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# Supramolecular Structures, Organization and Surface Behavior at Interfaces

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**Summary:** The surface behavior of Supramolecular Structures as inclusion complexes[1] were studied. The inclusion complexes (ICs) obtained from the threading of $\alpha$-cyclodextrin ($\alpha$-CD) with poly($\varepsilon$-caprolactone) (PEC) and derivatives as precursor homopolymers were prepared and characterized by $^1$H-NMR and FT-IR Microscopy. In order to investigate the influence of the chemical structure of the other precursor homopolymers as poly(ethylene oxide) (PEO) and poly(tetrahydrofuran) (PTHF), the inclusion complexes (ICs) were also obtained from the threading of $\alpha$-cyclodextrin ($\alpha$-CD) with these polymers. Surface pressure-area isotherm ($\pi$-A) at the air-water interface were determined by the Langmuir Technique for all the ICs and their polymers. Due to solubility reasons, different spreading solvents were used. In a set of control experiments, it was observed that the spreading volume did not influence significantly the isotherms for any polymeric systems studied. It was found that the hydrophobic and hydrophilic balance changes with the increasing of the methylene and hydroxyls groups number in the chemical structures of the precursor polymers involved in the ICs. The degree of hydrophobicity of the different supramolecular systems was also estimated from the determination of the surface free energy (SE) values using the wettability measurements.[2] In order to describe the experimental behavior of the ICs and the precursor polymers, molecular dynamics simulation (MDS) were performed. The radial distribution functions (RDF) between water molecules and hydrophilic and hydrophobic moieties of the polymeric systems studied were analized. By this way it was possible to visualize the orientation and the organization of these supramolecular structures at the air-water interface.

**Keywords:** hydrophilic-hydrophobic balance; inclusion complexes; molecular dynamic simulation; precursor homopolymer; surface free energy

## Introduction

A growing interest in the last decade toward supramolecular structures has been increasing. Specifically the self-assembly of macromolecular systems have been reported.[1–4] The importance of non-covalent interaction in biologycal systems has motived much of the current interest in supramolecular assemblies.[5] The term supramolecular invokes a non-classical chemistry. A convenient way to define a supermolecule is like an assembly of molecules that is held together by relatively weak intramolecular bonds. Supramolecular systems are maintained by a variety of weaker (non-covalent) interactions as hydrogen bonding, electrostatic interaction and van der Waals interactions. Supramolecular structures as inclusion complexeses (ICs),[6] diblock copolymers and dendronized polymers[7] have been quite noticeable to design new functional materials and also to medical applications. Cyclodextrins (CDs) are an interesting class of compounds that can form supramolecular structures as inclusion complexes (ICs)

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with a wide range of low molecular weight compounds.[2,8] The most common hosts include crown ethers,[9] cryptants,[10] calixarenes[11] and cyclodextrins.[12] Harada et al.[13,14] have included polymers of various molecular weight inside $\alpha$-, $\beta$- and $\gamma$-CD. The selectivity of the ICs formation is very high. In general, ICs formation depends on the cross-sectional area of the polymers and correlates very well with the cavity size of CDs. On the other hand, the majority of ICs are formed with hydrophilic polymer, but also some complexes can be obtained with hydrophobic polymers. Some complexes of $\alpha$-CD with linear polymers present a columnar structure.[14] In other cases, it has been reported that a cage-type structure is more probable.[15] The aim of this work is the study of the surface behavior of some supramolecular systems as inclusion complexes at the air – water interface. The orientation and the interactions of these systems have been also estimated. In order to describe the orientation of the supramolecular systems at the interfaces, molecular dynamic simulation (DMS) was performed.

## Materials and Methods

### Materials

$\alpha$-CD (Sigma–Aldrich), poly(ethylene oxide) (PEO), poly(tetrahydrofuran) (PTHF), poly($\varepsilon$-caprolactone) (PEC) with molecular weights (Mw) of 65000 and 80000 (PEC65000)(PEC80000), poly($\varepsilon$-caprolactone) diol of Mw 900 and 2000 (PEC900) (PEC2000) and poly($\varepsilon$-caprolactone) triol of Mw 530 (PEC530) supplied by Merck–Schuchardt, Germany, were used as received. All solvents used were analytical grade. Water was purified by Millipore Milli – Q system (resistivity greater than 18.0 MΩcm). Preparation of the Inclusion Complexes: ICs were prepared following the procedure reported by Harada et al.[13] 20 mg of polymer was introduced into tubes with heating above the melting temperature. A satured aqueous solution of CD ($\alpha$-CD $1.8 \times 10^{-4}$ mmol in 1,2 mL and $\gamma$-CD $1.1 \times 10^{-4}$ mmol in 0,6 mL) was added and the heterogeneous mixtures were ultrasonically agitated during 10 min with heating and then allowed to stand overnight at room temperature. They were collected by centrifugation, dried under vacuum up to 373 K washed with water and dried under vacuum and then washed with THF and dried under vacuum to obtain ICs. The mixture became turbid and the complexes were obtained as white crystalline precipitates. This procedure was performed for all the ICs.

### Inclusion Complex Characterization

The inclusion complexes were characterized by Fourier Transform Infrared spectroscopy (FT - IR) in KBr and $^1$H - NMR in $CDCl_3$.

### Surface Pressure-Area Isotherms

The surface pressure-area isotherms for spreading films of ICs from $\alpha$-CD with PEC and derivatives at different molecular weight (Mw) and the other ICs with PEO and PTHF were studied using the Langmuir Technique. The surface pressure-area isotherms ($\pi$-A) were performed with a surface balance of Langmuir Nima 611 at 298 K. The compression velocity was 10 cm$^2$/min. Water subphase was purified by Mili-Q-system (18 MΩcm). The spreading solvents used were dimethylformamide (DMF), Toluene, Chloroform ($CHCl_3$) and the binary mixture DMF/$CHCl_3$. The polymeric solution concentration was 1 mg/mL. The surface- pressure isotherms were established by compression.

### Surface Free Energy

The surface free energy (SE) of the polymeric systems were determined by wettability measurements with 1- bromonaphtalene and diiodomethane. The wettability of the polymeric system films was determined by contact angle measurements. Contact angles were measured using a OCA Dataphysics system with a conventional goniometer and high performance video camera, controlated by SCA20 software.

### Molecular Dynamic Simulation (MDS)

In order to describe the experimental results of the supramolecular systems studied at the air-water interface, MDS was performed specifically for PEO, PTHF and PEC monolayers, as polymers and their ICs with $\alpha$-CD. Periodic boundary conditions were applied to rectangular boxes with X and Y dimensions of 10, 20 and 30 Å. The length of the boxes in Z dimension was large enough to prevent the contacts between the chains. Simulations were done at room temperature. In order to obtain information about the organization and stability of the monolayers, the order parameters S(r) were calculated[16] as:

$$S(r) = 0.5\left(3\cos^2\theta_{ij}(r) - 1\right) \qquad (1)$$

All simulations were carried out in the NVT ensemble with a time step of 0.001 ps. The simulation time was of 5ns for the precursor homopolymer monolayers and 8ns for the IC monolayers. The MDS were run in the software and force field NAMD[17] and the results were analyzed and visualized with the software VMD.[18]

## Results and Discussion

The precursor polymers studied are shown in Scheme 1.

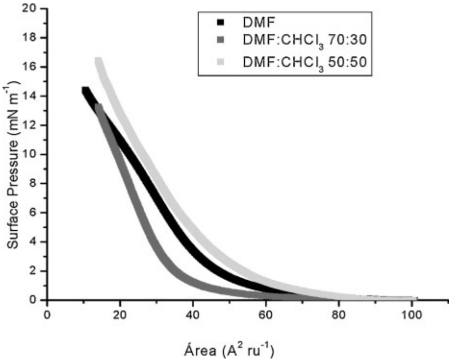
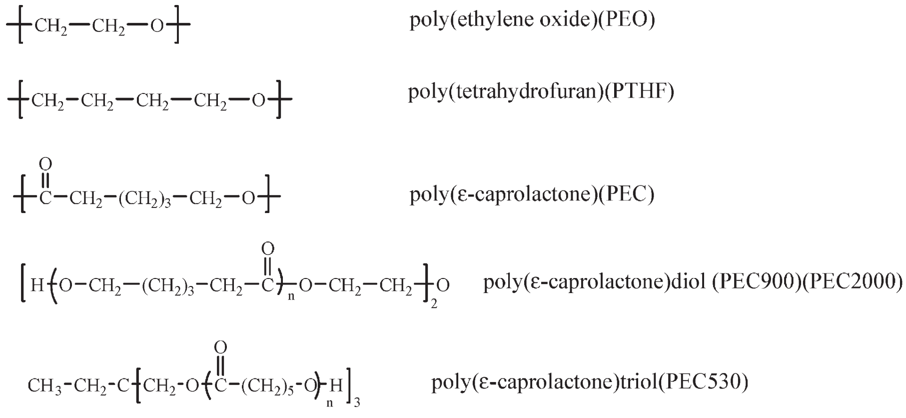


***Figure 1.***
Surface pressure-area isotherms ($\pi$-A) for IC-PEC2000 from different spreading solvents.

ICs monolayers spread at the air–water interface were studied by Langmuir technique. Due to solubility reasons several spreading solvents were used. The influence of the spreading protocol behavior, was investigated. Monolayer experiments under different conditions were performed. In a set of control experiments, changing the spreading volume did not influence significantly the isotherms. This behavior was observed for PEO, PTHF, and PECs. The effect of the nature of the spreading solvent on the surface pressure-area isotherms of the inclusion complexes of $\alpha$-CD with PEC2000 (IC-PEC2000) is shown in Figure 1. When the percentage of DMF decreases, it was observed that the stability



$\left[\mathrm{CH_2-CH_2-O}\right]$ poly(ethylene oxide)(PEO)

$\left[\mathrm{CH_2-CH_2-CH_2-CH_2-O}\right]$ poly(tetrahydrofuran)(PTHF)

$\left[\mathrm{\overset{O}{\overset{\|}{C}}-CH_2-(CH_2)_3-CH_2-O}\right]$ poly(ε-caprolactone)(PEC)

$\left[\mathrm{H\left(O-CH_2-(CH_2)_3-CH_2-\overset{O}{\overset{\|}{C}}\right)_n O-CH_2-CH_2}\right]_2\mathrm{O}$ poly(ε-caprolactone)diol (PEC900)(PEC2000)

$\mathrm{CH_3-CH_2-C\left[CH_2-O\left(\overset{O}{\overset{\|}{C}}-(CH_2)_5-O\right)_n H\right]_3}$ poly(ε-caprolactone)triol(PEC530)

***Scheme 1.***

***Table 1.***
Surface parameters for IC-PEC2000.

| Solvent | $\pi_C$ (mNm$^{-1}$) | $A_0$ (Å$^2$/ru) | $A_C$ (Å$^2$/ru) |
|---|---|---|---|
| DMF | 14 | 48 | 10 |
| DMF/$CHCl_3$ (70/30) (v/v) | 13 | 36 | 14 |
| DMF/$CHCl_3$ (50/50) (vv) | 17 | 53 | 14 |

of the isotherm increases and the $\pi_c$ value is larger when the percentage of DMF decreases in the binary mixture. Table 1 summarizes the main surface parameters of the isotherms taken from Figure 1 for this IC. There is no a correlation between the surface parameters and the solvent composition, what could be attributed to a preferential adsorption of one the components of the solvent mixture.

### Influence of the Molecular Weight and the Chemical Structure

The influence of the molecular weight and the chemical structure on the surface activity of poly($\varepsilon$-caprolactone) and derivatives and their inclusion complexes ICs with $\alpha$-cyclodextrin ($\alpha$-CD), was determined. Figure 2 shows the surface-area ($\pi$-A) isotherms for PECs using DMF as spreading solvent. Figure 3 represents the isotherms for ICs using also DMF as spreading solvent. As it can be observed in Figure 2, the influence of the molecular weight and the chemical structure of PEC diol or triol seems to have not significative effect on the isotherms.

Figure 3 represents the surface isotherms for IC-PEC at different molecular weights. The obtained isotherms are of the condensed type,[19] i.e. surface pressure increases gradually upon monolayer compression and the compressibility of the monolayer is higher when the molecular weight increases. However in the case of ICs, a strong influence of the molecular weight and the chemical structure on the isotherms of IC-PEC was found. (See Figure 3). We have tried to explain this peculiar behavior in terms of the insertion of hydroxyl groups that can contribute to a larger monolayer hydrophilicity.[20] The isotherms shown in Figure 3 reflect at least two effects,. i.e. by one hand, the effect of the molecular weight and the influence of the chemical structure on the other. The effect of the molecular weight can be observed in the case of IC-PECdiol with two molecular weights having a lower surface activity than IC-PECtriol and

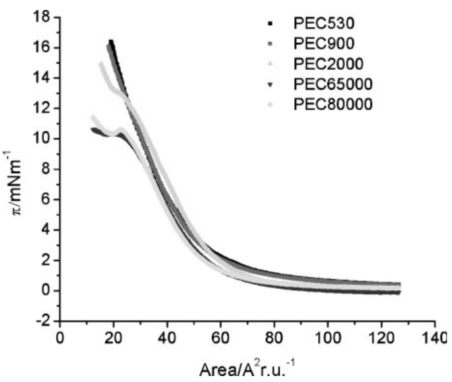


***Figure 2.***
Surface pressure-area isotherms ($\pi$-A) for all the PECs at different molecular weights. DMF was used as spreading solvent.

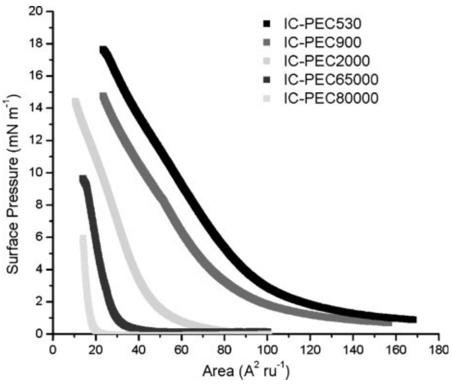


***Figure 3.***
Surface pressure-area isotherms ($\pi$-A) for all ICs at different molecular weights. DMF was used as spreading solvent

***Table 2.***
Surface parameters for ICs of different molecular weights.

| Inclusion Complex (IC) | Minimum area ($A_o$) at $\pi = 0$ (Å$^2$ ru$^{-1}$) | Collapse pressure $\pi_c$ (mNm$^{-1}$) |
|---|---|---|
| IC-PEC530-triol | 103,3 | 17,7 |
| IC-PEC900-diol | 90,0 | 14,8 |
| IC-PEC2000-diol | 48,3 | 14,4 |
| IC-PEC65000 | 28,4 | 13,1 |
| IC-PEC80000 | 18,0 | 5,8 |

higher to IC-PEC without modification. Nevertheless, the effect of the molecular weight can be clearly observed. Table 2 summarizes the main surface parameters of these ICs, $A_0$ and $\pi_c$ values for all the ICs studied. $A_0$ and $\pi_c$ values decrease when the molecular weight increases according to the surface isotherms obtained from Figure 3. At the same time when the hydrophilicity increases, the monolayers present a greater resistence to collapse. This behavior is in good agreement with with the results reported previously.[20]

Both $A_0$ and the $\pi_c$ values decrease when the molecular weight of the ICs increases. Therefore, hydrophobic-hydrophilic balance is also less favorable when the molecular weight increases. On the other hand, another possible explanation for the different isotherms shown in Figure 3 and the decreasing values of minimum area $A_o$ of the ICs (see Table 2) is the formation of multilayers at the air-water interface, that is to say, the monolayer could be structured in other dimension (3D behavior, no larger in pseudo 2D) as the molecular weights increases. Fowkes has suggested that in the case of expanded films polymer segments are miscible with water molecules in the surface layer, while in condensed films the polymers chains are in contact and water is substantially excluded.[21]

The driving forces leading to the inclusion complexation of cyclodextrins have been abundantly reviewed,[11,15] which included the electrostatic interaction, van der Waals interaction, hydrogen bonding, release of conformational strain, exclusion of cavity-bound high-energy water and charge-transfer interaction and they are important factors to be taken into account in the explanation of this behavior. Nevertheless, it is still often claimed that the driving forces leading to CD complexation remain unclear or controversial. In order to clarify the influence of the chemical structure of the precursor homopolymers (See Scheme 1), the interfacial properties of the supramolecular inclusion complex (ICs) obtained from the threading of $\alpha$-cyclodextrin ($\alpha$-CD) onto poly(ethylene oxide) (PEO) Poly($\varepsilon$-caprolactone) diol (PEC2000) and Poly(tetrahydrofuran) (PTHF) were studied at the air-water interface by surface pressure and contact angle measurements.

ICs and the three polymers form stable Langmuir monolayers. Surface pressure-area isotherms ($\pi$-A) at the air-water interface for polymers PEO, PTHF and PEC2000 are shown in Figure 4.

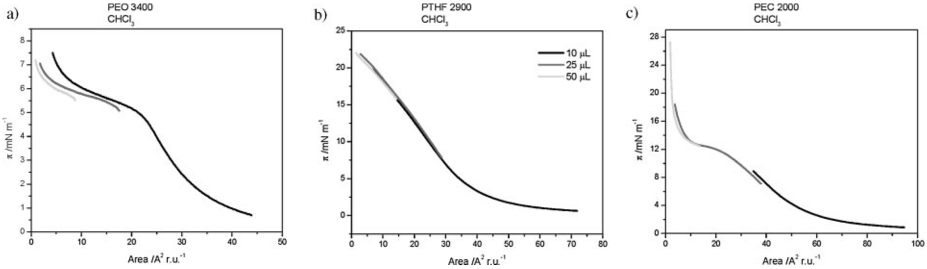


***Figure 4.***
Surface pressure-area isotherms for a) Poly(ethylene oxide); b) Poly(tetrahydrofuran) and c) Poly($\varepsilon$-caprolactone) diol.

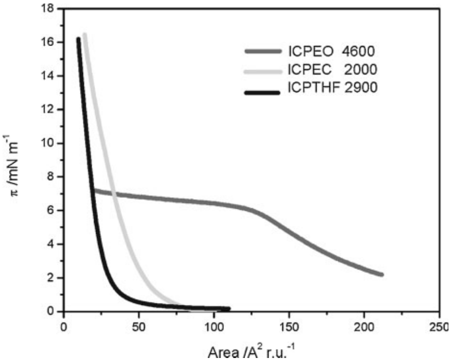


***Figure 5.***
Surface pressure-area isotherms of ICs.

The surface activity and the isotherms of Inclusion Complexes (ICs) obtained from the threading of $\alpha$-cyclodextrin ($\alpha$-CD) and poly(tetrahydrofuran) (PTHF), and poly($\varepsilon$-caprolactone)diol (PEC2000) are larger and more stable than that of the IC from $\alpha$-CD and poly(ethylene oxide) (PEO). Figure 5 presents these results.

PTHF, IC-PEC and IC-PTHF surface isotherms are of the condensed type, whereas that for PEO, PEC and IC-PEO is of the expanded type. Langmuir films of PEO are stable for low surface pressure. Upon compression the monolayer collapse and the water soluble PEO chains can dissolve in the water subphase for pressures that are molecular weight dependent (maximum collapse pressure value 10 mNm$^{-1}$ for high molecular weight PEO). Finally the monolayer stability decreases on the interface by PEO < PTHF < PEC. These results demonstrate that the hydrophobic and hydrophilic balance has been changed, with the increasing of the methylene groups number in the chemical structures of the polymers involved in the IC.

### Contact Angles. Surface Energy

The wettability of PEO, PEC, PTHF and their ICs corresponding was determined by contact angle measurements. To be confidence about the degree of hydrophobicity of polymers and ICs,the total surface energy was estimated (SE). Table 3 and 4 summarize the contact angle (CA), total surface energy (SE) dispersion force ($\gamma^d$) and polar contribution ($\gamma^p$) values for the precursor polymers and the inclusion complexes with $\alpha$-CD. From the SE values for ICs and polymers, we can conclude that the ICs present a degree of hydrophobicity higher than that of the polymers except for IC-PEC. This result is in agreement with

***Table 3.***
Contact angle (CA), total surface free energy (SE), dispersion contribution ($\gamma^d$) and polar contribution ($\gamma^{p)}$ values for PEC(2000), PEO(3400), PTHF(2900).

| Polymer | CA[a)] | CA[b)] | SE (mNm$^{-1}$) | $\gamma^d$ (mNm$^{-1}$) | $\gamma^p$ (mNm$^{-1}$) |
|---|---|---|---|---|---|
| PEC(2000) | 43,2 ± 0,9 | 48,3 ± 0,6 | 34,7 ± 0,8 | 33,2 ± 0,8 | 1,5 ± 0,8 |
| PTHF(2900) | 21,5 ± 0,8 | 30,8 ± 0,4 | 43,2 ± 0,6 | 41,4 ± 0,6 | 1,8 ± 0,6 |
| PEO(3400) | 34,2 ± 0,7 | 17,9 ± 0,5 | 55,3 ± 0,6 | 37,1 ± 0,6 | 18,2 ± 0,6 |

[a)] 1-Bromonaphtalene.
[b)] diiodomethane.

***Table 4.***
Contact angle (CA), total surface energy (SE), dispersion force ($\gamma^d$) and polar contribution ($\gamma^p$) values for ICs and $\alpha$-CD.

| IC | CA[a)] | CA[b)] | SE (mNm$^{-1}$) | $\gamma^d$ (mNm$^{-1}$) | $\gamma^p$ (mNm$^{-1}$) |
|---|---|---|---|---|---|
| IC- PEC(2000) | 32,8 ± 0,8 | 42,8 ± 0,5 | 38,4 ± 0,5 | 37,6 ± 0,8 | 0,8 ± 0,8 |
| IC- PEO(4600) | 27,2 ± 0,6 | 46,1 ± 0,4 | 40,0 ± 0,5 | 39,6 ± 0,5 | 0,4 ± 0,5 |
| IC- PTHF(2900) | 25,5 ± 0,8 | 38,9 ± 0,7 | 40,5 ± 0,5 | 40,2 ± 0,8 | 0,3 ± 0,7 |
| $\alpha$-CD | 24,1 ± 0,2 | 34,4 ± 0,2 | 50,7 ± 0,2 | 37,0 ± 0,2 | 13,7 ± 0,2 |

[a)] 1-Bromonaphtalene.
[b)] diiodomethane.

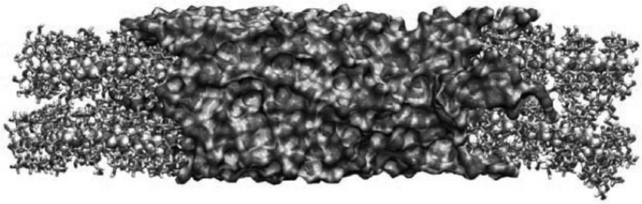


*Figure 6.*
Snapshots of the configuration of the system IC-PTHF at the beginning of the simulation run. The cyclodextrins are drawn with line style, and PTHF with van der Waals style. The drawing method for water molecules are solid surface. Carbon, hydrogen and oxygen atoms are green, white and red respectively.

its surface activity. The behavior observed can be explained in terms of the particular chemical structures of the different groups of the polymers.

**Molecular Dynamic Simulation (MDS)**

The order parameter S(r) and the radial distribution function (RDF) were determined from MDS to describe the orientation, organization and stability of the monolayers. Figure 6 shows the snapshots of the configuration of the system IC-PTHF at the begininng of the simulation run in which is in good agreement with the well-known picture of one system organization at the air-water interface. Figure 7 presents the S(r) variation as function of time for these polymers. 1.0 value for S(r) is indicative that the unit vector in different chains are parallel to each other. From the results shown in Figure 7, it is clear that PEC is more organized at the air-water interface than PTHF and PEO. These results are in good agreement with the experimental data. Comparing the S(r) for the PEC, PTHF and PEO and their ICs it can observe that the ICs are more ordered at air-water interface than their precursor polymers. Figure 8 a, b and c show these results. The conclusions are also agreement with the experimental data. From these simulations, it seems that the ICs have a better ordered monolayer. In the case of the polymers, the order of chains becomes worse, particularly for PEO. Figure 8c shows the S(r) for the IC-PEO.

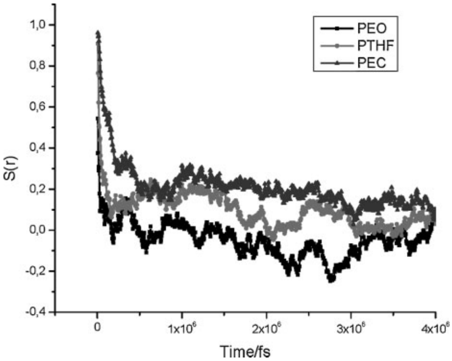


*Figure 7.*
Order parameter S(r) for precursor polymers from DMS.

The radial distribution function (RDF) between different atoms and atomic groups were analyzed. By this way it could also be possible to visualize the organization of the polymers at the air-water interface. Figure 9 and 10, present the results obtained. RDF between water molecules and the atoms oxygen in PEC displays the first peak at 3.9 Å, Figure 9 a). The plots for PEO and PTHF displays the first peak at 1.9 Å, (Figure 9 b and c). It could be observed that for the three systems exist a second peak. This could be considered as a representation of the second coordination shells. For PEO and PTHF the peaks were found at 3.4 Å and 3.6 Å and for PEC the peaks was at 4.9 Å. In the second case (Figure 10), The RDF between aliphatic moiety for the three polymers the first peak was found at 1.6 Å. This value is indicate that also the hydrophobic interactions are present between methylene groups of the different chains.

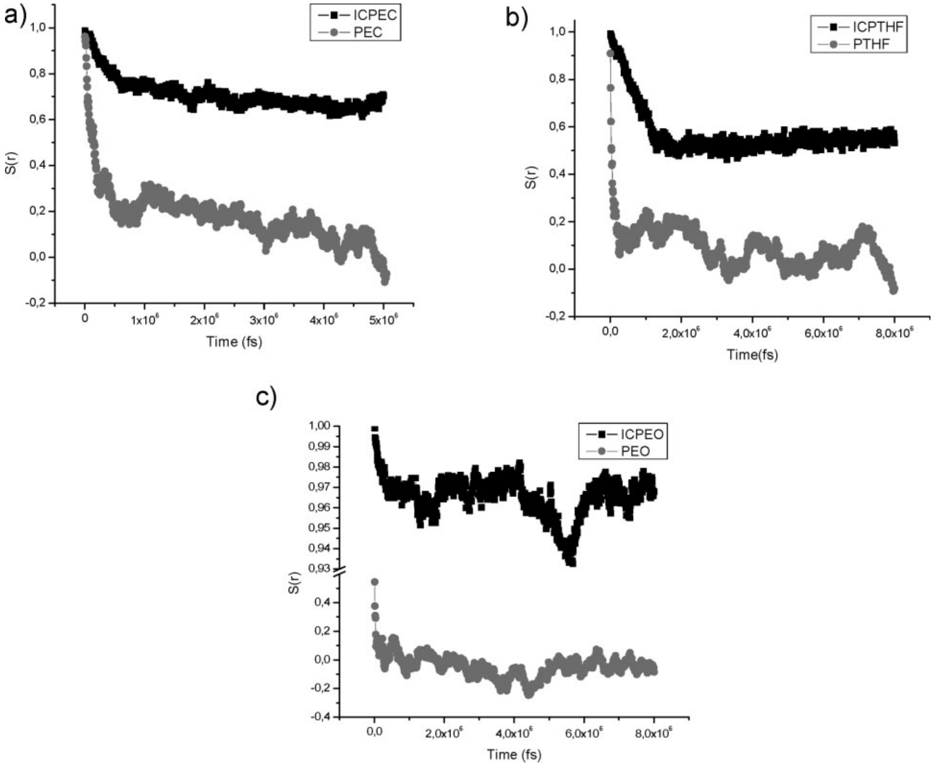


***Figure 8.***

Order parameter S(r) for a) PEC and IC-PEC; b) PTHF and IC-PTHF, c)PEO and IC-PEO.

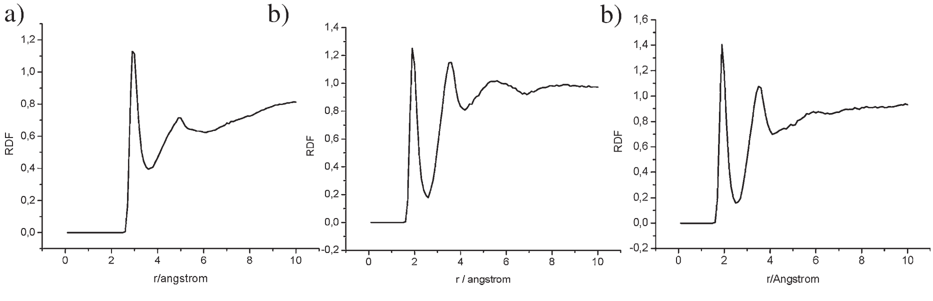


***Figure 9.***

RDF between oxygen atoms of the precursor polymer and water molecules for a) PEC, b) PEO and c) PTHF.

## Conclusions

The spreading experiments show that all the polymers and Inclusion Complexes studied form stable monolayers, despite of the sensibility of polymeric monolayers to the choise of spreading solvent. An important influence of the molecular weight and the degree of functionalization of PEC on the IC-PEC monolayers was found. Polymer monolayers stability depends on the number of methylene groups on the chemical structure and on the insertion of the hydroxyl number of functional groups in PEC. IC monolayers are more stable than that of the polymers.

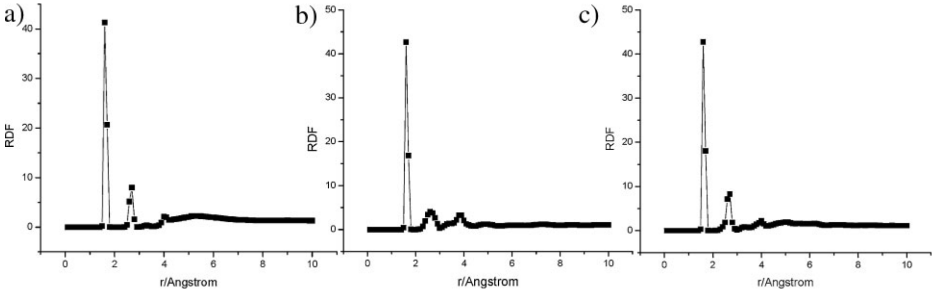


***Figure 10.***
RDF between $CH_2$-$CH_2$ of different chains for a) PEC, b) PEO and c) PTHF.

The experimental data were well described by molecular dynamic simulation in terms of the organization and stability of the monolayer at the air-water interface.

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