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N-1-alkylitaconamic acids-*co*-styrene copolymers. Surface characterization

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Abstract

A serie of six *N*-1-alkylitaconamic acids-*co*-styrene copolymers with alkyl groups varying in side chain length from 3 to 12 was used in this study. The surface behaviour of the copolymers has been studied as function of the side chain length. Contact angle data for two of these copolymer surfaces were obtained in water and several liquids. From this information the surface energy was determined. Differences in the wettability of *N*-1-alkylitaconamic acid-*co*-styrene are found. The results are discussed in terms of hydrophobic and polar effect of the copolymers. Results on spread monolayers characteristics of these copolymers on water surfaces are also reported. Surface pressure–area (π–A) isotherms on a pure water subphase exhibit a transition region depending on the length of the alkyl side chain of the itaconamic acid moiety. It was also analyzed the phase transition in the monolayer at the air/water interface by brewster angle microscopy (BAM). Molecular mechanics approach was used to obtain predictions about the local interaction energies between segments. It was possible to conclude that the local interaction energies of propyl and decyl derivatives are quite similar while the hexyl derivative has higher interaction energy. The analysis of the coulombic energies together with the dispersion van der Waals energies (VDW) would be indicative, in first approximation, that carbonyl groups are more exposed in the case of propyl than in the other copolymers studied.

Keywords: *N*-1-alkylitaconamic acids-*co*-styrene copolymers; Surface pressure–area (π–A) isotherms; Air/water interface

1. Introduction

Increasing attention is currently being directed to the synthesis of copolymers containing both hydrophilic and hydrophobic segments, i.e. amphiphilic polymers [1]. Multifunctionalization of polymers and copolymers is a suitable way to obtain amphiphilic polymer systems [2]. Copolymers with variable amounts of both types of structures can be considered as good models to study interactions in biological systems, mainly because of the possibility to produce a chemically homologous series of surfaces varying principally in hydrophobicity [3]. Copolymers containing itaconate units are of interest due to the variety of structures that are possible to obtain. Particularly interesting are mono-*n*-alkyl-itaconates as comonomers because they have the capacity to interact via hydrogen bonds through the free carboxylic groups [4,5]. On the other hand, poly(itaconamic) acids are a family of polymers derived from itaconic acid which can be classified as strong interacting amphiphilic polymers [6,7]. In fact, these polymers show a free carboxylic and amide groups per repeating unit, which should be able to interact specifically by hydrogen bonding formation with different acceptor polymers, what is of interest in the study of polymer–polymer miscibility. The alkyl side chain, in these polymers, can be varied obtaining polymers with different length in the side chain thus controlling the hydrophobicity [6,7]. Therefore, it should be expected that a balance between the length of the alkyl side chain and the free carboxylic group would allow to obtain particular surface behaviour.

In this paper, we investigate the surface properties and Langmuir monolayer characteristics of a novel family of the amphiphilic copolymers: (*N*-1-alkylitaconamic acids-*co*-styrene) (NAIA-*co*-S) (Scheme 1). In order to know the effect of the length of the side chain on the surface pressure–area isotherms (π–A) and on the surface energy, copolymers containing 1-Propyl (NPIA), 1-Butyl (NBIA), 1-Hexyl (NHIA), 1-Octyl (NOIA), 1-Decyl (NDIA) and 1-Dodecyl (NDoIA) groups were studied.

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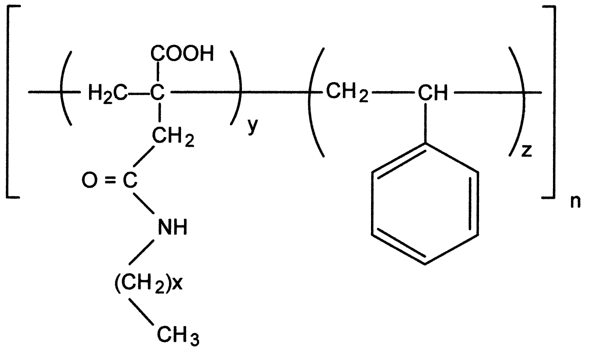

x = 2 : NPIA-co-S
x = 3 : NBIA-co-S
x = 5 : NHIA-co-S
x = 7 : NOIA-co-S
x = 9 : NDIA-co-S
x = 11: ND_0IA-co-S

Scheme 1.

2. Experimental

2.1. Monomer and copolymer preparation

N-1-alkylitaconamic acids (NAIA) were synthesized by reaction of itaconic anhydride with the corresponding 1-alkylamine in chloroform following procedures previously reported and improved by us [6,7]. A sample of styrene from Merck previously distilled under vacuum was used for copolymerization. Copolymerization of the monomers was carried out in bulk at 354–388 K (depending on the *N*-1-alkylitaconamic acid used) under nitrogen, using α,α'-azobisisobutyronitrile (AIBN) (0.6 mol%) as initiator. The conversion of most of the copolymers were rather low ($<10\%$). Purification of the copolymers was achieved by reprecipitation with methanol in THF solution, before vacuum drying [7,8].

2.2. Copolymer characterization

Copolymers were characterized by ^{1}H NMR in a Bruker AC-200 spectrometer using TMS as internal standard and chloroform as solvent [8]. FTIR spectra were recorded on a Vector 22 Bruker Fourier transform infrared spectrophotometer. The spectra were recorded with a resolution of 1 cm^{-1}. The samples were prepared directly in KBr pellets. Composition of the copolymers were determined by elementary analysis measurements following the nitrogen content in the copolymer [8]. The molecular weight of the copolymers was in the range 60,000–80,000 and the molecular weight polydispersity (MWD) was 1.84.

2.3. Surface energy

The surface energies of the copolymers was determined in water, bromobenzene and a series of liquids by wettability measurements. Films of the copolymers were spin-casted onto glass slides for optical microscopy. The casted films were dried for 30 min at 120 °C. The wettability of the copolymer films with several liquids was then determined by static contact angle measurements. Static contact angles were measured using a contact angle system OCA by Dataphysics with conventional goniometer and high performance video camera, controlled by SCA20 software. A syringe connected to a Teflon capillary of about 2 mm inner diameter was used to supply liquid into the sessile drop from above. A sessile drop of about 0.4–0.5 cm radius was used. The three-phase contact line of the drop was then slowly advanced by supplying more liquid from above through the capillary which was always kept in contact with the drop. The maximum contact angles were measured carefully from the left and right side of the drop and subsequently averaged. The above procedures were repeated for six drops of each liquid on three new surfaces. All readings were then averaged to give an averaged contact angle. All experiments were performed at room temperature.

2.4. Surface pressure isotherms

Surface pressure–area (π–A) isotherms for spread films of the copolymers at the air/water interface were obtained using a NIMA model 611 surface film balance (NIMA Instruments, Coventry, UK). The entire system was covered with a box of poly(methyl methacrylate). The copolymer monolayers were deposited on the water surface (Milli-Q its resistivity was always higher than 18 MΩ, and its surface tension at 298 K was 72.12 mN m^{-1}) from chloroform solutions with concentration of ca. 0.1% (w/v). The initial state of the film was always chosen to have surface pressure, π, close to zero. After total evaporation of the solvent and stabilization of the film (about 20 min), the film is continuously compressed. The data were obtained at a constant compression rate of 10 cm^2 min^{-1}. Water sub-phase pH was adjusted by adding HCl or NaOH solution to obtain a constant pH.

2.5. Brewster angle microscopy

Brewster angle microscopy (BAM) was employed to visualize the structure of the monolayer at the air/water interface. The conditions to carried out this study of the topography are the same described to obtain the isotherms. We use a Microscopy that consists of a p-polarized laser 30 mw which is reflected off the air/water interface with an incident angle of 52–54°. The lateral resolution is 2 μm. The reflected beam passes through a focal lens into an analyzer at a known angle of incident polarization and finally a CCΔ camera.

2.6. Molecular simulation

In order to estimate the interaction energy as a first approach, two conformations of the *N*-alkylitaconamic acid (NAIA) fragment were selected randomly from data collection. If it is assumed that miscibility and other properties are determined by the enthalpy of mixing ΔH_{mix}, that ΔH_{mix} is dominated by the local interactions between segments of the polymer chains and, furthermore that $P\Delta V_{\mathrm{mix}}$ contribution can be ignored (making $\Delta H_{\mathrm{mix}} = \Delta E_{\mathrm{mix}}$), the polymer miscibility and other properties can be estimated from interaction energies calculated from molecular mechanics studies on pairs of small polymer fragments [9]. A simple molecular mechanics approach has been proposed by a number of groups [10–12]. A Blends (MSI) packaged was used, where this approach was implemented. Relatively large polymer segments (10 backbone bonds) were used. To obtain an accurate prediction of the local interaction energies between chain segments, it is important to use a representative sample of the available conformations for each chain. These were generated using five simulated annealing cycles. Each cycle consists in 200 ps of simulation with a mean temperature of 700 K and a minimum temperature of 200 K. The temperature was incremented each 20 K by 1 ps. Finally a molecular dynamic of 100 ps at 500 K was run and used like data collection. To calculate the interaction energy, two conformations of NAIA fragment are selected randomly from data collection. These are initially placed so that their centers of mass coincide. One oligomer is then oriented at a random angle and the centers of mass are moved apart until either the intermolecular energy drops below a predefined threshold. This process is repeated many times to generate 100,000 oligomer pairs. Then the interaction energy is calculated for each pair and statistically analyzed. This is done using either molecular mechanics, with the force field UFF.

3. Results and discussion

Surface energy. The wettability of the copolymer films with a series of liquids was determined by static contact angle measurements. Since these copolymers interact with wetting liquids mainly by dispersion forces, the empirical wetting relation developed by Zisman [13] is a useful way to present wetting data [14]. Plotting the cosine of the contact angle of wetting (cos θ) versus the surface tension of the wetting liquid (γ_L) yields a straight line with the slope *m*. Extrapolation to the condition of complete wetting of the copolymer surface (cos $\theta = 1$) gives the critical surface tension γ_C. In order to compare the surface energy of these copolymers, we have chosen two of them. NPIA-*co*-S, with a short alkyl chain and NDoIA-*co*-S, with a larger alkyl chain. Copolymer composition used along this work was 20% S. Fig. 1 shows Zisman plots for two copolymers, NPIA-*co*-S and NDoIA-*co*-S. Extrapolated values for the critical surface tension γ_C of the two copolymers are summarized in Table 1. As can be observed the γ_C values for *N*-1-propylitaconamic acid-*co*-styrene and *N*-1-dodecylitaconamic acid-*co*-styrene are very similar. Contact angles values increase with increasing side chain length. The total surface energy of the films was estimated, and the dispersion force component (γ^d) and the polar component (γ^P) were calculated for the two copolymers by Owens and Wendt [15] and Kaelble [16] methods. We can observe that the polar contribution γ^P to the total surface energy are very different, for these copolymers.

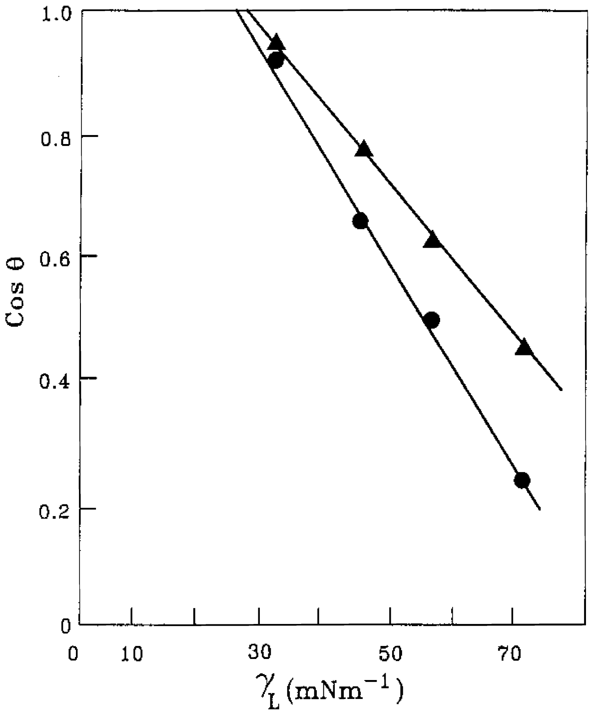

Fig. 1. Zisman's plots cos θ versus surface tension of the liquids γ_L (Table 1) (●) NPIA-*co*-S and (▲) NDoIA-*co*-S.

Surface pressure isotherms. Fig. 2 shows the spreading surface pressure–area (π–A) isotherms of the monolayers of a) ①: *N*-1-propylitaconamic acid-*co*-styrene (NPIA-*co*-S); (a) ②: *N*-1-butylitaconamic acid-*co*-styrene (NBIA-*co*-S); (b) ①: *N*-1-hexylitaconamic acid-*co*-styrene (NHIA-*co*-S); (b) ②: *N*-1-octylitaconamic acid-*co*-styrene (NOIA-*co*-S); (c) ①: *N*-1-decylitaconamic acid-*co*-styrene (NDIA-*co*-S), (c) ②: *N*-1-dodecyl itaconamic acid-*co*-styrene (NDoIA-*co*-S) at the air/water interface. The copolymer composition is the same for all the copolymers studied (20% S). Depending on the alkyl chain length on the *N*-1-alkylitaconamic acid moiety, different types of isotherms have been found. The shapes of the isotherms of NPIA-*co*-S, NDIA-*co*-S and NDoIA-*co*-S differed from that of NBIA-*co*-S, NHIA-*co*-S and NOIA-*co*-S. The decyl and dodecyl aliphatic chains shifted the curves towards lower areas, the collapse pressure π_c was lower and a plateau regions were formed on pure water subphase (pH 5.6). The NPIA-*co*-S also exhibits a plateau region (Fig. 2(a) ①). There are several factors that may cause the appearance of a plateau region in surface pressure isotherms. There are a lot of examples in the literature:

Table 1
Surface characterization of two copolymers studied: NPIA-*co*-S and NDoIA-*co*-S

Liquids	γ_L (mN/m)	θ^a				
		NPIA-*co*-S	NDoIA-*co*-S			
cis-Decalin	31.5	14.5	19.6			
Diethyleneglycol	45.2	38.2	48.2			
Formamide	56.9	51.8	60.0			
Water	72.1	63.0	77.1			
Copolymer	θ_{water}	$\theta_{bromobenzene}$	SE	γ^d	γ^p	$\gamma_c{}^b$
NPIA-*co*-S	64.9	9.8	41.7	26.8	14.9	~29.0
NDoIA-*co*-S	79.4	16.3	35.5	27.2	8.3	~28.0

[a] Contact angle.
[b] Using the Zisman empirical relation.

Coexistence of monolayer phases such as gas–liquid, liquid-expanded and liquid-condensed in phospholipid monolayers [17]; Collapse of the monolayer film into multilayer film as observed for biphenyl and terphenyl derivatives [18]; Molecular orientational changes upon films compression in physiologically active compounds [19]; A combination of both orientational changes and monolayer collapse in carboxylic acid substituted triphenylbenzene compounds [20]; Disolution of monolayer material in the water subphase upon film compression as in the case of monolayers of some polypeptides [19]. We have tried to investigate the possible origin of the plateau in the surface pressure–area isotherms of NPIA-*co*-S, NDIA-*co*-S and NDoIA-*co*-S.

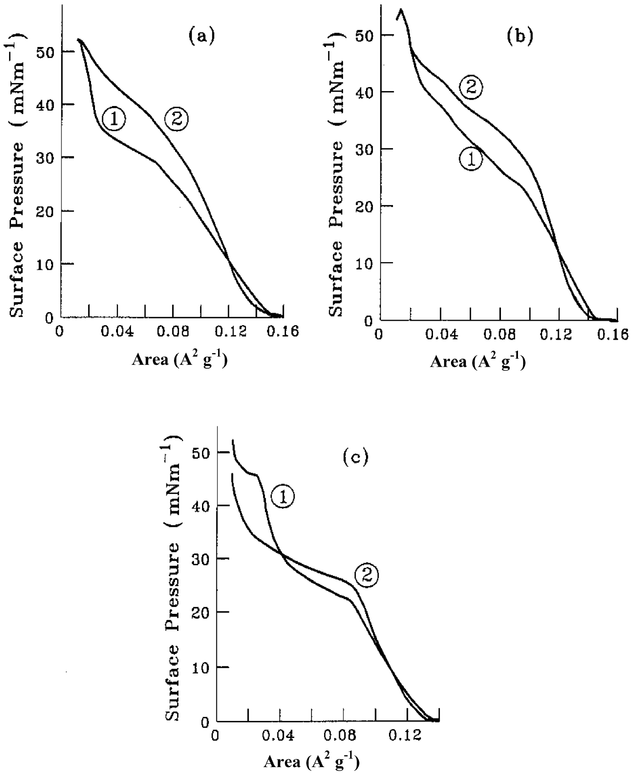

Fig. 2. Isotherms π–A of spreading of copolymers. (a) ①: *N*-1-propylitaconamic acid-*co*-styrene (NPIA-*co*-S); (a) ②: *N*-1-butylitaconamic acid-*co*-styrene (NBIA-*co*-S); (b) ①: *N*-1-hexylitaconamic acid-*co*-styrene (NHIA-*co*-S); (b) ②: *N*-1-octylitaconamic acid-*co*-styrene (NOIA-coS); (c) ①: *N*-1-decylitaconamic acid-co styrene (NDIA-*co*-S); (c) ②: *N*-1-dodecylitaconamic acid-*co*-styrene (NDoIA-*co*-S) at 80/20% composition (20% S) and water subphase pH 5.6.

In general, the isotherms of many classical amphiphiles, such as glycolipids [21] or long-chain carboxylic acids [22], corresponds to first order liquid-expanded to liquid-condensed transition. As can be seen, the isotherms of NPIA-*co*-S, NDIA-*co*-S and NDoIA-*co*-S exhibit three distinct regions. At low pressures the monolayers of (a) ① and (c) ② are relatively incompressible. At intermediate pressures of approximately 25 mN m^{-1} the compressibility increases to reach finally the collapse pressure π_c.

Morphology. In order to correlate microscopy observations with macroscopic monolayer properties, we have tried to obtain morphological information about the monolayers from BAM measurements.

Video images show that for NDoIA-*co*-S forms immediately after the copolymer has been spread on the water surface some heterogeneities (as small particles) moving freely across the water surface. This is consistent with the results at very low pressures where the copolymer chains should be in a gas analogous phase (Fig. 3(a)). As the compression proceeds the particles are observed to coalesce into a more homogeneous structure (Fig. 3(b)). As the plateau region is approached ($\pi > 30$ mN m^{-1}) the film, as visualized by BAM, becomes more rigid and appears uniform (Fig. 3(c)). It is interesting to note in Fig. 3 that the increase in the degree of ordering seems to be correlated to the plateau region. In Fig. 3(d), we can see the collapse pressure of the monolayers. These results could be interpreted by means of a simple molecular interaction model. At low coverage we could have dispersed molecules at the interface, where attractive interactions are compensated. However, when the monolayer is compressed, the hydrophobic interactions become stronger and the lateral chains began to orient in a perpendicular way at the interface. These attractive interactions have enough force as to draw up the carboxylate groups between themselves,

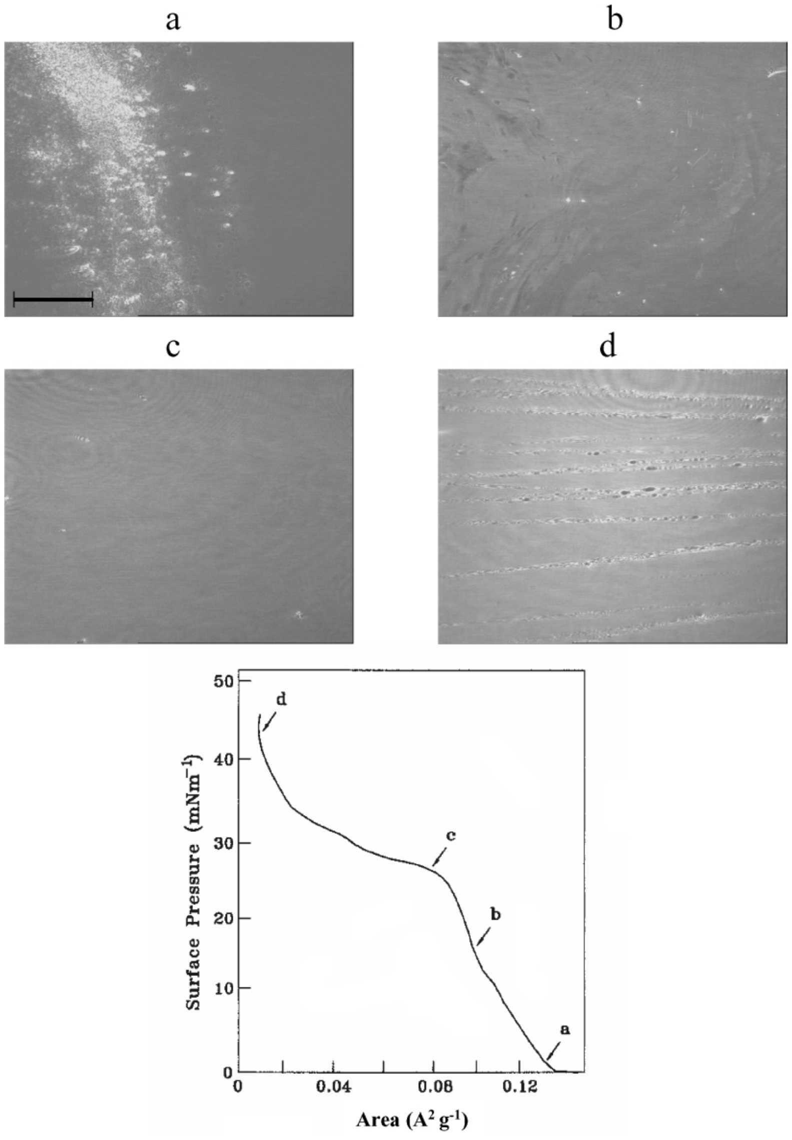

Fig. 3. Pressure–area isotherms of *N*-1-dodecylitaconamic acid-*co*-S at (80/20)(20% S) and 298 K and BAM images for the successive surface pressures: (a) 2 mN/m, (b) 15 mN/m, (c) 26 mN/m, (d) 42 mN/m (collapse pressure). The bar represents 500 μm.

generating hydrogen bonds between amide and carboxylate groups. At this moment, the monolayer shows the initiation of the plateau region. Here, the compression process decreases the area but the surface pressure remains constant. In this situation, the repulsive interactions between the carboxylates groups are shielded. This effect could be attributed to the increases of the electrostatic potential due to the approximation of the carboxyl groups when the pressure increases. In this point a lowering of the pK_as of the carboxyl groups can promote the protonation of some of them. This effect, gives rise to new hydrogen bonds because of the short distance between these groups, which would structured the lateral chains. Finally, upon further compression, the surface pressure increases and the monolayer is packed with an organized structure.

3.1. Molecular simulation

The system was simulated under two conditions, one of them is neutral, assuming that the system is far of the water effect. Solvent molecules have been neglected at the polymer–solvent interface in this preliminary molecular simulation. The other is a charged system, where all carboxylic groups are charged. Next is shown the interaction energies between two equal segments for both systems. It is interesting to observe that in the neutral system the total interaction energies between propyl (NPIA) and decyl (NDIA) are quite similar while the hexyl (NHIA) have the higher interaction energy. The coulombic energy is close to zero in the decyl and hexyl derivatives, while NPIA has a considerable contribution, because the carbonyl groups are more exposed in this case, while the others are

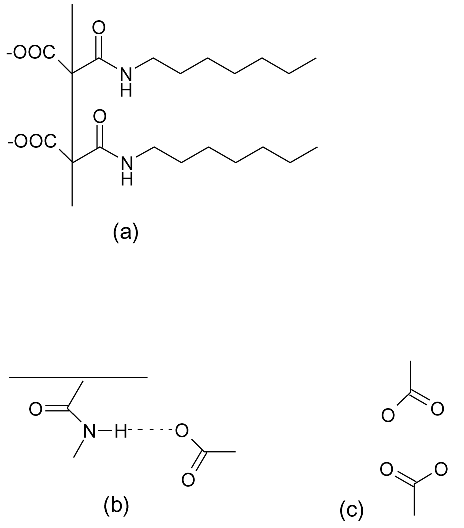

Fig. 4. The schematic representation of: (a) VDW attractive interaction; (b) hydrogen bond attractive interaction and (c) repulsive interaction that competes with the two attractive interactions (a) and (b) for all fragment structures studied.

Table 2
Neutral and charged systems using 10 monomers

NC[a]	Total energy (Kcal/mol)	VDW energy (Kcal/mol)	Coulomb energy (Kcal/mol)
Neutral system			
10	− 15.02	− 15.00	− 0.02
6	− 12.56	− 12.50	− 0.06
3	− 14.28	− 9.33	− 4.95
Charged system			
10	− 20.22	− 14.00	− 6.22
6	− 17.01	− 12.60	− 4.41
3	− 19.40	− 13.30	− 5.33

[a] Number of carbon atoms in the side chain.

shielded by the hydrophobic groups. In the charged systems the coulombic energy takes larger values than in the neutral case. Three types of interactions can be observed. The main in the case of hexyl and decyl derivatives are hydrophobic interactions between aliphatic chains (Fig. 4(a)). From electrostatic point of view there are two types of interactions, one is attractive and the other is repulsive. The attractive one, takes place through hydrogen bonds between the carboxyl groups of one segment with the –NH of the amido group of the other segment (Fig. 4(b)). This interaction is also common between monomeric units, of some segments, mainly between –CO and the –NH of the amido group. This interaction increases when the monomeric units are deprotonated, because carboxylate groups have larger avidity to interact by hydrogen bonding formation. The other interaction is the repulsion between carboxylate groups (Fig. 4(c)). This interaction is a negative contribution to the join of segments and compete with attractive interactions. On the other hand, the hydrophobic interaction tends to interdenticulate the lateral chains between one segment and other. In the case of propyl derivative this fact favours hydrogen bonding interactions between carboxylates and amide groups (Fig. 5). In the case of hexyl and decyl derivatives the energy that stabilizes the interaction between segments is essentially hydrophobic. The length of the chains diminishes the possibility to hydrogen bonding formation between carboxylates and amide from different segments. Finally the systems show that the hexyl group has the largest energy, while the propyl and decyl have lower energies and very similar between them (Tables 1 and 2). This behaviour in the first case is due to the stabilization by van der Waals interaction and in the second case, at least two contributions stabilize the system, i.e. van der Waals and coulombic interactions. The molecular dynamics simulation of a monolayer is a very complex task and with a high computational cost. The styrene and water presence was neglected in this preliminary

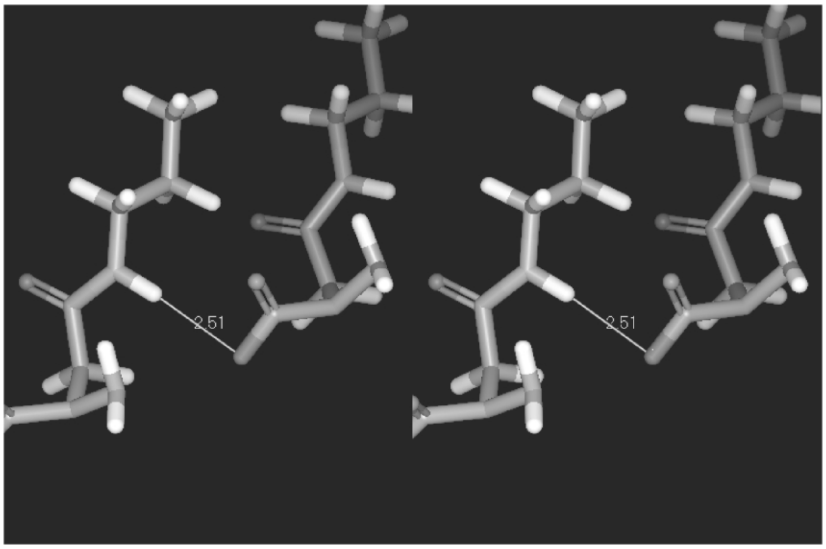

Fig. 5. Stereo picture for the interaction by hydrogen bonding between two units of different segments in the propyl derivatives.

simulations because it is a common factor along the systems studied and could be considered constant. Nevertheless, we accept that the interaction with styrene and water could produce some effect on the interactions.

4. Conclusions

In conclusion, this paper describes the surface behaviour of the six *N*-1-alkylitaconamic acids-*co*-styrene copolymers with alkyl groups varying in side chain length from 3 to 12. It was found that the surface properties depend on the length of the alkyl chain of the itaconamic acid moiety. We have studied monolayers of 1-*N*-alkylitaconamic acid-*co*-styrene at a water/air interface. These data together with the wettability measurements have been used to obtain the surface behaviour of these copolymers. An important and unexpected result is the similarity monolayer found for propyl derivative with decyl and dodecyl derivatives. To clarify this point a molecular mechanics approach was used to obtain prediction about the local interaction energies between segments. The analysis of the coulombic energies together with the dispersion van der Waals energies (VDW) (Table 2) seems to be indicative that carbonyl groups are more exposed in the case of propyl derivative than in the other copolymers studied.

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