

Poly(ester)s Containing Germanium and Silicon in the Main Chain, Part 2: Static and Dynamics Behavior of Monolayers at the Air–Water Interface

Ligia Gargallo,¹ Beatriz Miranda,¹ Luz Alegría,¹ Angel Leiva,¹ Luis Hernán Tagle,² Deodato Radić¹

¹Departamento de Química Física, Casilla 306, Santiago 22, Chile

²Departamento de Química Orgánica Facultad de Química, Casilla 306, Santiago 22, Chile

Received 18 January 2011; accepted 22 June 2011

DOI 10.1002/app.33020

Published online 10 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The static and dynamic behavior of the Langmuir monolayers of poly(ester)s containing germanium and silicon in the main chain (Scheme 1) is reported. True monolayers are found for all the poly(ester)s studied. The isotherms of surface pressure versus surface area for poly(ester)s exhibit a behavior of the expanded-type monolayers and that of condensed-type monolayers. It was observed that the addition of an hydrophilic polymer such as poly(monomethyl itaconate) to the water subphase produces significant changes in the isotherm properties. The interfacial rheology of the poly(ester)s monolayers has also been studied by using

Oscillatory Barrier Experiments in a low-frequency range. It was found that the elasticity and the dilational viscosity increase from diluted monolayers until a surface concentration about $20 \times 10^{-5} \text{ mg cm}^{-2}$. The static and dynamic elasticities were found to be very similar for the poly(ester)s over the dilute range. It was possible to conclude that these poly(ester)s form extremely viscoelastic monolayers. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3126–3132, 2011

Key words: poly(ester)s; germanium; silicon; monolayer; interface; poly(monomethylitaconate); dilational viscosity

INTRODUCTION

The nature of a monolayer partially depends on the strength of interfacial interactions with substrate molecules and of polymer intersegmental interactions. It is therefore expected that both the viscoelastic properties of polymer monolayers and the nature of the water subphase are also dependent on these factors. If a polymer monolayer is viewed as a macroscopic viscoelastic continuum, several types of motions are possible.¹ Two main types of motions can be distinguished: capillary (or out of plane) and dilational (or in plane).² The first one is a shear deformation, while for the second one there are both a compression-dilation motion and a shear motion. Since dissipative effects do exist within the film, each of the motions consists of elastic and viscous components. The elastic constant for the capillary motion is the surface tension γ , while for the second it is the dilation elasticity $\varepsilon(\omega)$. The latter modulus depends upon the stress applied to the monolayer. For an uniaxial stress the dilational modulus is the

sum of the compression and shear moduli,^{3,4} given by eq. (1):

$$\begin{aligned}\varepsilon(\omega) &= \varepsilon_k + \varepsilon_S \\ \varepsilon_k &= \kappa + i \omega \eta_k \\ \varepsilon_S &= S + i \omega \eta_S\end{aligned}\quad (1)$$

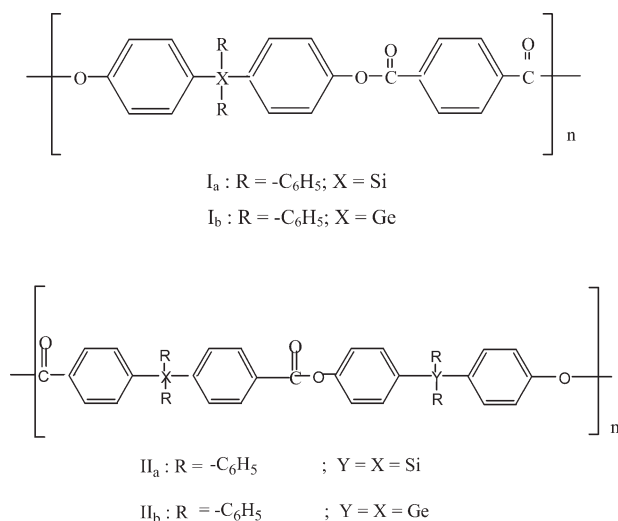
where ω denotes the angular frequency and $\omega\eta'_S$ are the loss components of the compression and shear motions. $\varepsilon(\omega)$ and κ are the dilational elasticity and viscosity, respectively.⁴ ε_S in this case can be considered as zero because fluid monolayer is present. There are several experimental techniques for studying $\varepsilon(\omega)$. In this work, oscillatory barrier experiments were performed. This technique will be used in the low-frequency range (<1 Hz). In this kind of experiments, the frequency of the oscillations is varied for a given area. From the experimental parameters, the real and the imaginary components of the dilational elastic modulus can be calculated.¹ From the surface pressure Π versus surface concentration Γ (Π - Γ) curves, it is possible to calculate the static elasticity modulus or static compressibility modulus.

$$\varepsilon_0 = \left(\frac{\partial \Pi}{\partial \ln \Gamma} \right)_T \quad (2)$$

which would correspond to the ε_0 defined in eq. (2) for an instantaneous deformation of the monolayer and therefore without any dissipative effects.

Correspondence to: D. Radić (dradic@puc.cl).

Contract grant sponsor: Fondecyt; contract grant numbers: 1080026, 1080007, 1070778.



Scheme 1 Chemical structure of poly(oxy-1,4-phenylene-diphenylsilyl-1,4-phenylene-oxycarbonyl-1,4-phenylene-carbonyl)(I_a); poly(oxy-1,4-phenylene-diphenylgermyl-1,4-phenylene-oxycarbonyl-1,4-phenylene-carbonyl)(I_b); poly(carbonyl-1,4-phenylene-diphenylsilyl-1,4-phenylene-carbonyl-oxy-1,4-phenylene-diphenylsilyl-1,4-phenylene-oxy)(II_a); Poly(carbonyl-1,4-phenylene-diphenylgermyl-1,4-phenylene-carbonyl-oxy-1,4-phenylene-diphenylgermyl-1,4-phenylene-oxy)(II_b).

Because of the excellent adhesion of condensation polymers containing Si films,⁵ it is interesting to study the interfacial behavior of these poly(ester)s at the air–water interface. The formation of Langmuir Blodgett monolayer of condensation polymer, as poly(ester)s containing Si and Ge in the main chain can present promising potential applications in areas such as catalysis, metallic conductors, semiconductors, bactericides, and cancer chemotherapeutic agents, as we have reported previously.⁶

The aim of this work is the comparison of dynamic and static elasticities for the poly(ester)s containing silicon or germanium or both i.e., poly(oxy-1,4-phenylene-diphenyl-silyl (or germyl)-1,4-phenylene-oxycarbonyl-1,4-phenylene-carbonyl) (X = Si = I_a ; X = Ge = I_b); poly(carbonyl-1,4-phenylene-diphenyl-silyl (or germyl)-1,4-phenylene-carbonyl-oxy-1,4-phenylene-diphenyl-silyl (or germyl)-1,4-phenylene-oxy) (X = Si = II_a ; X = Ge = II_b). The chemical structures of the polymers are shown in Scheme 1. The dynamic viscoelastic parameters $\varepsilon(\omega)$ and κ were calculated using oscillatory barrier experiments, assuming $\mu = 0$; being μ the transverse surface viscosity.

EXPERIMENTAL

Polymers

The preparation of poly(ester)s were reported previously.^{7,8} Poly(esters) I_{a-b} were synthesized from ter-

ephthaloyl dichloride and the diphenols bis(4-hydroxyphenyl)-diphenylsilane or germane under phase transfer catalysis conditions.⁹ The diphenols were obtained from 4-bromophenol and dichloro diphenylsilane or germane, according to a procedure described in the literature.¹⁰

Poly(esters) II_{a-b} were synthesized from the same diphenols and the acid dichlorides bis(4-chloroformylphenyl)-diphenylsilane or germane under phase transfer catalysis conditions.⁸ The acid dichlorides were obtained from bis(4-methylphenyl)-diphenylsilane or germane, which were oxidized with KMnO₄ and then reacted with thionyl chloride, according to a described procedure. Bis(4-methylphenyl)-diphenylsilane or germane were obtained from 4-bromotoluene and dichlorodiphenylsilane or germane, according to a described procedure.

Monomers and poly(esters) were characterized by IR and ¹H and ¹³C NMR spectroscopy, and the results were in agreement with the proposed structures.

Poly(monomethyl itaconate) (PMMel) was synthesized by radical polymerization in bulk using α - α' azo-bisobutyronitrile (AIBN) as previously reported.¹¹

Surface pressure-area isotherms

The surface pressure-area (Π -A) isotherms for spread films of the poly(ester)s 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 poly(ester)s monolayers were deposited on the water surface (Milli-Q whose resistivity was always higher than 18 M Ω , and surface tension γ at 298 K was 72.12 mNm⁻¹). The spreading solvent used to prepare poly(ester)s monolayers was spectrograde chloroform and used it without further purification. The initial state of the monolayer was always chosen to have surface pressure, Π , close to zero. After total evaporation of the solvent and stabilization of the film (30 min), the monolayer was continuously compressed. The data were obtained at a constant compression rate of 10 cm² min⁻¹. Water subphase pH was adjusted by adding HCl or NaOH solution. NaCl was added to obtain a constant ionic strength.

The spreading protocol was systematically studied. In fact, experiments in which measurements were performed by varying the evaporation times. By this way it was concluded that 30 min is the optimum time for the best stabilization of the film and there is not evidence that the evaporation time affect the film and no crystallization is observed. The effect of the spreading solvent with different evaporation rates could not be analyzed because of solubility reasons. Nevertheless, it is well known that chloroform is the best spreading solvent in this technique. The

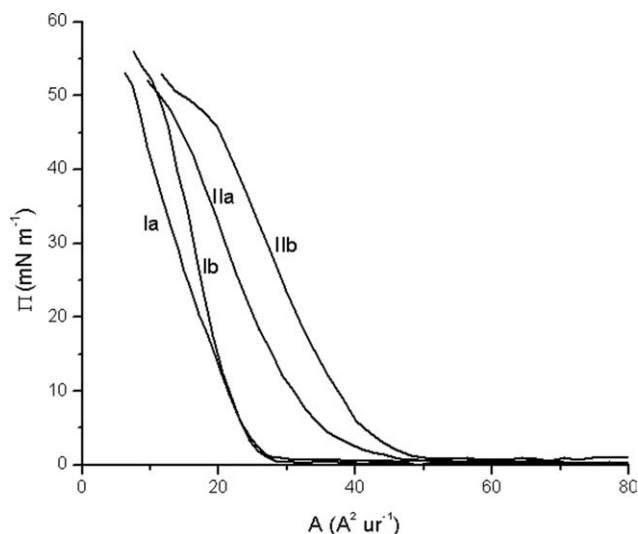


Figure 1 Surface pressure-area (Π - A) isotherms of four poly(ester) monolayers on water subphase at 298 K.

spreading solution is applied with a Hamilton microsyringe at different parts on the the surface. To confirm the stability of the monolayer two different forms for preparing the monolayers were used. In the first one the surface concentration was changed by subsequent addition of the polymer solution. The surface pressure is continuously measured and the equilibrium value was taken when the surface pressure Π had remained constant at least 10 min. In the second way, the monolayers were symmetrically compressed by moving two barriers under computer control after the spreading of the polymer Solution. The maximum barrier speed was 10 mm min^{-1} . Both isotherms agreed with each other.

Oscillatory barrier experiments

These experiments were carried out by inducing an oscillatory movement at the barrier. They were performed at constant barrier speed and the frequency was varied by changing the maximum area change ΔA . The technique of oscillatory barriers at low frequency allow to observe the variation of the rheological parameters with the surface concentration. The experiments were developed in triplicate to ensure reproducibility. For this reason the reported values are reproducible and the cattering do not affect the results and the interpretation of the data. This is a common procedure and generally accepted.

RESULTS AND DISCUSSION

Figure 1 shows the surface pressure Π plotted as a function of surface areas A per repeating unit (Π - A isotherms) for I_a , I_b , II_a and II_b monolayers. It is found that on pure water (pH: 5.6) the monolayer is

stable and collapses at high surface pressures. In general, Π gradually increases with decreasing A and finally shows a relatively steep increase before attaining a collapse region. The Π - A isotherm for the poly(ester) I_b monolayer has sharper increase in Π as A decreases compared with the poly(ester)s I_a , II_a and II_b monolayers. This is commonly attributed to the presence of strong lateral interchain interaction.¹² The limiting areas per repeating unit, A_0 extrapolated to $\Pi = 0$ through the linear portion of the Π - A isotherms are smaller for two poly(ester)s I_a and I_b than those with two silicon or two germanium (II_a and II_b). Table I summarizes these results. The critical surface area A_C values at $\Pi = \Pi_C$ increase from I_a to II_b as can be seen in Table I. Perhaps this behavior could be attributed to some effect due to the size of the heteroatom such as flexibility of the chain or crystallinity i.e., silicon has lower size than germanium. However, it could not be disregarded a possible aggregation process which is difficult to detect.

It is known that the Coulombic or electrostatic interaction is higher for polymers with Si atoms. This tendency is probably due to the lower electronic affinity or electronegativity than Ge specially lower than carbon.⁷

Influence of additives on the interfacial behavior and spreading characteristics of the poly(ester) monolayers were studied using PMMeI in the water subphase. The presence of PMMeI in water subphase modifies the shape and the position of the isotherms considerably when compared with those obtained on pure water.

Figure 2 illustrates this behavior for II_b at pH: 3.0 and 5.6, this finding could be indicative of appreciable interactions of PMMeI with poly(ester) II_b monolayers. An outstanding feature of the monolayer is the increasing in the area per repeating unit, A_0 , from 60 (without PMMeI) to 70 (with PMMeI) $\text{\AA}^2/\text{ru}$ approximately at pH: 3.0. The two isotherms at pH: 3.0 and 5.6 with PMMeI in the water subphase differ in the pressure at which the monolayer collapses $\Pi_C = 33$ and $43 \text{ (mNm}^{-1}\text{)}$ respectively. The addition of PMMeI in water gives rise to a destabilized monolayer when compared with the II_b monolayer at the same pH. Attempts to explain this behavior suggest to attribute

TABLE I
Monolayer Parameters

Poly(ester)	A_0 ($\text{\AA}^2/\text{ru}$)	Π_C (mNm^{-1})	A_C ($\text{\AA}^2/\text{ru}$)
I_a	23	53	7
I_b	24	54	10
II_a	33	53	15
II_b	41	53	20

The limiting area per repeating unit A_0 at $\Pi = 0$; the critical area A_0 at $\Pi = \Pi_C$. Water subphase pH: 5.6.

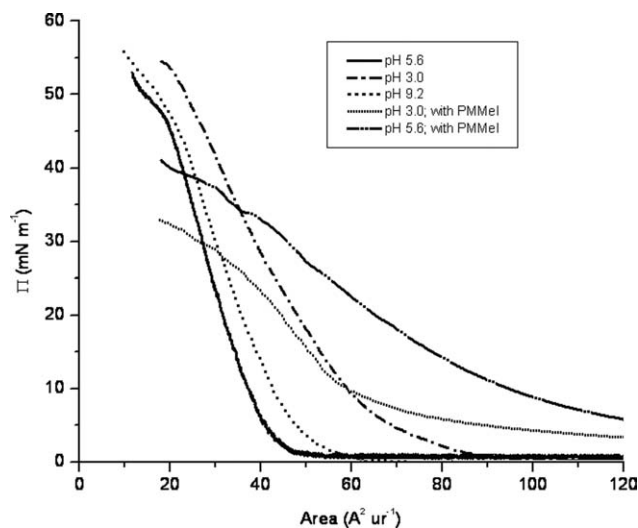


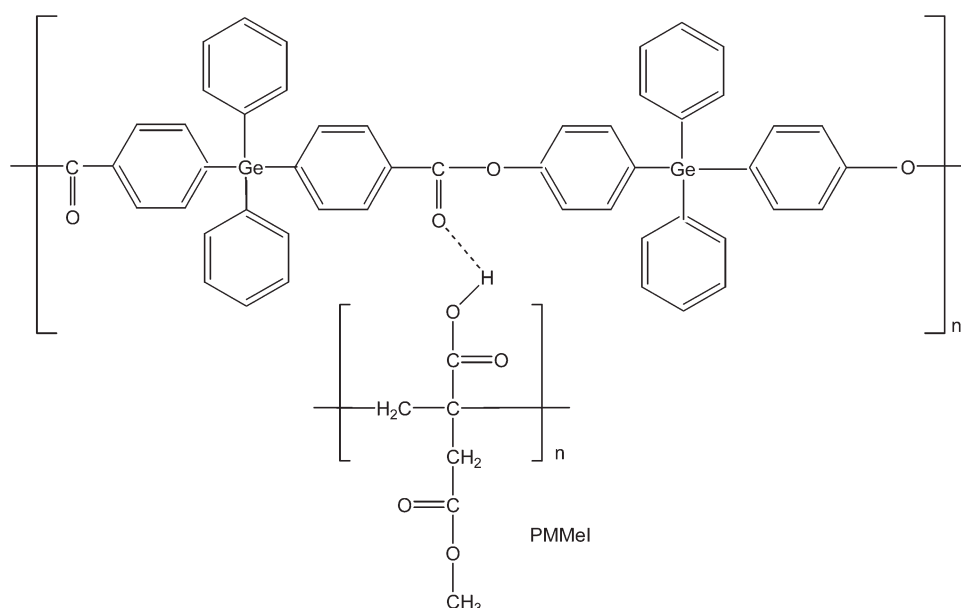
Figure 2 Surface pressure-area (Π -A) isotherms of Π_b at different pH of the water subphase; (—) pH 5.6, (---) pH 3.0, (····) pH 9.2, (— · —) pH 3.0 with PMMeI and (---) pH 5.6 with PMMeI.

this behavior to a strong specific interaction between poly(ester) and PMMI. This interaction could be of the hydrogen bonding type between the carboxylic groups of the poly(ester) and the carboxylic groups of the PMMeI, as illustrated in the schematic representation in Scheme 2. As it can be observed in Figure 2 the isotherm on the water subphase at pH: 3.0 with PMMeI produces a larger destabilized monolayer when compared with Π_b monolayer at pH 5.6 with

PMMeI. For this reason the hydrogen bond interaction should be the main responsible of this behavior. This interaction also would modify the hydrophobic/hydrophilic balance of the poly(ester) at the interface. From the present experimental results, a possible process of dissolution of the poly(ester) coming from the air–water interface to the aqueous subphase with compression processes cannot be disregarded. In general, it is well-known that compounds dissolved in the subphase combine with the hydrophilic moieties in amphiphilic materials and increase or decrease the stability of the monolayer formed at the air–water interface.^{13,14} However, to more clearly examine the changes in the monolayers, spectroscopic measurements should be used.

Viscoelastic properties of poly(ester) monolayers

This work provides a more quantitative aspect of monolayer dynamics in terms of the dilational elasticity $\varepsilon(\omega)$ and the corresponding viscosity κ in conjunction with the static elasticity ε_0 . The dynamic viscoelastic parameters $\varepsilon(\omega)$ and κ were calculated assuming the transverse surface viscosity $\mu = 0$. The optimum resonant coupling between the capillary waves (controlled by the surface tension γ) and the longitudinal waves (controlled by $\varepsilon = \varepsilon' - i\omega\kappa$) take place^{15–17} when the ratio of ε_0/γ reaches a value of about 0.2. If ε_0/γ exceeds 0.2 as Γ is increased then the resonance condition is weakened. ε_0 was determined from static Π - Γ isotherm via eq. (2) [Fig. 3(A,B)].



Scheme 2 Schematic representation of specific interaction like hydrogen bond type between poly(carbonyl-1,4-phenylene-diphenylgermyl-1,4-phenylene-carbonyl-oxy-1,4-phenylene-diphenylgermyl-1,4-phenylene-oxy) and poly(monomethyl itaconate) (PMMI)

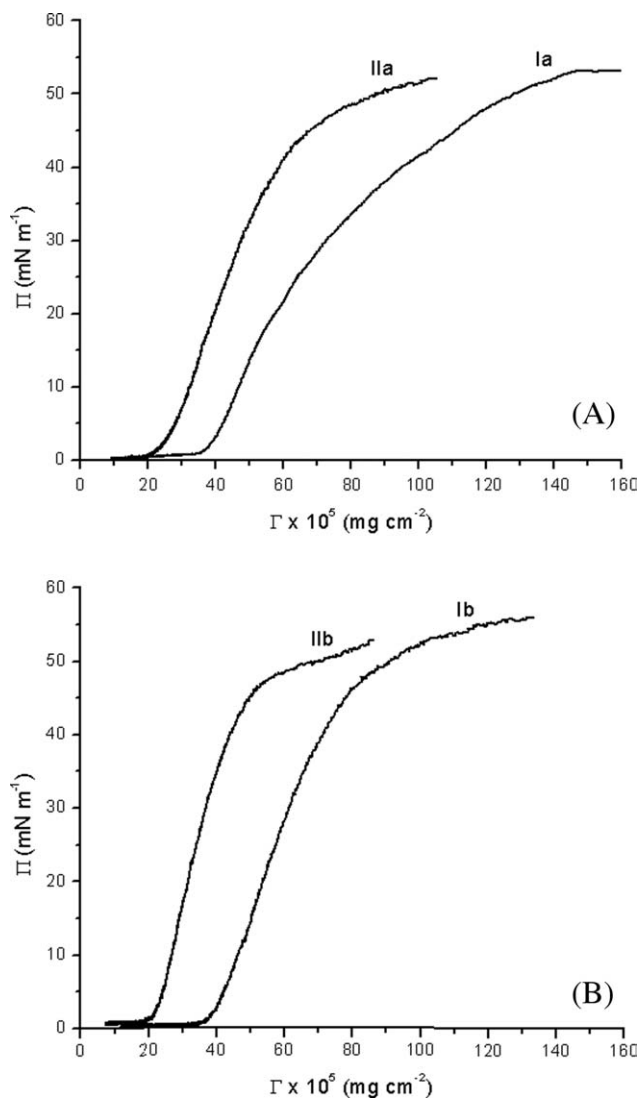


Figure 3 Surface pressure Π versus surface concentration Γ of (A) I_a and II_a and (B) I_b and II_b .

In a previous study,⁶ it has been possible to estimate the concentrations that mark the crossover from dilute to semidilute and from semidilute to concentrated regimes. Plots ε_0/γ versus Γ in mg m^{-2} are shown in Figure 4, where it can be distinguished the three concentration areas, and the ε_0/γ ratio values.

A comparison of dynamic and static elasticities for I_a , I_b , II_a and II_b is given in Figure 5(A–D), respectively. The dynamic viscoelastic parameters $\varepsilon(\omega)$ and κ were calculated with the eq. (1). The dynamic and static elasticities are identical for all the poly(ester)s within experimental error until the surface concentration reaches about $2.0 \text{ (mg m}^{-2}\text{)}$. From this point, the monolayer should presumably depart from 2D conformation by chain looping, or possibly more macroscopic film collapse. This behavior is more prominent with II_a . The corresponding surface viscosity κ , which is a combination of compressional

and shears components was also estimated. The values of κ in Figure 5(A–D) are approximately zero at low concentrations and then begin to increase as ε_0 and $\varepsilon(\omega)$ increases and seem to reach a maximum at about a Γ of $2.5\text{--}3.0 \text{ (mg m}^{-2}\text{)}$ for II_a .

A significant influence of the type of heteroatom on the monolayer behavior was found. Particularly in the cases of I_b and II_a it can be seen an increasing of the elasticity $\varepsilon(\omega)$ close to the crossover from semidilute to concentrated regimes. This behavior can be explained by a balance between a maximum connectivity between the segment contacts and moderate lateral repulsion. This situation produces a minimum of compressibility. Another observation is that the ε_0 values in both cases (I_b and II_a) are not the same in the concentrated regime. In the other case, I_a , an increase of the $\varepsilon(\omega)$ value is observed, which demonstrates that the same surface pressure for the reorganization of the material allows states with greater accumulated elastic energy.

At low surface concentration, in the dilute or semidilute area, the dynamic parameter values are similar to the compression elasticity equilibrium values. This situation corresponds to a system as a fluid where the shear component is zero. On the contrary, in the concentrated area there are shear components which produce an increase of the storage elastic modulus relative to the equilibrium value. The coupling modes are not possible when the surface concentration increases. In the region with a high cover the viscous components are dominant in relation to the elastic component. This condition corresponds to a film as a gel. At low frequency the motions should correspond to reptation motions of the chains.¹⁸ $\varepsilon(\omega)$ for II_a are larger than those for II_b , taking into

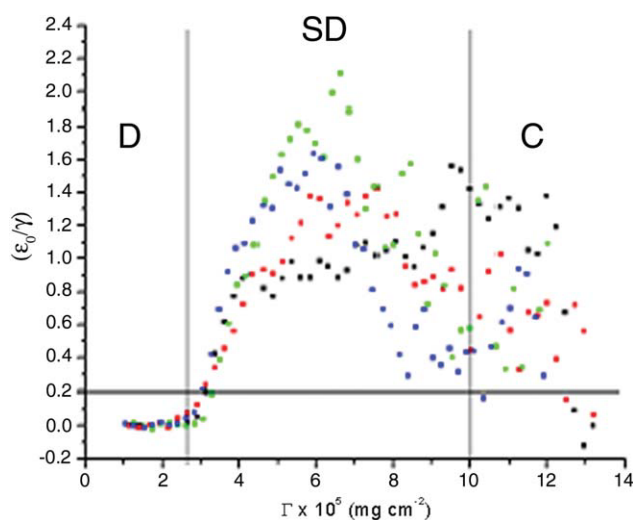


Figure 4 Elasticity/surface tension (ε_0/γ) ratio versus surface concentration Γ of (black) I_a , (green) I_b , (red) II_a and (blue) II_b . D, SD, and C are dilute, semidilute, and concentrate area, respectively.

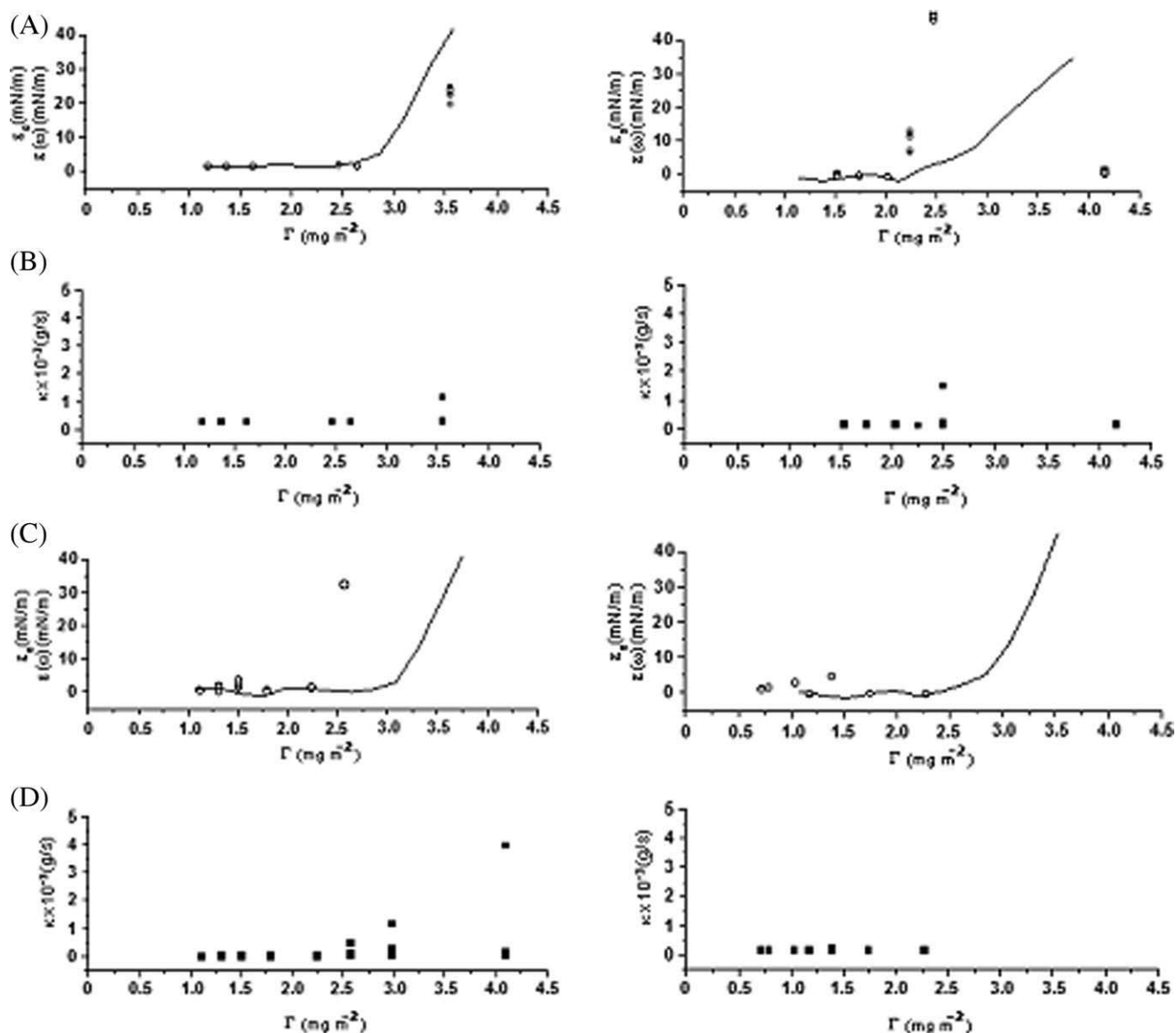


Figure 5 Surface elasticity versus surface concentration Γ . The static dilational elasticities ε_0 are represented by the solid curve and the dynamic elasticity $\varepsilon(\omega)$ are represented by (o). Surface viscosity κ versus Γ are represented by (■). (A) for I_a , (B) for I_b , (C) for II_a , and D for II_b .

account the beginnings of semidilute region. $\varepsilon(\omega)$ values for I_b are larger than for I_a . In general, the $\varepsilon(\omega)$ values can be only compared in the dilute region for each polymer. The comparison of the results observed for the poly(ester)s in Figure 5 should show that all of these poly(ester)s form extremely viscoelastic monolayers.

CONCLUSION

In conclusion, an influence of the type of hereoatom of the poly(ester) on the monolayer behavior was found. The zero pressure limiting area per repeating unit A_0 , increases from 23 and 24 $\text{\AA}^2/\text{ru}$ for I_a and I_b to 33 and 41 $\text{\AA}^2/\text{ru}$ for II_a and II_b , respectively.

The critical area, A_c , increases from 7 to 20 $\text{\AA}^2/\text{ru}$ from I_a to II_b .

At low surface concentration, in the dilute or semidilute area, the dynamic parameter values are similar to the compression elasticity equilibrium values. This situation corresponds to a system as a fluid where the shear component is zero. On the contrary, in the concentrate area there are shear components which produce an increase of the accumulated elastic energy relative to the equilibrium.

When the surface concentration increases, the coupling of modulus is not possible. In the region with a high coverage the viscous components are dominant relative to the elastic component. This condition

should correspond to a film as a gel. At low frequency the motions could correspond to reptation motions of the chains.

The presence of PMMeI causes a significant difference in the shape and position of the isotherms of Π_b at pH: 3.0 and 5.6.

References

1. Noskov, B.A.; Zubkova, T.U. *J Colloid Interface Sci* 1995, 1, 170.
2. Kawaguchi, M. *Prog Polym Sci* 1993, 18, 341.
3. Monroy, F.; Ortega, F.; Rubio, R. G. *Phys Rev* 1998, E58, 7629.
4. Goodrich, F. C. *Proc R Soc Lond Ser* 1981 A374, 341.
5. Thames, S. F.; Patel, S. F. *J Coating Technol* 1989, 61, 53.
6. Gargallo, L.; Miranda, B.; Leiva, A.; González, A.; Sandoval, C.; Radic', D.; Tagle, L. H. *J Macromol Sci Phys* 2006, 45, 105.
7. Tagle, L. H. *Macromol Symp* 2003, 199, 499.
8. Tagle, L. H.; Díaz, F. R.; Vega, J. C.; Valenzuela, P. *Eur Polym J* 2003, 39, 407 (and references therein).
9. Tagle, L. H.; Díaz, F. R.; Nuñez, M.; Canario, F. *Int J Polym Mat* 2003, 52, 287.
10. Davidson, W.; Laliberte, B. R.; Goddard, C. M.; Henry, M. C. *J Organomet Chem* 1972, 36, 283.
11. Gargallo, L.; Radic', D.; Yazdani-Pedram, M.; Horta, A. *Eur Polym J* 1989, 25, 1059.
12. Gargallo, L.; Miranda, B.; Ríos, H.; Radic', D. *Polym Int* 2001, 50, 858.
13. Gargallo, L.; Miranda, B.; Leiva, A.; Radic', D. *Polimery (Warsaw)* 2001, 46, 828.
14. Makino, M.; Kamiya, M.; Ishii, T.; Yoshikawa, K. *Bull Chem Soc Jpn* 1996, 69, 3429.
15. Kawaguchi, M.; Sauer, B. B.; Yu, H. *Macromolecules* 1989, 22, 1735.
16. Noskov, B. A. *Colloid Polym Sci* 1995, 273, 263.
17. Earnshaw, J. C. *Adv Colloid Interface Sci* 1996, 68, 1.
18. Makino, M. *Langmuir* 1997, 13, 7125.