Poly(ethylene oxide)s hydrophobically modified. Adsorption and spreading at the air–water interface

Angel Leiva [a,*], Marcela Urzúa [b], Ligia Gargallo [a], Deodato Radić [a]

[a] *Departamento de Química Física, Facultad de Química, Pontificia Universidad, Católica de Chile, Casilla 302, Correo 22, Santiago, Chile*
[b] *Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Correo Central, Santiago, Chile*

Abstract

A comparative study of spread and adsorbed monolayer of poly(ethylene oxide)s of different molecular weight hydrophobically modified with alkyl isocyanates of different length chain is reported. The modification of the polymer was carried out according to reported procedures. The polymers obtained were studied at the air–water interface by Langmuir isotherms for spread monolayers and by Gibbs isotherms for the adsorption process. Isotherms obtained are interpreted in terms of the hydrophobic and hydrophilic balance of the polymers. Limiting area per repeating unit (A_0) and collapse pressure (π_c) from spread monolayers were obtained. Spread monolayers of the hydrophobically modified polymers show larger collapse pressure values than unmodified polymer monolayers. In the adsorption process the excess surface concentration Γ^{∞}, area per repeat unit σ, and efficiency of the adsorption were determined. The values of the area occupied per repeat unit in adsorbed monolayer (σ) were larger than those of the spread monolayer. The efficiency of the adsorption of poly(ethylene oxide)s increases with the hydrophobic modification and with the alkyl chain length.

Keywords: Biodegradable polymer; Air–water interface; Monolayer; Adsorption

1. Introduction

Biodegradable polymers actually are subject of numerous studies due to their use in new applications and to replace non-biodegradable materials by biodegradable polymers and therefore to contribute to diminish the environmental problem. The study of the interfacial properties of these materials is very interesting, from technological and scientific point of view. These properties have direct relation with the behavior in a great number of applications such as pharmacology, biomedical dispositives, food, and materials. Poly(ethylene oxide) (PEO) is an important biodegradable nonionic synthetic water-soluble polymer. This polymer is widely used in different fields, such as production of pharmaceuticals, cosmetics, lubricants, and dispersions stabilizant. The evolution of synthetic biodegradable polymers has been achieved through modulating their chemical compositions using several polymerization techniques and, to a lesser extent, chemical modification of presynthesized polymers [1].

In this work the interfacial behavior of the hydrophobic derivatives of (PEO)s at the air–water interface is studied.

Poly(ethylene oxide)s hydrophobically end-capped are known as associative polymers [2–5] and show interesting rheological behavior when dispersed in aqueous solutions. This kind of polymers has a great number of applications, for example, as new building block for biomaterials [6].

(PEO)s form insoluble monolayers at the air–water interface and the monolayers are stable despite being PEO water-soluble at moderate temperature [7,8].

The adsorption behavior of the poly(ethylene oxide) at the air–water interface has been systematically characterized with respect to adsorption kinetics [9], segment density profiles [10], and thermodynamic characterization [11,12]. Adsorption of the PEO capped at one end with fluorocarbon groups has been re-

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* Corresponding author. Fax: +56 2 6864744.
  E-mail address: aleivac@puc.cl (A. Leiva).

ported by Richards and Sarica [13], and they have concluded that the adsorption of PEO from aqueous solution at the air–water interface is considerably enhanced by a hydrophobic fluorocarbon group inserted at one end of the macromolecule. PEOs spread at the air–water interface has been studied by wave damping [7], surface dynamic elasticity [14], and the thermodynamic and the collapse parameters have been obtained [8]. Co-polymers containing PEO blocks have been also studied at the air–water interface [15–18].

In this report we have studied the spread and adsorbed hydrophobically modified PEOs at the air–water interface. We have tried to explain the results obtained in terms of the macromolecule arrangements at the air–water interface and to compare these results with the behavior of PEO without modification at the same interface.

2. Experimental

2.1. Poly(ethylene oxide)s modification

The chemical modification was carried out by reaction between PEO and alkyl isocyanate in toluene solution and in the presence of 1,4 diazabyciclo-2,2,2-octane (DABCO) as catalyst, following a reported method [4,19]. Isocyanates with three different length chains [octyl, dodecyl, and octadecyl isocyanate] and PEO of 1000 and 10,000 g/mol number average molecular weight ($\overline{M}_n$) were used. All the reactions were carried out at 60 °C under nitrogen atmosphere during 72 h. The modified polymers were purified by repeated precipitation process with benzene-petroleum ether as solvent and nonsolvent pair and dried under vacuum during 48 h.

2.2. Polymer characterization

The polymer was characterized by Fourier transform infrared spectroscopy (FTIR) in KBr and ^{1}H NMR in CDCl₃.

2.3. Monolayers at the air–water interface

Monolayers were obtained by spreading of polymer fractions on aqueous subphase from chloroform. The concentrations of the spread solutions for different fractions were 0.39 and 0.41 mg/ml and the temperature was 298 K. Water subphase was purified by Millipore Milli-Q system (resistivity greater than 18.0 MΩ cm).

2.4. Surface pressure/area isotherms

Polymer monolayers on aqueous subphase were studied by the Langmuir technique. Surface pressure/area (π/A) isotherms 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) in order to prevent environmental perturbations. Constant compression rate of 30 cm²/min was used in all experiments. The experiments were developed in triplicate to ensure reproducibility.

2.5. Surface tension measurements

Surface tension of the aqueous polymer solutions was measured at 298 ± 0.1 K by the pendant drop method using a contact angle system OCA Dataphysics. Water Milli-Q quality with a surface tension value of >71.0 mN m^{-1} was used. The polymer concentration was from 0.01 to 0.09 ± 0.0001 mol monomer units per liter (mol m.u./L). Low concentrations were achieved by dilution.

3. Results and discussion

The polymers obtained were labeled according to PEO molecular weight and the chain alkyl length as PEO1-octyl, PEO1-dodecyl, and PEO1-octadecyl for the three polymers obtained from PEO 1000 g/mol (PEO1) and PEO2-octyl, PEO2-dodecyl, and PEO2-octadecyl for the three polymers obtained from PEO 10,000 g/mol (PEO2). The possible chemical structures obtained are summarized in Scheme 1.

For all polymers the FTIR and the ^{1}H NMR spectrum shows signals which corroborate the alkyl chains incorporation. The FTIR spectrum shows signals of the O–H ≈ 3423 cm^{-1}; C=O, C–N, and N–H 1695–1543 cm^{-1}; C–H ≈ 1467 cm^{-1}; and C–O–C of the PEO ≈ 1114 cm^{-1}. In the ^{1}H NMR spectrum the following signals are observed: CH₃ ≈ 0.87 ppm; CH₂ $\approx$ 1.68 ppm of the alkyl groups; and CH₂ ≈ 3.63 ppm of the PEO.
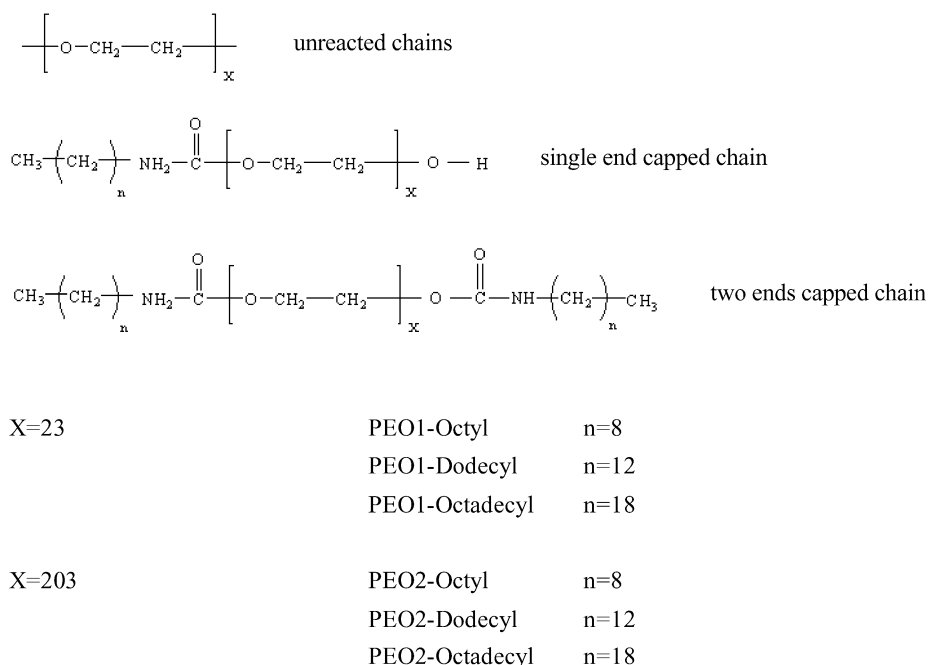
In order to quantify the percentage of unreacted hydroxyl groups at the chain ends of otherwise modified PEOs, it was necessary to convert them to naphthyl groups so that they could then be characterized by UV spectroscopy [4]. Naphthyl isocyanates are considerably more reactive than alkyl isocyanates toward hydroxyl groups. Both precursors and alkylated PEOs were treated with naphthyl isocyanate in THF. UV–vis spectroscopy was performed using ethanol as solvent. A calibration curve was performed using 1-naphthyl carbamate.

Table 1 summarizes the percentage of the unreacted hydroxyl groups in the chain ends obtained for the polymers studied. These results indicate that the modification in the PEOs ends was partial and the polymer samples obtained are a mixture of the structures shown in Scheme 1. Although the obtained percentages were between 60 and 70%, the samples considered to be of the same order of substitution due to the uncertainty of the measurements.

Polymers monolayers spread at the air–water interface were studied by the Langmuir technique. In all cases the spreading solvent was chloroform. Fig. 1a shows the Langmuir isotherms

Table 1
Percentage of unreacted hydroxyl groups at the chain ends of the modified PEOs

Polymer	% OH free
PEO1-octyl	63
PEO1-dodecyl	70
PEO1-octadecyl	57
PEO2-octyl	67
PEO2-dodecyl	59
PEO2-octadecyl	63

unreacted chains

single end capped chain

two ends capped chain

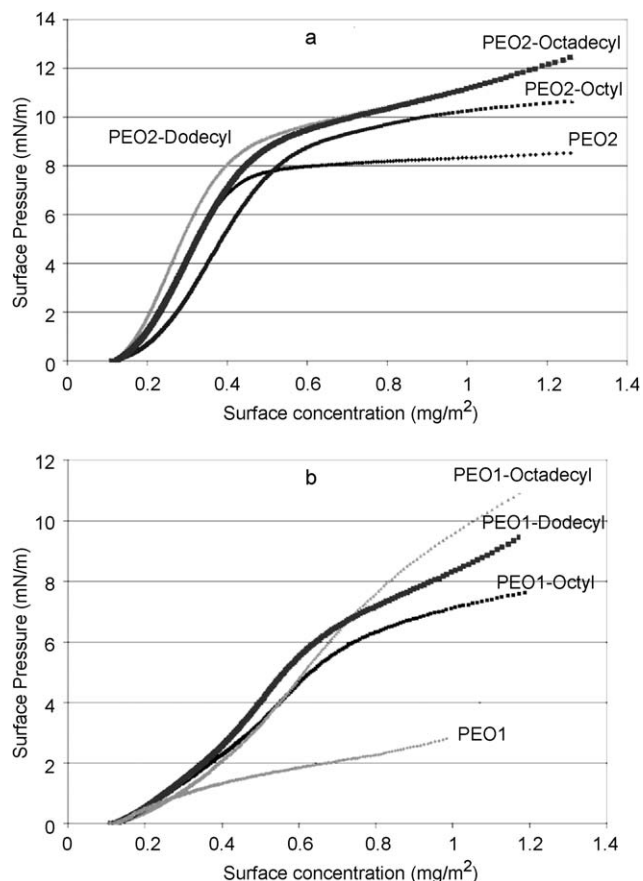| X=23 | PEO1-Octyl | n=8 |
	PEO1-Dodecyl	n=12
	PEO1-Octadecyl	n=18
X=203	PEO2-Octyl	n=8
	PEO2-Dodecyl	n=12
	PEO2-Octadecyl	n=18

Scheme 1.

Fig. 1. Langmuir isotherms for (a) PEO2 and their derivatives and (b) PEO1 and their derivatives.

obtained by monolayer compression of the PEO2 and the respective alkyl derivatives at the air–water interface. In all cases the isotherms are of the expanded type [20,21]. This behavior

Table 2
Area for monomer unit projected to zero surface pressure (A_0) for PEO 1000 and 10,000 g/mol and their derivatives

Polymer	A_0 (Å^2/m.u.)
PEO1	23 ± 2
PEO1-octyl	22 ± 2
PEO1-dodecyl	21 ± 2
PEO1-octadecyl	22 ± 2
PEO2	32 ± 2
PEO2-octyl	30 ± 2
PEO2-dodecyl	35 ± 2
PEO2-octadecyl	33 ± 2

is indicative that the polymers have similar affinity for the water subphase [20]. Fowkes [22] suggests that in expanded films the polymer segments are miscible with water molecules in the surface layer, while in condensed films the polymer chains are in contact and water is substantially excluded. The surface pressure π increases gradually by monolayer compression. Three different qualitative regions can be distinguished in the isotherms: at low surface concentration in a pseudo gas state π increases slowly when the monolayers are compressed, in the semidilute region when the pseudo liquid state is reached π rises rapidly and at high surface concentration the pseudo solid state is reached and π increases slowly again before the collapse. The areas per monomer unit projected to zero surface pressure, obtained from the linear variation of π with the surface concentration (A_0) in the semidilute region [21] for the polymers, are summarized in Table 2. The values obtained in all cases were very similar. Fig. 2a shows the Langmuir isotherms where the surface concentration is expressed as area per repeat unit (Å^2/r.u.) and shows graphic determination of A_0 for PEO2.

The correspondence between area per repeat unit A and surface concentration Γ (mg/m^2) is $A = \Gamma N_A \times 10^{-23} M^{-1}$,
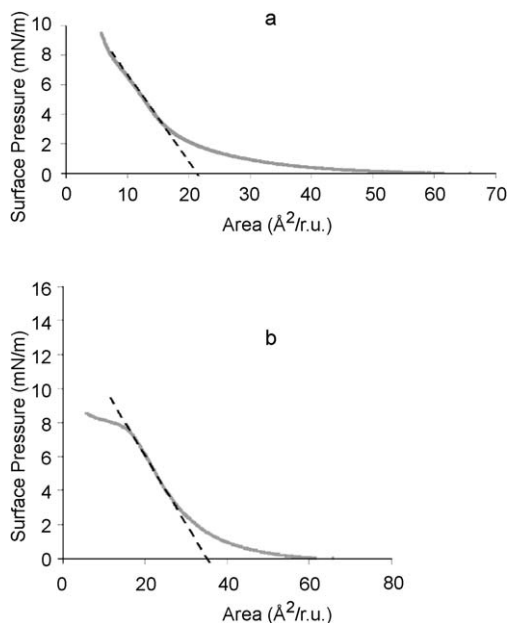
Fig. 2. A_0 determination for (a) PEO2 and (b) PEO1-octadecyl.

Fig. 3. Adsorption isotherms for PEO1, their derivatives, and PEO2.

where M is molar mass (g/mol) of the repeat unit and N_A is the Avogadro number.

The isotherms have a very defined collapse pressure, ≈ 7.5 mN/m for PEO2 and ≈ 8.5 mN/m for the respective alkyl PEOs derivatives. These values are in agreement with the tendency reported by Xu and co-workers [23]. The collapse condition was corroborated by means of repeating of the isotherms before and after the collapse point. When the monolayer is collapsed, it is not possible to reproduce the isotherm by expansion followed by a compression process. These results indicate larger resistance to collapse by monolayer of the alkyl derivatives than unmodified PEO. The collapse is close to 0.4 mg/m^2 surface concentration, these results are in agreement with those reported by Kuzmenka and co-workers [8]. When the monolayer at the air–water collapses the molecules are ejected from the interface toward the subphase (hydrophilic molecules) and toward the air (hydrophobic molecules). In the case of PEO, monolayer collapses into the aqueous substrate [22], due to the high hydrophilic character of PEO. In the case of the modified PEOs, the alkyl chains turn more difficult to collapse into the aqueous subphase.

Kawaguchi and co-workers [24] have reported that the air–water interface is a good solvent for PEO, we have corroborated this condition in semidilute zone where π follows a power law in Γ [25], according to $\pi = \Gamma^{2\nu/(2\nu-1)}$, the ν value found was 0.72.

Fig. 1b shows the Langmuir isotherms obtained for PEO1 and their derivatives, the isotherms are also the expanded type and present lower collapse pressure, ~ 1.5 mN/m for PEO and ~ 5.5 mN/m for derivatives. The same explanation given for PEO2 and its derivatives seems reasonable here for the alkyl chain effect but in this case the effect over the PEO1 is larger due to the short length of the PEO macromolecules. The A_0 values obtained are summarized in Table 2. Fig. 2b shows the graphic determination of the A_0 for PEO1-octyl. The lower A_0
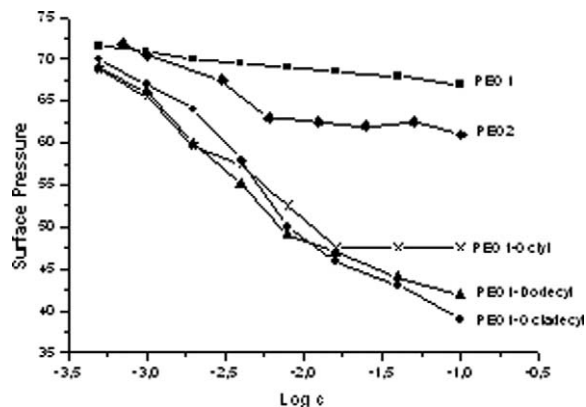
values could indicate a more efficient package for short PEOs chains.

We have also studied the adsorption process of the PEO1 and its derivatives and PEO2.

Fig. 3 shows the behavior of the interfacial tension γ_{int} as a function of the polymer concentration c (mol L^{-1}) of monomeric units in water, in the high dilution zone. As can be seen in all cases there is a decrease of the γ_{int} with c reaching a plateau. The decrease of the γ_{int} is more pronounced for PEOs hydrophobically modified than that found for PEO1 and PEO2.

In order to quantify the adsorption process, the following form of the Gibbs equation was used [26]:

$$\Gamma = -(RT)^{-1} c \left(\frac{\partial \gamma}{\partial c} \right), \tag{1}$$

where Γ is the excess surface concentration, R and T have their usual meaning. In order to evaluate the slopes, $(\delta\gamma/\delta c)$, experimental data of γ vs c were adjusted to the empirical equation of Szyszkowski:

$$\gamma_{\text{int}} = \gamma_{\text{int}}^0 - \gamma_{\text{int}}^0 B \log[[c/A + 1]]. \tag{2}$$

Here γ_{int}^0 is the interfacial tension between pure phases and A, B are two empirically adjusted parameters which are related to the standard free energy of adsorption $\Delta \bar{G}_{\text{ads}}^0$ and to the areas covered by monomer unit at the interface, respectively.

By differentiation of Eq. (2), it is possible to obtain

$$d\gamma/dc = -\gamma_{\text{int}}^0 B/[c + A], \tag{3}$$

which can be related to Eq. (1) to obtain the Gibbs–Szyszkowski equation

$$\Gamma = \gamma_{\text{int}}^0 Bc/[RT[c + A]]. \tag{4}$$

At low c values, Γ is nearly linear with c while at high c values, Γ is practically independent of the polymer concentration.

If $c \gg A$

$$\Gamma^\infty = \gamma_{\text{int}}^0 B/RT, \tag{5}$$

$$\sigma = [\Gamma^\infty N_A]^{-1}, \tag{6}$$

where Γ^∞ and σ are the limiting excess surface concentration and the area covered per monomer unit, respectively.

Table 3

Adsorption parameters obtained from adsorption isotherms of the PEO 1000 g/mol, their derivatives, and PEO 10000 g/mol

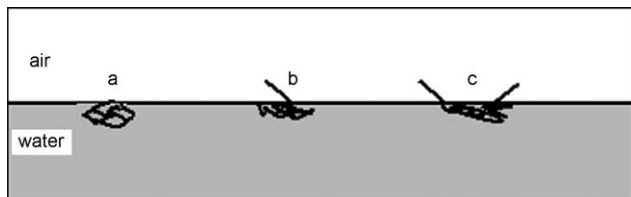| Polymer	Γ^∞ (mol/m²)	σ (m²/m.u.)	σ (Å²/r.u.)	pC_{20}	ΔG^0_{ads} (kJ/mol)
PEO1	1.28×10^{-6}	1.30×10^{-18}	124.7	–	–
PEO1-octyl	4.96×10^{-6}	3.35×10^{-19}	33.5	2.2	−26.5
PEO1-dodecyl	4.19×10^{-6}	3.96×10^{-19}	39.6	2.2	−27.2
PEO1-octadecyl	4.54×10^{-6}	3.66×10^{-19}	36.6	2.0	−25.7
PEO2	1.52×10^{-6}	1.10×10^{-18}	109.5	–	–

Fig. 4. Schematic representation of (a) PEO chain adsorbed at the air–water interface, (b) single end capped PEO chain adsorbed at the air–water interface, and (c) double end capped chain adsorbed at the air–water interface.

The values of Γ^∞ and σ are summarized in Table 3, the σ value obtained for PEO1 was higher than those for the derivatives. These results provide evidence that the alkyl chains favor some organization of the polymers at the air–water interface. The segment surface density should increase.

Schick's data [27,28] about the surface tension measurements for poly(oxyethylenes) adsorbed at the air–water interface from aqueous solutions determined as a function of ethylene oxide chain length indicate that the ethylene oxide chains instead of lying flat in the water surface as was true for insoluble films, the ethylene oxide chains form coils in the aqueous phase with the hydrophobic groups above the interface. In the case of the hydrophobically modified PEOs adsorbed at the air–water interface we can visualize that the alkyl chains in a single and double end capped PEOs act as float and contribute to reach a higher number of the ethylene oxides segments lying at the interface and by this way the σ values obtained are lower. This behavior is represented graphically in Fig. 4.

The PEO2 derivatives were partially soluble in water and their adsorption isotherms were not possible to obtain. For this kind of polymers aggregation processes have been reported [4,29]. By dynamic light scattering we corroborated this aggregation. Bi-modal size distribution from the correlation curve was obtained.

A convenient estimation of the efficiency of adsorption is the negative logarithm of the concentration of surfactant in the bulk phase required to produce a 20 mN/m reduction in the surface or interfacial tension of the solvent $-\log C(\Delta\gamma = 20) = pC_{20}$.

The ideal measure of the efficiency of adsorption would be function of the minimum concentration of surfactant in the bulk phase necessary to produce maximum adsorption (saturation) at the interface. pC_{20} is close to the minimum concentration to produce saturation adsorption at the interface.

The relationship of pC_{20} to the free energy change on adsorption at infinite dilution (ΔG^0_{ads}) can be seen by the use of the Langmuir and Szyszkowski equations [30]. In this case,

$$\Delta G^0_{ads} = -2.303RT\left[pC_{20} + 1.74 + 20\big/\left[2.303RT\,\Gamma^\infty\right]\right]. \quad (7)$$

The pC_{20} and ΔG^0_{ads} values obtained from Fig. 3 are summarized in Table 3. We can conclude that hydrophobically modified PEOs of PEO1 present larger surface activity than their respective precursor, similar results were obtained by Richards and co-workers using fluorocarbons groups as substituent [13]. The enhanced surface activity is reflected in the adsorption isotherms shapes and in the Γ^∞ and pC_{20} values.

The adsorption processes are spontaneous as can be inferred from the negative values of the standard free energies of adsorption.

For alkylated PEO1 the values of the area covered per monomer unit σ obtained from the adsorption isotherms are larger than the surface area occupied by monomer unit A_0 obtained from the Langmuir isotherms for the same polymers. For nonmodified PEO the difference is noticeably higher. Meader and Criddle [31] have obtained results for derivatives of poly(ethylene oxide)s, such as ethylene oxide adducts of fatty alcohols which provide evidence that, in the films of such polymers spread at the air–water interface as monolayers, the hydrophilic ethylene oxide monomeric unit lies flat in the interface with every ether oxygen atom in the water, whereas the hydrophobic groups were oriented away from surface and into the atmosphere.

By this explanation it is possible to understand the high area per monomer unit value found in the case of the monolayer formed by adsorption from solution relative to the spread monolayer. In the last case, there could be more ethylene oxide monomer units lying flat at the air–water interface. On the other hand, in monolayers adsorbed from solution, part of the ethylene oxide monomer units tend to form coils into the subphase.

4. Conclusions

The partial incorporation of the isocyanate chains at the terminal hydroxyl groups of the PEOs has direct consequences on the behavior at the air–water interface of the polymers monolayers in both spread and adsorbed monolayers. The larger hydrophobicity conferred by alkyl chains make the spread monolayer more resistant to the collapse. The adsorption of poly(ethylene oxide) from water solution to the air–water interface is considerably enhanced by a hydrophobic group placed at ends of the molecules. For PEO1 and its derivatives the area per monomer unit occupied in the adsorbed monolayer at the air–water interface is higher than the area per monomer unit occupied in the spread monolayer.

Acknowledgment

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