collapse point of a monolayer is difficult. Indeed, it is not always possible to determine with some precision the value of the collapse pressure π_c . An interesting example can be given by observing the results found and reported for the monolayer of the poly1-phenyl 1-propyl methacrylate [28].

The monolayer was analyzed using Brewster angle microscopy (BAM) during compression. This technique allowed estimating the collapse pressure π_c of the one copolymer system with relative accuracy. Figure 1 illustrates the observed results.

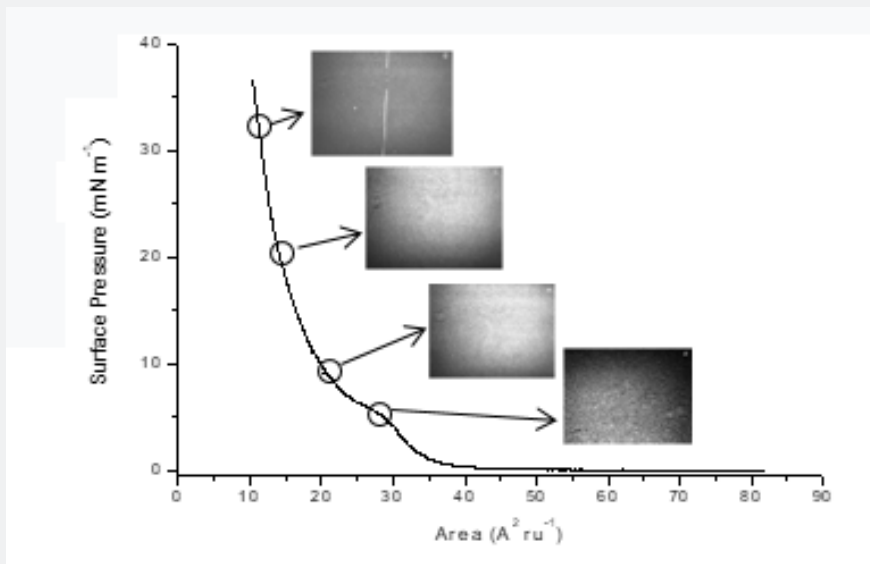


Figure 23: Surface pressure-area isotherm (π -A) of the Langmuir monolayer of the poly1-phenyl 1-propyl methacrylate analyzed BAM during compression [28].

Some attempts for theoretical interpretations of the (π -A) isotherm of polymer monolayers spread at the air-water interface have been made in terms of statistical thermodynamics since the development of the theory of Singer, who assumed that the model

of the surface was a two-dimensional quasi-lattice where a linear polymer chain moves out with various orientations, which is analogous to the three-dimensional Flory and Flory and Eichinger solution theory [29,30].

The equations of the state based on the lattice model could not fit isotherms in the higher surface pressure region. To improve this failure, Huggins [31] proposed an equation of state that is expressed as a virial series and applies to the entire surface concentration range. From fitting isotherms, the fraction of polymer attached at the interface could be determined and thus could be related to the molecular interaction energy [32]. Since the Langmuir technique was first used to study the behavior of polymeric films, many surface pressure-area measurements have been performed on various polymer films. Crisp [14] was the first author to study and systematically discuss the monolayer properties of polymeric materials, especially polyacrylates and polymethacrylates. While it is true that the Langmuir technique was first used to study the behavior of polymer films, today, many techniques have made it possible to study the behavior of polymers at interfaces, including electron spin resonance (ESR), [33,34] ellipsometry, [35-37] and BAM. [38-40].

A. Effect of the spreading solvents

Different macromolecular arrangements at the air-water interface can be induced by either changes in the nature of the subphase or by changes in the spreading solvent. Few studies have described and reported the effect of spreading solvent on the behavior of monolayer's surface pressure areas of polymethacrylates or polyitaconates. Years ago, interesting work was published on this topic. Maleev et al. [41] investigated the effect of different spreading solvents on the compressional behavior of polymethacrylates monolayers relative to some polyacrylates monolayers. They observed that the compressional behavior of polymethacrylate monolayers is affected by the nature of the solvent to a much higher degree than that of polyacrylate monolayers. It was possible to relate this behavior with the polymer glass transition temperature T_g of the polymers studied.

In general, little information is available on how a change in spreading conditions can affect the behavior of polymer monolayers at the air-water interface Maleev et al. [41] suggested that polymers having a T_g higher than the temperature at which their monolayers are spread essentially independent of compression configuration. This would be the case with polymethacrylate monolayers. Conversely, polymers with T_g lower than the temperature at which their monolayers are spread may form several kinds of arrangements resulting from intramacromolecular chain rearrangements, which occur upon the compression of these monolayers. This will be the case with polyacrylates. Another alternative possible explanation for the influence of the spreading solvent could be its thermodynamical quality. The better the solvent, the larger the dimensions of the random coil in solution, which should facilitate the conformational rearrangement into a 2D monolayer. However, Hendlinger et al. [42] concluded that the expansion of the polymer coils in the spreading solutions is not related to the ability or inability to form well-organized monolayers. Different conformations are stable in several spreading solvents, and the effect of the spreading solvent on the stable conformation in the monolayer has been also

investigated [43-45].

B. Effect of the chemical structure of the polymer

Over the past decades, extensive data have been accumulated about the relationship between the chemical structure of amphiphilic polymers and their behavior at the air-water interface. Polymethyl methacrylates and polyitaconates containing either cycles, aromatic, or linear side groups have been synthesized and characterized in solution and the solid state. However, to our knowledge, no studies describe the behavior of this type of polymer at the air-water interface. Monolayers of polymethyl methacrylates containing either aromatic or linear side groups were studied at the air-water interface by Caminati et al. [46]. These authors determined the orientation and the interaction energies of the monolayers of polymethacrylic ester compounds with aromatic substituents of polyphenyl methacrylate (PPMA) and polybenzyl methacrylate (PBeMA). Polyhexyl methacrylate (PHMA) monolayers were also studied for comparison. It was observed that the shapes of the isotherms of PPMA and PBeMA differ from that of PHMA. The aromatic polymers shifted the surface pressure isotherm curves toward lower areas. On the contrary, the surface isotherms of the PHMA move toward larger areas, particularly when the temperature increases. With the increase in temperature, the monolayers of the PPMA and PBeMA become more condensed. This type of behavior has also been observed in other compounds [47] and was explained as a type of structural organization of water molecules around groups anchored on the surface. With these results, Caminati [46] attributed an important role to the geometric factor and the steric impediments in determining the interfacial distribution of each polymer at the air-water interface. In fact, the orientation of PPMA and PBeMA was slightly horizontal, and in turn, the angles between the aromatic rings and the interfacial plane are small. Many researchers have studied hydrophilic polymers hydrophobically modified to establish relationships between chemical structures and interfacial characteristics [48-50].

Results on the behavior of monolayers of functionalized polymethacrylate shown in Scheme 1 have been reported [51]. These polymethacrylate derivatives form a stable film at the air-water interface. The surface pressure area curves (π -A) are the condensed type, which tends toward isotherms more condensed when the number of the methylene groups in the lateral chain increases [51]. It was also observed that the A_0 values of the boundary surface area decrease when the number of methylene groups in the side chains of the polymer increases. The variation of A_0 with the chemical structure of the polymers was explained in terms of the flexibility of the side chain, which is known to depend on the length of the spacer group. With these polymer systems, molecular dynamic simulation (MDS) calculations were performed to describe the experimental behavior found for the three polymers at the air-water interface. Figure 2 shows the variation of the order parameter $S(r)$ as a function of time for the three polymers.

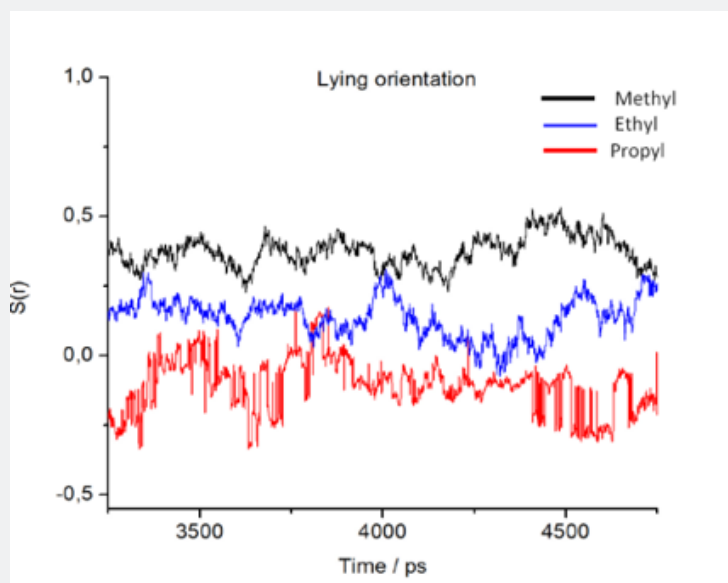
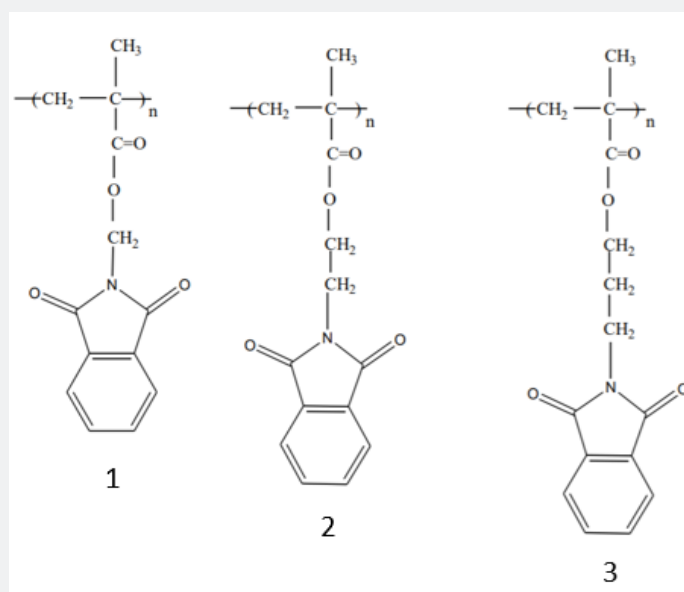


Figure 2: Variation of $S(r)$ as a function of time for the three polymers [51].



Scheme 1: 1) PolyN-phthalimidomethyl methacrylate (PNPMMA), 2) PolyN-phthalimidoethyl methacrylate (PNPEMA), 3) PolyN-phthalimidopropyl methacrylate (PNPPMA) [51].

From these results, considering that the value of 1.0 for $S(r)$ indicates that the unit vectors in different chains are parallel to each other. From the results shown in Figure 2, the authors concluded that (PNPMMA) presents greater organization at the air-water interface than (PNPEMA) and (PNPPMA). The structures, specifically the amount of conformational order associated with monolayer films at the air-water interface of polymers, such as polyoctyldecyl acrylate, containing long, and

flexible side chains, have also been reported [52]. The results of these studies have shown that methylene stretching vibrations are sensitive indicators of the degree of order in the hydrocarbon side chains. The superficial concentration of polymeric monolayers scattered at the air-water interface is easily adjusted by compressing or expanding the monolayer and obtaining a surface isotherm surface pressure area [53]. It is also possible to draw an analogy between the intervals of superficial concentration and the

corresponding within the face that are frequently used in polymer science. Thanks to this analogy, the area extrapolated under pressure zero surface pressure, A_0 , and the collapse pressure or critical surface pressure, π_c , respond to phenomena that take place in the concentrated region [26]. In the region of semi-diluted concentration, the pressure surface obeys a power law of surface concentration according to the concepts of scale [54]. The surface pressure in the region semi-diluted varies with the surface concentration according to the expression: $\pi = \Gamma^2 \nu / (2\nu - 1)$ where Γ is the surface concentration and ν is the critical exponent of volume excluded [3]. Despite the importance of studying the behaviors just mentioned, there are few studies on this topic.

Indeed, comparative studies of thermodynamic and morphological properties of Gibbs monolayers with corresponding Langmuir monolayers have been scarce [55]. A more recent work, in this regard, corresponds to polymethacrylate containing cycles in the lateral chain [26]. Leiva et al. performed a comparative study of polytetrahydropyranyl-2-methyl methacrylate (PTHMPM) in solution and at the air-water interface. They demonstrated the analogy between the properties of this polymer in solution (3D) and at the air-water interface (2D). The authors demonstrated two different theta conditions for this polymer, the binary solvent toluene/cyclohexane at 298 K and the air-water interface at 298 K, respectively. [26]. The morphological features of the condensed phase structures of the Langmuir monolayers and the adsorption layers agree completely [53].

Studies have also addressed the equilibrium and surface properties of Langmuir monolayers of polymethyl methacrylate (PMMA) at the air-water interface [56]. These were determined as a function of concentration and molecular weight. Dilational and shear complex elasticity moduli covering a frequency range from 10–3 to 0.2 Hz have been discussed. It was found that the air-water interface behaves as a poor solvent for PMMA monolayers, thus suggesting that the polymer coils take collapsed soft-disks (pancakes) shape at the interface. The equilibrium and dynamic results suggest a fluid-to-soft-glass transition as the polymer concentration increases above a critical packing fraction at a constant temperature. This behavior was in agreement with the results previously discussed for the dilational rheology of poly-4-hydroxystyrene [57]. The dependence on the relaxation dynamics of the monolayers suggests that the gel state may be considered as a fragile soft glass.

Crisp [14] was the first author to study and systematically discuss the monolayer properties of polymeric materials, especially polyacrylates and polymethacrylates. The stereostructural difference in a polymer is expected to induce variation in the shape of surface pressure-area isotherms owing to steric hindrance. The stereostructural difference in a polymer is expected to induce variation in the shape of surface pressure-area isotherms owing to steric hindrance. A typical and known

example corresponds to polymethyl methacrylate (PMMA). Beredjick et al. [58,59] were one of the first to report results that the surface pressure area (π -A) isotherm of isotactic PMMA is more expanded than that of syndiotactic PMMA and the former PMMA has a limiting area twice as large as the latter PMMA. Brinkhuis and Schouten [60] performed detailed surface pressure measurements of PMMA films as a function of molecular weight and tacticity. These authors also reported results about the effect of the tacticity on the behavior of polymethyl methacrylate with short ester side chains such as methyl, ethyl, and isobutyl [60].

The observed (π -A) isotherms for isotactic and syndiotactic PMMA were in agreement with the findings of Beredjick. The isotactic PMMA film showed a transition at about 8 mN/m and an area of about 0.2 nm²/monomer unit. From studying the transition as a function of molecular weight and compression speed, it was deduced that the transition corresponds to two-dimensional pseudo crystallization with a double-helix conformation in the PMMA films. The (π -A) isotherms of the isotactic PMMA depended on its molecular weight.

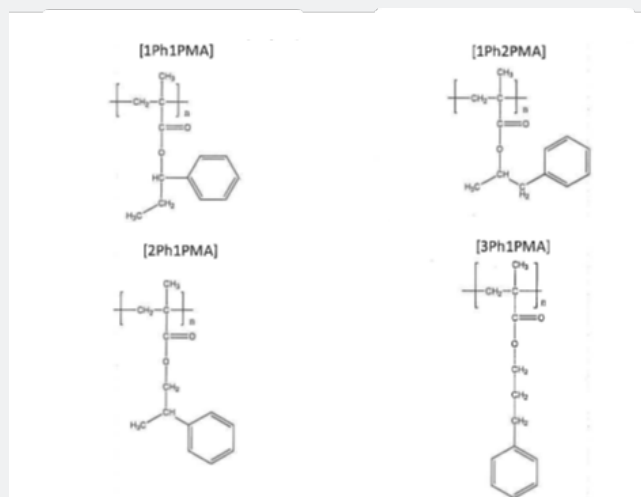
The surface behavior of monolayers of the functionalized polymethacrylates polymethacrylate 1-phenyl 1-propyl (1Ph1PMA) polymethacrylate 1-phenyl 2-propyl (1Ph2PMA), polymethacrylate 2-phenyl 1-propyl (2Ph1PMA) and polymethacrylate 3-phenyl 1-propyl (3Ph1PMA) at the air-water interface were investigated at 298 K on an aqueous subphase [28]. Scheme 2 shows the chemical structures of the polymers (1Ph1PMA), (1Ph2PMA), (2Ph1PMA), and (3Ph1PMA).

The monolayer characteristics of (1Ph1PMA), (1Ph2PMA), (2Ph1PMA), and (3Ph1PMA) were studied and compared in terms of surface pressure-area (π -A) isotherms, surface compressional modulus-surface pressure (C_s - π) curves, static elasticity-surface concentration curves, hysteresis phenomena, and phase images observed with BAM. The results showed that the polymers studied gave rise to stable monolayers, and the isotherms presented pseudoplateau regions at different surface pressure values depending on the chemical structure of the polymer. Small differences in the chemical structures of functionalized polymethacrylates allow us to explore the influence of the position of the different groups of the side chain; in other words, how this isomeric characteristic affects the behavior of the polymer at the air-water interface [28]. Figure 3 shows the surface pressure isotherms (π -A) of the (1Ph1PMA), (1Ph2PMA), (2Ph1PMA), and (3Ph1PMA).

It is important to take into account and to remember that structurally PMMA and polymethyl acrylate (PMA) differ only in the replacement of a methyl group with a hydrogen on the backbone in the repeat unit. However, this small change has a profound effect on the steric hindrance to the rotation of bonds in the polymer backbone, which produce differences in chain

stiffness. It was observed that the rigid steric hindrance has a significant influence on the type of surface isotherm obtained. The (π -A) isotherm of PMA is the expanded type where a finite value of the surface pressure is observed over a wide range of the surface area. The isotherm of PMMA, however, is of the condensed type where the surface pressure increases more steeply than that of PMA, and its limiting value is lower than that of PMA. Sutherland and Miller [61] also studied the (π -A) isotherms of polytert-butyl acrylate and polytert-butyl methacrylate as a function of tacticity. They interpreted the differences in the isotherms as being due to different packing efficiency of the polymer segments of different tacticity in the films. Similar experiments have been performed by Mumby et al. [62] for polyoctadecyl methacrylate (PODMA) and polyoctadecyl acrylate (PODA). Both polymers have a long alkyl

chain on the ester group in the repeating unit. The (π -A) isotherm of PODMA was substantially different from that of PODA. The surface pressure of PODMA was observed at a larger surface area than that of PODA since rotations about bonds in the polymer backbone are sterically more hindered for methacrylates, as compared with acrylates, due to the presence of the methyl side group. In the isotherm of PODMA, there are two distinct regions where the surface pressure rises approximately linearly with the decrease in surface area. The first rise in the isotherm was interpreted as resulting from trying to force the backbone of the polymer into a closely packed, two-dimensional structure. The second rise in the isotherm was attributed to interactions between the long aliphatic side chains. The lower steric hindrance in PODA allows the long alkyl side chain to be compressed easily.



Scheme 2: Chemical structures of the polymers (1Ph1PMA), (1Ph2PMA), (2Ph1PMA), and (3Ph1PMA).

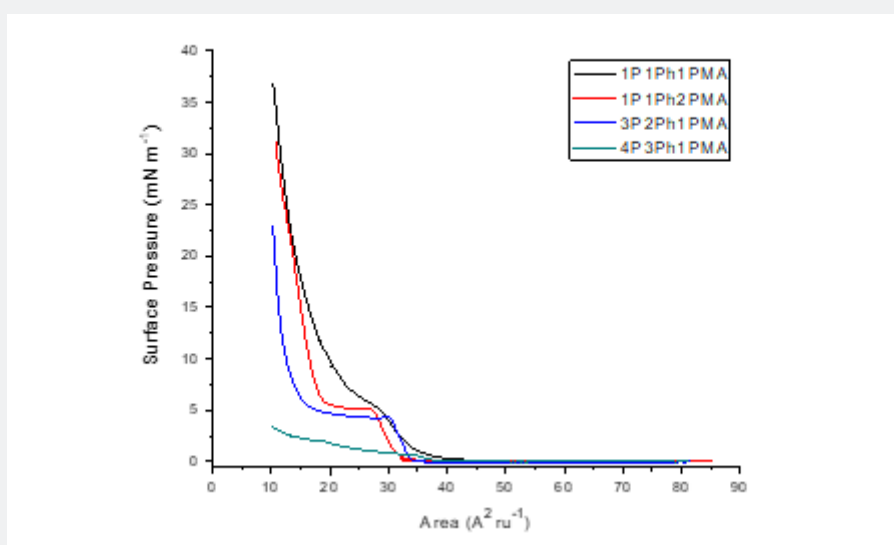


Figure 3: Surface pressure isotherms (π -A) of the (1Ph1PMA), (1Ph2PMA), (2Ph1PMA), and (3Ph1PMA).

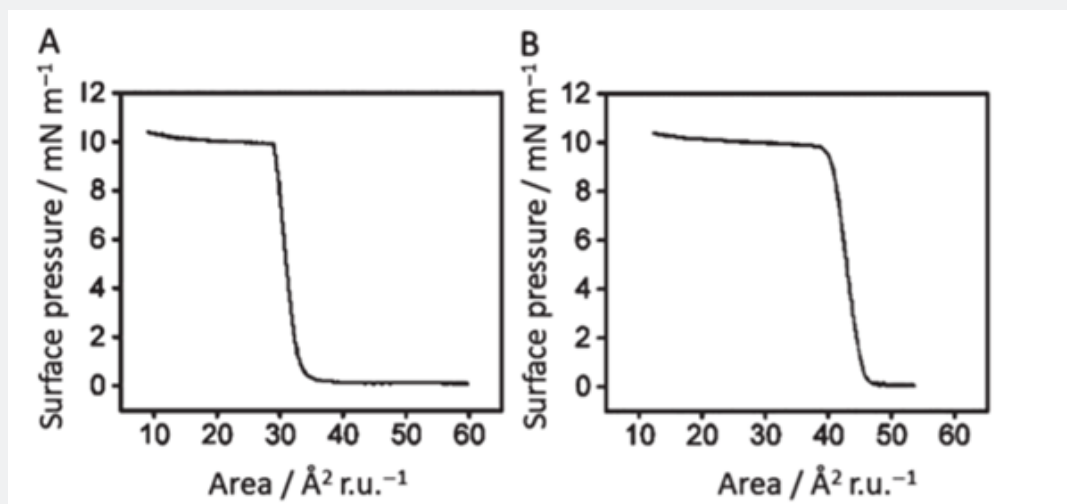


Figure 4: Surface pressure-area (π -A) isotherms for: (A) PEHMA -b- PDMA, and (B) PEHMA-b-PDMA.

Concerning polyitaconates and their derivatives, numerous studies on polymers derived from itaconic acid have been reported [63-67]. These polymers have attracted much attention mainly due to their interesting and peculiar physicochemical behavior [68-71]. Despite the numerous studies reported and that this type of polymer has attracted much attention due to its applications, [72] research on behavior at the air-water interface is less frequent. As has been profusely pointed out, for a stable polymer monolayer formation at the air-water interface, the polymer must present an appropriate hydrophilic-hydrophobic balance in its structure [11]. That is how polymer derivatives of itaconic acid, such as polymonoesters, polydiesters, and copolymers, present remarkable amphiphilic characteristics. In its structure, it has two carboxylic acid groups (hydrophilic segments) and a hydrocarbonated chain (hydrophobic segment). Polyitaconates and their derivatives have been studied primarily in terms of their synthesis [66,67], characterization, [68-72], and interpolymer complexation [73,74].

However, reported investigations about these polymers' behavior at the air-water interface are less frequent. Monolayers spread at the air-water interface have been studied for polymonoethyl itaconate (PMOI), polymonodecyl itaconate (PMDI), polymonododecyl itaconate (PMDoI), polymonobenzyl) (PMBzI), polymethyl dodecyl itaconate (PmeDoI), and the alternating copolymer (monoethyl itaconate-alt-maleic anhydride) (MOI-alt-MA) [23]. The chemical structures of the polymers are shown in Scheme 3.

All polymers shown in Scheme 3 were spread at the air-water interface, and their respective Langmuir isotherms were obtained. These surface pressure/area isotherms (π -A) were obtained by monolayer compression for all the indicated polymers: (PMOI), (PMDI), (PMDoI), (PmeDoI), (PMBzI), and (MOI-alt-MA). In all cases, the isotherms are of the expanded type [11]. The surface

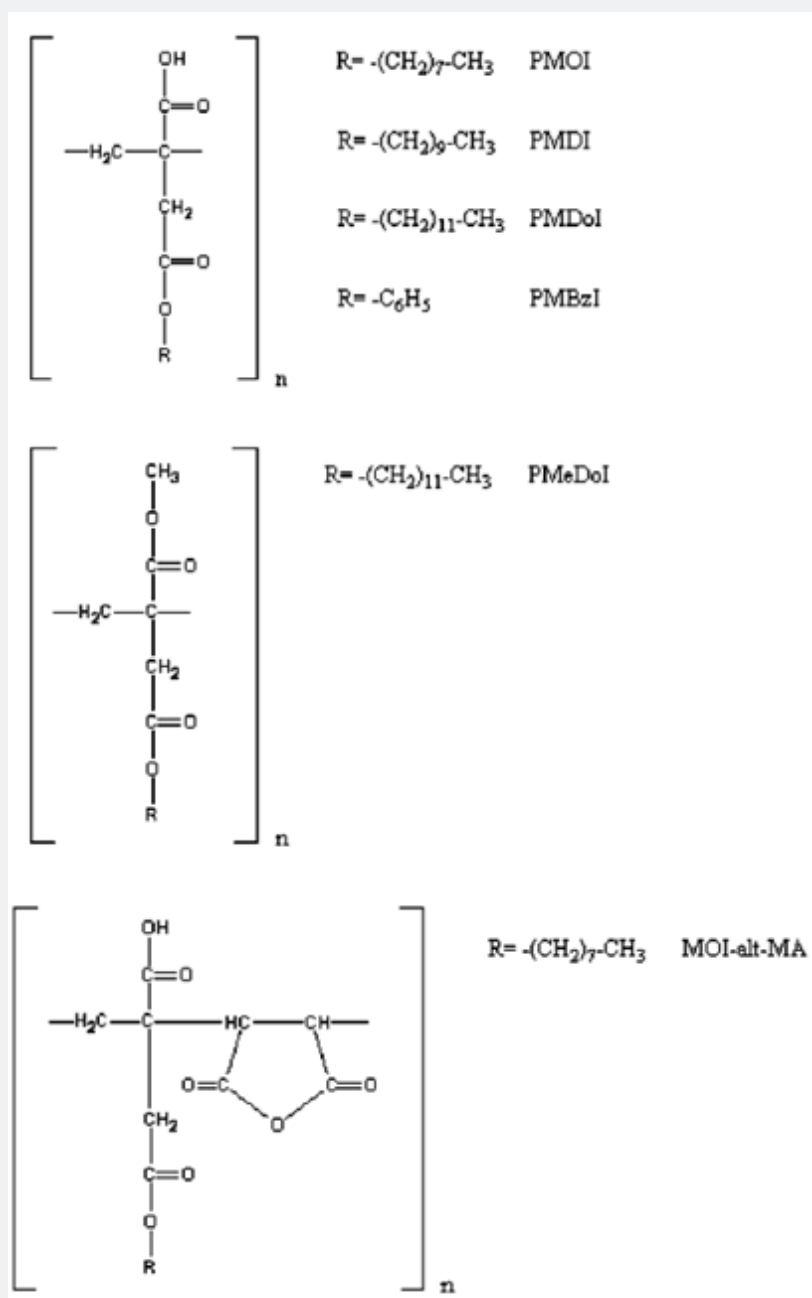
pressure increases gradually through monolayer compression. These isotherms present a defined collapse pressure.

The projected area to zero surface pressure A_0 was obtained from the linear variation of π with a surface concentration in the condensed region; the collapse pressure π_c was also determined. As usual, in the polymer, the monolayer spread at the air-water interface begs an analogy between the intervals of superficial concentration and the regimes of concentrations of solutions frequently used in polymeric science. By this analogy, the extrapolated area to zero surface pressure and the collapse pressure respond to phenomena that happen in the concentrated region (in 2D) [10]. In the semidilute concentration region, surface pressure obeys the power law of the surface concentration and is independent of the molecular weight [11]. In this concentration regime, that is, in a moderately concentrated solution, the polymer chain partially interpenetrates each other. According to the scaling concepts, [12,13] the surface pressure in the semidilute region varies with the superficial concentration according to the following expression $\pi = \Gamma^2 v / (2 v^{-1})$ where Γ is the surface concentration and v is the critical exponent of volume excluded [3,14]. Applying this equation, the values for the excluded volume parameter v of the polymers studied were calculated. They are summarized in Table 1.

The v values summarized in Table 1 are very similar; these results indicate similar likeness with the interface for the six polymers, which is reasonable according to the similar stability of the monolayers reflected by their similar collapse pressures. In conclusion, the polymers spread at the air-water interface show similar behavior. In agreement with the polymeric scale concepts and second virial expansion in semidilute and dilute regions, respectively, for these polymers, the air-water interface at 298 K is a bad solvent, very close to the theta solvent.

Table 1: ν values obtained from the linear region of Log π vs log Γ plots.

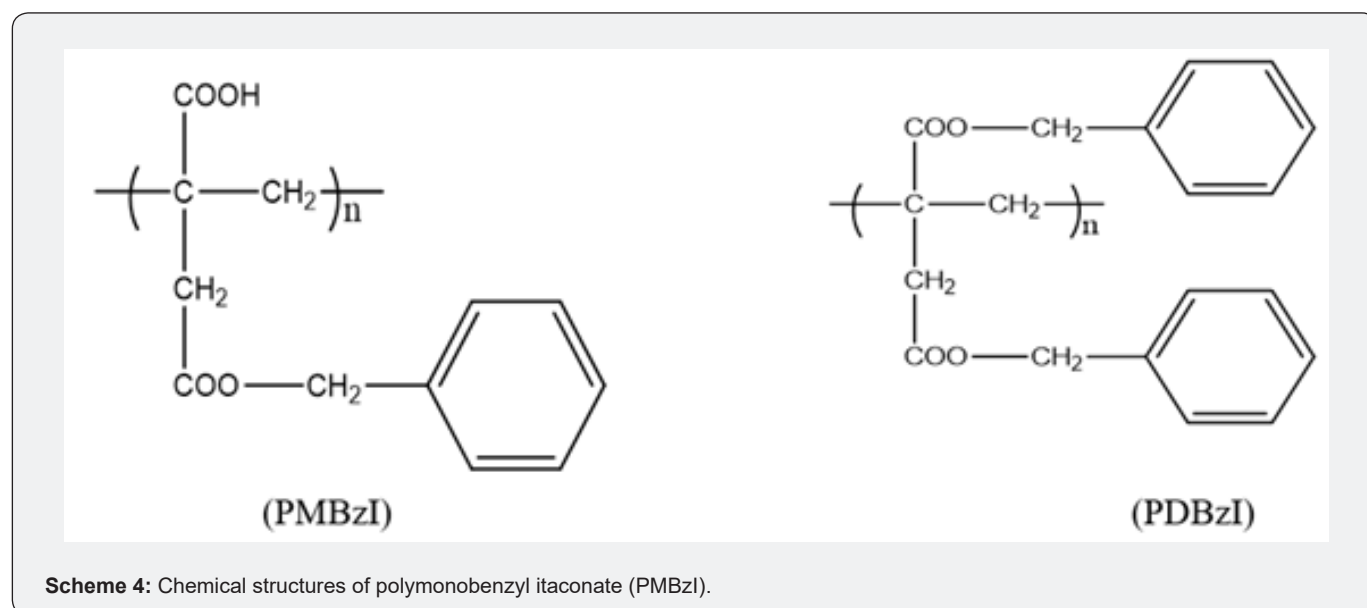
polymer	$\nu \pm 0.01$
PMOI	0.51
PMDI	0.51
PMDoI	0.52
PMeDoI	0.51
PMBzI	0.52
MOI-alto-MA	0.51


Scheme 3: Chemical structures of the polymers [23].

Polymers derived from itaconic acid containing saturated rings as side chains show significant mechanical and dielectric activity when they are affected by force fields [63,64]. This is partly due to the flexibility of the saturated rings, which can flip between two conformational states, e.g., chair-to-chair [65]. 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 [4-6].

In previous articles, the relaxational behavior of polymonobenzyl itaconate (PMBzI) [5] and polydibenzyl

itaconate (PDBzI) [4] was explored by dynamic, mechanical, and dielectric spectroscopy. From the relaxational behavior of the two polymers, it was concluded that the small differences in their chemical structures also gave rise to significant differences in relaxational behavior [65]. The peculiar relaxational behavior of polymono and dibenzyl itaconates warranted a comparative study of the surface behavior of this kind of polymer at the air-water interface [7]. Polymonobenzyl itaconate (PMBzI) [25] and polydibenzyl itaconate (PDBzI) form stable monolayers at the air-water interface. Scheme 4 shows the chemical structures of polymonobenzyl itaconate (PMBzI) and polydibenzyl itaconate (PDBzI).



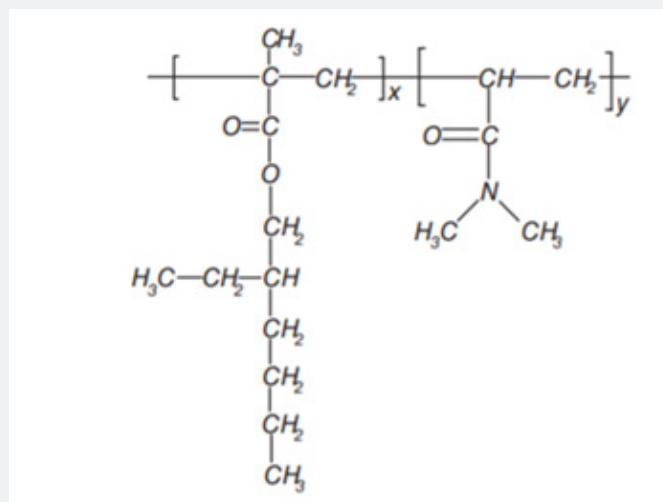
Scheme 4: Chemical structures of polymonobenzyl itaconate (PMBzI).

The chemical structures of PDBzI and PMBzI significantly affect the shape of the surface isotherms (π -A), irrespective of the pH level in the water subphase. The results reported 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 (A_0 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. At the same time, PDBzI is less hydrophilic than PMBzI according to the level of surface free energy, which is consistent with the chemical structures of the polymers [25].

Currently, in Langmuir's film work, his training has been imaged and analyzed using BAM to complement the data obtained from surface-pressure measurements. It is important to remember that BAM is a useful tool for investigating the dynamic process of monolayer compression at the air-water interface and the polymer morphological texture of the Langmuir film. The advantage of BAM is that the morphology of the monolayers at

the air-water interface can be visualized without affecting the monolayer [75-77]. Studies about the behavior at the air-water interface of block copolymers containing methacrylates or itaconates are scarce. Interesting examples include those with a second hydrophobic block. Among them, the block copolymer monolayers of polystyrene-polymethyl methacrylate at the air-water interface were studied [77].

The surface behavior of two diblock copolymers of (2-ethyl hexyl methacrylate-b-(N-N-dimethylacrylamide) (Scheme 5) with different molecular weights of the hydrophobic segment was described to understand the effect of both molecular weight and the confinement of these systems. The results were compared with those obtained for the corresponding homopolymers of each block to understand their role in the overall behavior of diblock copolymers. The surface activity of two amphiphilic diblock copolymers containing (2-ethyl hexyl methacrylate-b-N-N-dimethylacrylamide) (EHMA-b-DMA) with different chain lengths of the hydrophobic segment was studied. Such studies aim to identify the effects of the hydrophobicity degree of these systems on their surface behavior [78].



Scheme 5: Chemical structure of (2-ethyl hexyl methacrylate-b-N, N-dimethylacrylamide) copolymer (EHMA-b-DMA) [78].

Surface pressure-area isotherms' (π -A) static and dynamic elasticities and ν exponent of the excluded volume were also obtained. Scheme 5 shows the chemical structures of (2-ethyl hexyl methacrylate-b-N, N-dimethylacrylamide) (EHMA-b-DMA). Figure 4 shows the Langmuir monolayers for EHMA-b-DMA (A) and EHMA-b-DMA (2) (B) of different molecular weights. To obtain further information on the role of each block on the

surface behavior of the diblock copolymer, the surface isotherm for the hydrophilic block and the hydrophobic block were also determined. The surface pressure isotherm corresponding to the hydrophilic block is shown in Figure 5A. This is a condensed isotherm very different from that of copolymers. In contrast, the surface isotherm of the hydrophobic block (Figure 4B) is very similar to that of the copolymer, as shown in Figure 5B.

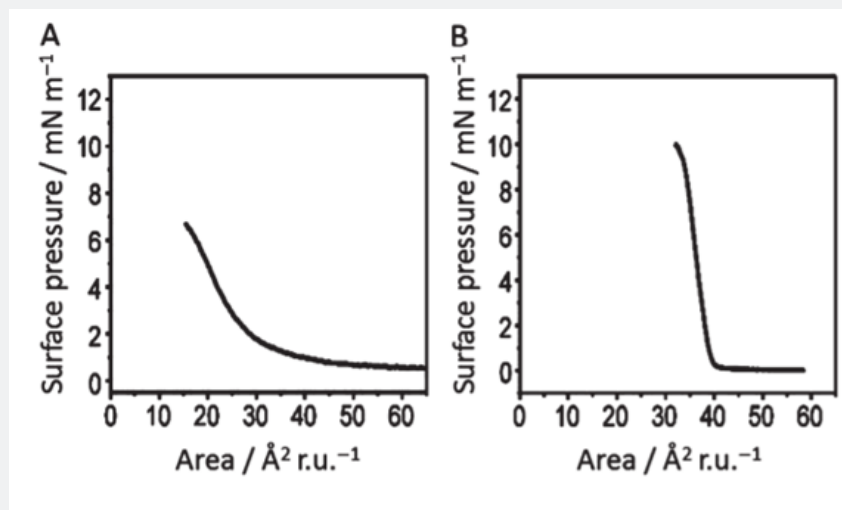


Figure 5: Langmuir isotherm of polyN, N-dimethylacrylamide using chloroform as a spreading solvent at 298 K. B: Langmuir isotherm of poly(2-ethyl hexyl methacrylate).

From the results of this work, the amphiphilic diblock copolymers based on (2-ethyl hexyl methacrylate) and (N, N-dimethylacrylamide) formed stable monolayers at the air-water interface. The isotherms of the copolymers show regions with pseudoplateaus and plateaus, which can be attributed to phase

transitions or the monolayer collapse, respectively, according to the experimental results of hysteresis and BAM images. No significant effect of the molecular weight of the hydrophobic block was found either in the morphology or the collapse pressure of these monolayers, as observed by BAM [21].

C. Effect of the presence of other polymers in the water subphase

Few studies have directly addressed the effect of the presence of other polymers in the water subphase. The properties of polyamphiphilic monolayers at the air-water interface are also strongly affected by water-soluble polymers and surfactants present in the subphase [77]. One of these investigations was performed by Gargallo et al. [79] The addition of surfactants or polymers to a subphase is used to obtain stable mono or multilayers. These studies serve to facilitate possible applications or to obtain more information on the interactions involved and the possible formation of interpolymer complexes [18]. Results have been reported on the effect of the presence of polymonomethylitaconate (PMMel) in the form of maleic anhydride-alt-stearic methacrylate (IMA -alt-StM) isotherms at pH 3.0 and 7.0. The isotherm of MA-alt-StM with water-PMMel subphase at pH 3 had a higher critical surface pressure π_c than the isotherm at pH 7.0 under identical conditions [79].

D. Effect of temperature

Another aspect analyzed in the present review is how the temperature on the surface pressure of monolayers of polymethacrylates and copolymers containing metacrylates can modify the surface isotherms. For example, the case of polymethacrylates with n-alkyl groups containing from 9 to 18 carbon atoms [80]. Two kinds of phase transitions have been observed in surface pressure-area isotherms, and these have been investigated extensively [81] The phases observed are well characterized and analogous to the specification of 3D phases. Comparative studies between Langmuir monolayers of functionalized polymethacrylates and polyacrylate have been frequent. Among them, Yoo and Yo [82] measured the surface pressures of polyN-butyl methacrylate (Pn-BuMA) monolayers at different temperatures. All isotherms were of the condensed type, and the temperature coefficient of the surface pressure in the transition region was positive and negative in the plateau region. Another case of block copolymer monolayers of a polystyrene-polymethyl methacrylate at the air-water interface has been studied [77] They observed an important effect of temperature on the interfacial behavior of this copolymer. In the plot vs. surface area per repeating unit, the monolayer changed from the gas phase to the liquid expanded phase.

Conclusion

In conclusion, the main factors affecting the behavior of polymers at the air-water interface have been indicated in this review, some of which warrant further exploration.

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