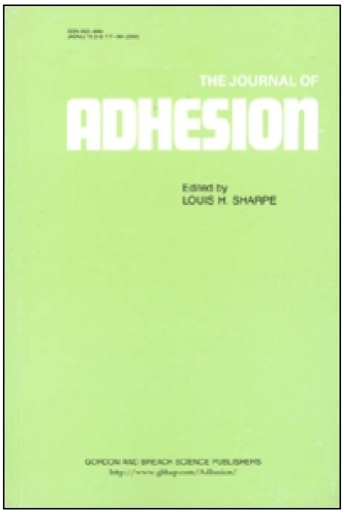

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Ringard-Lefebvre, Catherine and Baszkin, Adam(1997) 'Adhesion of Polymer Monolayers to the Water Subphase. Effect of Solvents and Polymer Functionality', The Journal of Adhesion, 63: 1, 99 — 119
To link to this Article: DOI: 10.1080/00218469708015216
URL: http://dx.doi.org/10.1080/00218469708015216

J. Adhesion, 1997, Vol. 63, pp. 99–119
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Adhesion of Polymer Monolayers to the Water Subphase. Effect of Solvents and Polymer Functionality*

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(Received 30 October 1995; In final form 18 April 1996)

The properties and the organization of poly (D, L-lactic acid) monolayers spread at the air/water interface were shown to be dramatically dependent on whether these monolayers have been spread from a good or a bad solvent. Whereas a good solvent, such as chloroform, favored the deployment of polymer chains from their coiled structure in solution to the unfolded structure, a bad solvent, as exemplified by acetone, enhanced strong intersegment interactions resulting in the formation of microdomains capable of respreading and favored adhesion of the polymer monolayer to water.

Independently carried out experiments with monolayers of ester derivatives of hyaluronic acid demonstrated that the nature of a chemical group substituted on the glucuronic acid moieties of the polymer can considerably influence surface properties of these monolayers. Thus, if monolayers of the ethyl ester derivative were shown to be rather compressible, those of the benzyl ester derivative were more rigid and, relative to the ethyl ester derivative, they exhibited increased adhesion to the water subphase within a wide range of areas.

It has been shown that the van Oss-Chaudhury-Good theoretical approach applied to the calculation of interfacial free energies of these monolayers with water, obtained from the contact angle data on their Langmuir-Blodgett films, was perfectly adapted to explain the observed differences in their adhesion properties.

Keywords: Poly (lactic acid) monolayers; hyaluronic acid derivative monolayers; contact angles; polymer LB films-water energies of adhesion

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*One of a collection of papers honoring Robert J. Good, the recipient in February 1996 of *The Adhesion Society Award for Excellence in Adhesion Science, sponsored by 3M.*

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INTRODUCTION

It has long been established that the surface of many polymer systems are significantly different in composition from the bulk structure. The surface properties such as wettability, friction, lubrication, biological compatibility and chemical reactivity were shown to be primarily dependent upon the chemical and physical molecular structure at the surface of a polymer. Because of minute amounts of material present in a surface zone, the surface requires special tools that can directly probe it. Thus, surface analysis should provide information on both the chemical and physical characteristics of the surface. Whereas the former would mainly concern the type of exposed chemical functionality and its associated features such as lateral distribution of surface density, translational ordering, composition and depth distribution of functionality, the latter includes roughness, void content, mass density and defects. However, such an analysis, which would enable one to emphasize selected features of interest, is often difficult to realize mainly because of the difficulties encountered in correlations of database polymer properties and structures with those for the polymer surface of interest [1]. Moreover, polymer structure and properties are essentially non equilibrium structures and, as such, exhibit a range of relaxation times in response to changing environments and external stimuli.

A thermodynamic consideration of a surface formation process for homopolymers or simple copolymers imply that the main chain or side chains will orient in response to the new environment to minimize the interfacial free energy. Such changes do not necessarily require long range segmental motion that would produce a conformational change of a polymer or migration of large polymer segments, but may be achieved by a relatively short range motion such as rotational motion of segments present at the surface. Thus, the motion or reorientation of apolar groups or segments of a polymer towards the interface with vacuum or air will always take place, while the motion of polar phases, blocks, segments or side chains towards the aqueous phase would constitute the main driving force leading to the minimization of its free energy at this interface.

More than twenty years ago, and for the first time, we showed that potassium chlorate/sulfuric acid-oxidized low density polyethylene has temperature dependent contact angles and rapidly becomes hydrophobic when heated in air [2]. The reduction in polymer surface functionality was explained by migration of polar groups which dominate the polymer-air surface into the bulk phase. The magnitude of the driving force for this reaction, *i.e.* minimization of the surface energy, was calculated for various degrees of oxidation of the polymer [3, 4]. Later, Gagnon and McCarthy [5], who worked with this relaxed-surface film, demonstrated that treatment of the film with warm aqueous sodium hydroxide followed by dilute hydrochloric acid, causes diffusion of the polymer's polar carboxylic acid and sulfonate groups back from the bulk to the surface, while the reheating of the dried surface in air brings them again into the bulk of the polymer. The authors concluded that with such surface oxidized polymer films it is possible to control the surface polarity rationally by concentrating polar functional groups at the surface or away from the surface.

Surface dynamic effects that permit the surface of a polymer to restructure were shown to be particularly pronounced in aqueous media. Holly and Refojo [6] who studied acrylic hydrogels reported that these gels appear to be hydrophobic with an advancing water contact angle measurement and highly hydrophilic with a receding water measurement. They attributed this observation to the mobility of surface polymer chains and their side groups or segments. Thus, in the case of studied poly (hydroxyethyl methacrylate) hydrogels, the apolar side chain and alpha-methyl group would dominate the surface in air whereas the hydrophilic, hydroxyl group containing the ester side chain dominates the surface in water. The latter reduces the interfacial tension of water while the former exercizes the same effect on the surface energy in air.

Following these pioneering works, surface reorientation of polymer solids and its dependence on different environments was exhaustively studied during the recent two decades. Many polymers were shown to exhibit differences in surface polymeric chain orientations which are particularly evident at air and water interfaces. Examples include hydrogels, block copolymers, graft copolymers and radio frequency sputtered polymers. Some main references to this considerable range of studies is given in References [7–27].

However, if the phenomenon of the surface dynamics and molecular rearrangement at the surface of polymer solid films is today well documented by different analytical methods and well understood, the surface mobility of polymer segments in monolayers spread at the aqueous subphase and the influence of various factors upon the inter- and intra-segment interactions is still in its infancy. The question which should be adressed is that raised by Gaines [28]: how likely is it that spreading of polymers from organic solvents at the aqueous subphase can produce monolayers in which every polymer segment can extend at the interface?

MONOLAYERS OF POLYMERS

Ultrathin polymer films with thicknesses of the order of 10 to 100 nm are of considerable importance in several key industrial operations such as detergency, lubrication and solvent-casting processes. The organization of these films, their interfacial properties and mobility are different from those of three-dimensional solid films, in that polymer chains in the ultrathin films are confined to small spatial dimension perpendicular to the film surface. This results in a smaller, conformational entropy of an individual chain relative to three-dimensional solid state. The conformation and packing analysis of the aggregation state of polymer chains in ultrathin films [29, 30], reveals also that the segment density distribution of an unperturbed Gaussian chain having no excluded volume is the same along the direction parallel to the surface as along that perpendicular to it. Conversely, for the case where a perturbed chain with excluded volume is restricted in a small spatial dimension along the direction paralled to the surface, the excluded volume affecting the segment density distribution along this direction is augmented by that along the direction parallel to the surface. This results in a perturbed chain dimension along the direction parallel to the surface larger than the perturbed chain dimension in the three-dimension state [29–31]. The above considerations clearly show that both the conformation and packing of chains, as well as their mobility, may well vary form polymer to polymer.

Though polymers were among the first types of materials investigated in the form of monolayers at the air/water interface [32–36], these studies were mainly restricted to the classification of their surface pressure-area (π-A) isotherms and to the evaluation of limiting areas per segment [37–47]. By comparing an extrapolated area to the zero surface pressure with a projected area of a monomer unit from molecular models, information on molecular orientation and packing of these polymer monolayers could often be obtained. However, such comparisons are only valid if the assumption that polymer molecules which in a bulk solution form tightly bound three-dimensional coils could, during the spreading process from organic solvents onto the aqueous subphase, extend to cover the available area with every polymer segment in the surface layer.

Studies of the effect of solvents and polymer functionality on monolayer characteristics are sparse. A part from the early work of Maleev *et al.* [48], who studied compressional behavior of poly (acrylate) and poly (methylacylate) monolayers and attributed differences in their behavior to the differences in polymer glass transition temperatures, that of Malcom [49] and of Loeb and Baier [50] as well as that of Baglioni *et al.* [51], on poly (γ-methyl L-glutamate) monolayers should be mentioned. The authors show that the polymer may form either an α helix or a β sheet conformation depending on whether the spreading solvent did or did not contain pyridine.

In general, when molecular cohesion of a monolayer is high compared with its adhesion towards the aqueous phase, the molecules of a monolayer remain at least partly as three-dimensional clusters on the surface and incomplete spreading results. Conversely, high adhesion to the water subphase and low intermolecular monolayer cohesion will result in an unstable soluble film. By changing the chemical nature of the subphase or of the spreading solvents it is possible to obtain different intermediate states of a monolayer.

We concentrate in this article on two polymers: poly (D, L lactic acid) monolayers spread from different solvents at the air-water interface and on monolayers of ethyl and benzyl ester derivatives of hyaluronic acid spread from dimethyl sulfoxide. Both polymers find wide application as biomaterials [52, 53] or as bioresorbable drug carriers obtained by a solvent casting procedure [54, 55]. The dependence of poly (D, L lactic acid) monolayer behavior on the nature of the spreading solvent has already been reported by us previously [56] and we refer here only to some selected data from this work. The effect of the chemical nature of ester derivatives of hyaluronic acid on adhesion of its monolayers to the water interface is presented for the first time.

SURFACE FREE ENERGIES OF MONOLAYERS AND THEIR INTERACTION ENERGIES WITH THE WATER SUBPHASE

It is well known that interfacial energies between solids and liquids as well as those between solids and solids cannot be determined directly. However, such a determination may be possible *via* the surface tensions, γ_1 and γ_2, of the interacting materials 1 and 2, provided that an appropriate combining rule is available.

Developed some ten years ago, the so-called van Oss-Chaudhury-Good approach [57–60] allows a clear-cut delineation between the apolar Lifshitz-Vander Waals (LW) forces that account for all electrodynamic interactions on a macroscopic scale and the polar (AB) electron-acceptor-electron-donor (Lewis acid-base) interactions, and provides a fairly easy way of calculating these energies.

According to the authors, the surface tension of liquids and surface free energies of solids are essentially determined by these two types of interactions which are additive:

$$\gamma = \gamma^{\mathrm{LW}} + \gamma^{\mathrm{AB}} \tag{1}$$

If the γ^{LW} component of γ incorporates electrodynamic London dispersion and dipole interactions of a given material, the γ^{AB} component comprises two non-additive parameters resulting from electron-acceptor (γ^+) and electron-donor (γ^-) contributions. The γ^{AB} term of Eq. (1) can be expressed as:

$$\gamma^{\mathrm{AB}} = 2(\gamma^+\gamma^-)^{1/2} \tag{2}$$

The interfacial tension between two apolar condensed phase materials 1 and 2 becomes:

$$\gamma_{12}^{\mathrm{LW}} = [(\gamma_1^{\mathrm{LW}})^{1/2} - (\gamma_2^{\mathrm{LW}})^{1/2}]^2 \tag{3}$$

while the polar portion of the interaction between two condensed phase materials 1 and 2, for which the electron acceptor of 1 interacts with the electron donor of 2 and the electron donor of 1 interacts with the electron acceptor 2, is given by:

$$\gamma_{12}^{\mathrm{AB}} = 2[(\gamma_1^+ \gamma_1^-)^{1/2} + (\gamma_2^+ \gamma_2^-)^{1/2} - (\gamma_1^+ \gamma_2^-)^{1/2} - (\gamma_1^- \gamma_2^+)^{1/2}] \tag{4}$$

Combining Eqs. (3) and (4)and taking γ_1 as referring to the surface free energy of a solid LB film, its interfacial tension with the water subphase may be written in the form:

$$\gamma_{SL} = [(\gamma_S^{\mathrm{LW}})^{1/2} - (\gamma_L^{\mathrm{LW}})^{1/2}]^2 + 2(\gamma_S^+ \gamma_S^-)^{1/2} + (\gamma_L^+ \gamma_L^-)^{1/2}$$

$$- (\gamma_S^+ \gamma_L^-)^{1/2} - (\gamma_S^- \gamma_L^+)^{1/2}] \tag{5}$$

To solve Eq. (5) for γ_{SL}, containing three unknown terms, γ_S^{LW}, γ_S^+, and γ_S^-, we need the relations obtained with the aid of contact angle measurements. The formation of the SL interface at the cost of the *SV* and *LV* interfaces according to the Young-Dupré equation as

$$-(1 + \cos\theta)\gamma_L = \Delta G_{SL}^{\mathrm{tot}} \tag{6}$$

and taking into account that

$$\Delta G_{SL}^{\mathrm{tot}} = \Delta G_{SL}^{\mathrm{LW}} + \Delta G_{SL}^{\mathrm{AB}} \tag{7}$$

the total solid-liquid free energy of interaction may be obtained from the following expression:

$$(1 + \cos\theta)\gamma_L = -\Delta G_{SL}^{\mathrm{LW}} - \Delta G_{SL}^{\mathrm{AB}}$$

$$= 2[(\gamma_S^{\mathrm{LW}} \gamma_L^{\mathrm{LW}})^{1/2} + (\gamma_S^+ \gamma_L^-)^{1/2} + (\gamma_S^- \gamma_L^+)^{1/2}] \tag{8}$$

Thus, from contact angle measurements with three liquids of which two are polar with known γ_L^{LW}, γ_L^+ and γ_L^- values and one apolar (for which $\gamma_L = \gamma_L^{\mathrm{LW}}$) and using Eq. (8) three times, the γ_S^{LW}, γ_S^+, and γ_S^- of LB films were determined. Introducing these values into Eq. (5), the interfacial solid-water tensions, γ_{SW}, were calculated.

The calculated γ_S^{LW}, γ_S^+ and γ_S^- values make possible the determination of the total solid-liquid free energies of interaction between the monolayers and water ($\Delta G_{SW}^{\mathrm{tot}}$) from Eq. (8), as well as their Lifshitz-van der Waals ($\Delta G_{SW}^{\mathrm{LW}}$) and acid-base components ($\Delta G_{SW}^{\mathrm{AB}}$) from

$$\Delta G_{SW}^{\mathrm{LW}} = -2(\gamma_S^{\mathrm{LW}}\gamma_W^{L})^{1/2} \tag{9}$$

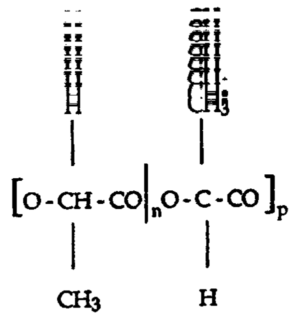
$$\Delta G_{SW}^{\mathrm{AB}} = -2[(\gamma_S^{+}\gamma_W^{-})^{1/2} - (\gamma_S^{-}\gamma_W^{+})^{1/2}] \tag{10}$$

where γ_W^{LW}, γ_W^{+} and γ_W^{-} refer to Lifshitz-van der Waals electron acceptor and electron donor components of water surface tension, respectively.

The reference liquids used for the contact angle measurements are presented in Table I.

MONOLAYERS OF POLY (D, L-LACTIC ACID) SPREAD AT THE AIR-WATER INTERFACE

Poly (D, L-lactic acid) monolayers were spread from various solvents in which the polymer was dissolved at 5 g/l concentration [56]. The polymer material was spread on the aqueous substrate over the maximum available area (780 cm^2) by means of a micropipette. The polymer used was purchased from Boehringer Ingelheim (Germany), with a molecular weight of 25000 and a polydispersity of 2.14. The polymer structure is:



$$\left[\mathrm{O}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{H}-\mathrm{CO}\right]_n\left[\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CO}\right]_p$$

PLAX (x = 100n/n+p)

where χ is the percentage of L repeating units in the polymer chain.

The organic solvents were allowed to evaporate for at least 15 min. before film compression. The compression-expansion cycling of spread polymer films was performed on a Langmuir type film balance (MCN Lauda, Germany), by first compressing a monolayer to a pressure below its collapse pressure and then after a 5-min. hold by decompressing

TABLE I Surface tensions and their components (in mJ/m^2) of reference liquids used for contact angle measurements on LB films

liquid	γ_L	γ_L^{LW}	γ_L^{AB}	γ_L^+	γ_L^-	*Ref.*
water	72.8	21.8	51.0	25.5	25.5	58
ethylene glycol	48.0	29.0	19.0	1.92	47.0	58
diiodomethane	50.8	50.8	0	0	0	59
α-bromonaphthalene	44.4	44.4	0	0	0	59

the film to the initial available area and again by compressing it at the same rate at which the first compression was done (34.5 cm^2/min).

The polymer monolayers were transferred from the air-water interface to hydrophilic glass slides using the conventional Langmuir-Blodgett (LB) vertical dipping method at a constant dipping speed of 3 mm/min, and at constant monolayer pressure corresponding to the polymer area of 125 m^2/g. All these experiments have been described in detail in a previously published work [56].

The contact angles on LB films were measureed using an automatic contact angle meter which assured a powerful user-independent image analysis of a liquid drop profile.

The surface pressure (π), surface area (A) isotherm of the films spread from acetone and chloroform are reproduced in Figure 1. A marked difference in the contour between these two isotherms is evident. While the monolayer spread from chloroform was characteristic of an expanded type π-A isotherm, that of acetone was rather of the condensed type.

Analysis of possible reasons that produced this dramatic difference in their spreading behavior was made through the determination of surface energetic parameters on the LB films sampled from these monolayers and by comparing the magnitude of the hysteresis exhibited by these monolayers on their expansion. The data summarized in Table II and those represented in Figure 2 served as a basis for interpreting these differences in behavior.

The most striking observation that may be made when comparing the data in Table II was that for LB films spread from both acetone and chloroform the ΔG_{SW}^{LW} values were essentially the same. This was not surprising since the polymer in both case was the same. However, a notable characteristic of a polymer which strongly interacts with

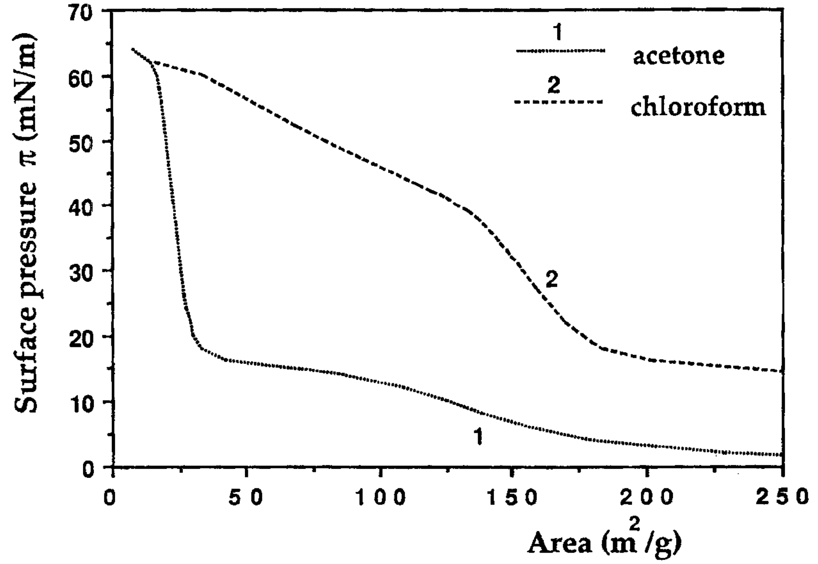


FIGURE 1 Surface pressure (π)-area (A) isotherms of poly (D, L-lactic acid) monolayers spread from acetone and chloroform at the air/water interface.

TABLE II Lifshitz-van der Waals (γ_S^{LW}), electron-acceptor (γ_S^+) and electron-donor (γ_S^-) components of the free energies of poly (D, L-lactic acid) LB films (in mJ/m^2)

Spreading solvent	$\theta°_{H_2O}$	γ_S^{LW}	γ_S^+	γ_S^-	γ_{SW}	ΔG_{SW}^{LW}	ΔG_{SW}^{AB}	ΔG_{SW}^{TOT}
acetone	41	36.0	0.1	44.9	−13.7	−56.0	−71.5	−127.5
chloroform	62	36.6	0	20.5	7.2	−56.5	−45.7	−102.2

water is that its ΔG_{SW}^{AB} values are large and negative [56]. Evidently, poly (D, L-lactic acid) reorients in contact with the water phase differently depending on the type and on the strength of inter-and intra-molecular interactions operating between polymer chains. Thus, if ΔG_{SW}^{TOT}, which is negative, has a large enough magnitude, γ_{SW} will also be negative [56]. Such negative values of γ_{SW} are characteristic of LB film sampled from the monolayers spread from acetone ($\gamma_{SW} = 13.7$ mJ/m^2) but not of those spread from chloroform (7.2 mJ/m^2).

Although both films exhibited monopolar base behavior ($\gamma_S^+ \approx 0$) the γ_S^- value of the films spread form acetone was almost twice as high

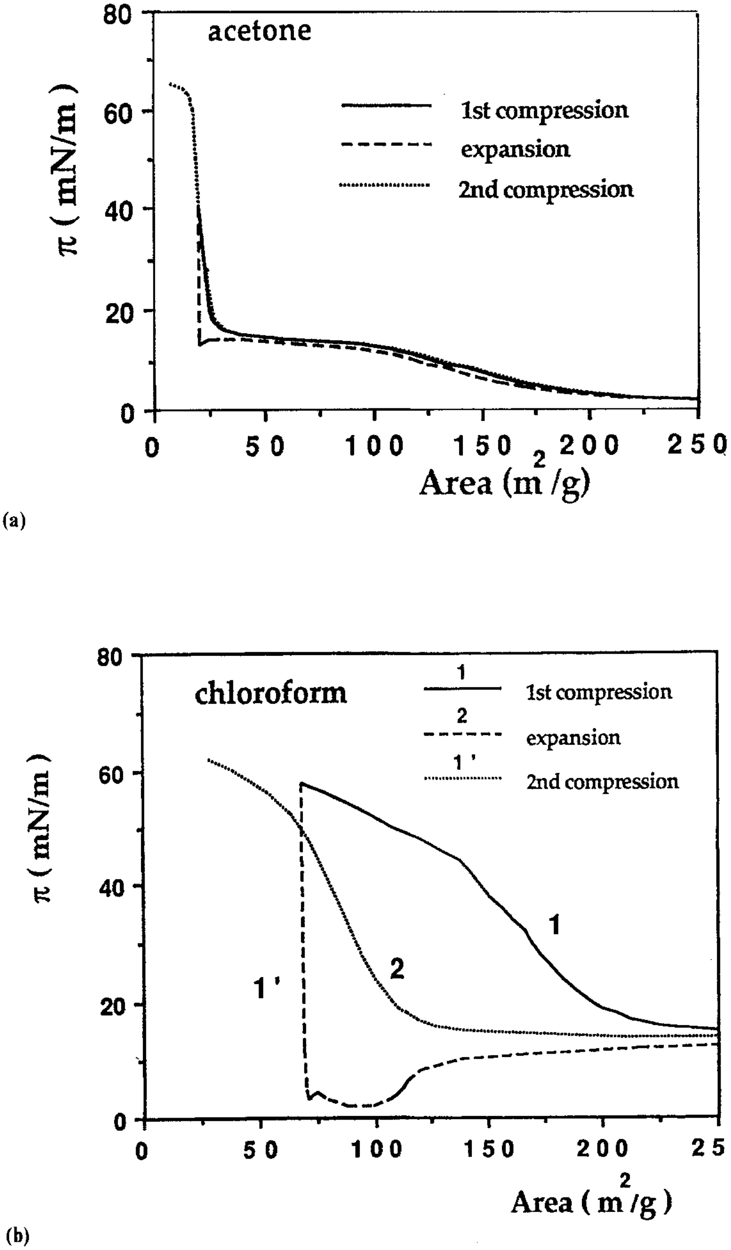


FIGURE 2 Compression/expansion cycles of poly (D, L-lactic acid) monolayers. Influence of the spreading solvent: acetone in Figure 2 (a); chloroform in Figure 2 (b).

as that sampled from monolayers spread from chloroform. This, in turn, yielded for the monolayer spread from acetone a greater interaction across the interface with water ($\Delta G_{SW}^{\text{TOT}} = -127.5$ mJ/m^2) than for the monolayer spread from chloroform ($\Delta G_{SW}^{\text{TOT}} = -102.2$ mJ/m^2). In both cases, these energies were higher than the cohesive energy of the polymer (roughly $2\gamma_S \approx 81.5$ mJ/m^2, from Eq. (1).

Differences in the polymer conformation induced by the spreading solvent are perfectly illustrated by the differences in their compression-decompression behavior (Fig. 2). Whereas the monolayer spread from acetone exhibited virtually reversible collapse behavior with practically no hysteresis, that spread from chloroform decompressed with the appearance of a pronounced hysteresis which was attributable to strong interaction or coagulation which would prevent respreading.

All these considerations led to the conclusion that the existence of strong adhesion of acetone-spread monolayers with the water subphase results from the intense hydrophobic polymer intersegment interactions, which would hinder turning of lactic units from inward to the bulk phase to outward orientation. This explained the contact angle on the acetone-spread LB film being lower than on the chloroform-spread one and accounted for the impossibility of the LB sampling of the former on the hydrophobicized glass slides.

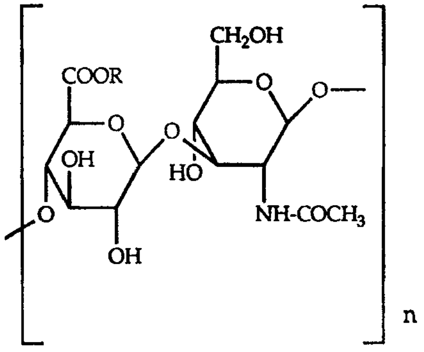
Surface pressure, viscosity and contact angle measurements unequivocally evidenced that spreading of poly (D, L lactic acid) from a good solvent (chloroform, ethyl acetate or dichloromethane) favored the deployment of polymer chains from their coiled structure in solution to the unfolded structure which resulted in high surface pressures, irreversible collapse and relatively low adhesion to the water subphase. Conversely, spreading from a poor solvent (acetone, tetrahydrofuran) enhanced strong intersegment interaction, which gave rise to the formation of microdomains capable of respreading and exhibited strong adhesion to the water subphase *via* the important electron donor (γ_S^-) contribution to Lewis acid-base interactions.

As already described in the section concerning polymer monolayers, in a good solvent the perturbed chain dimension along the direction parallel to the film surface would be larger than that in a three-dimensional coil. Consequently, polymer chain expansion would take place.

Such differences in a monolayer behavior, in terms of differences of the spatial orientation and conformation of polymer side groups, have recently been observed also for monolayers of poly (methyl methacrylate) and were interpreted to be a result of competing forces exerted on the polymer ester groups by the interfaces, the solvent and the surrounding segments in the monolayer [61].

MONOLAYERS OF HYALURONIC ACID DERIVATIVES

Hyaluronic acid (HA) is an unbranched polysaccharide made up of a basic repeating unit composed of alternating moieties of D-glucuronic acid and *N*-acetyl glucosamine linked by a *β*-1-3 glucosidic bond. Polymers used in this work were ethyl and benzyl esters of the acid. They were kindly provided by Fidia Research Laboratories at Abano Terme (Italy). Their degree of esterification corresponded to 100% and they are codified HYAFF 7 (for ethyl ester) and HYAFF 11 (for benzyl ester). The structure is:



$R = C_2H_5$ or C_6H_6

Structure of HA derivatives

where R is C_2H_5(HYAFF 7) or C_6H_6(HYAFF 11)

The molecular weight of the polymers as determined by the gas permeation chromatography method was 130,000 Da ± 15% with a polydispersity ($Mw/Mn = 2$) that the process of esterification did not significantly alter [62]. Hyaluronic esters were characterized by thermal analysis and solubility tests [62] and in the form of cast films by means of contact angle measurements, XPS and ATR/FR-IR spectroscopies, SEM, wide angle X-ray scattering (WAKS) and thermogravimetric analysis (TGA) [53].

HYAFF 7 and HYAFF 11 were dissolved in dimethyl sulfoxide (DMSO) at 3 mg. ml^{-1} concentration, and spread on the aqueous subphase of autorecording Langmuir-type film balance (MCN Lauda, Germany) over the maximum available area (780 cm^2) by means of a micropipette. Monolayers were left for about 15 min. before measurement. Surface pressure (π)-area (A) isotherms were recorded at 23°C at a constant rate (30 cm^2. $min.^{-1}$ which equals to 2 cm. $min.^{-1}$). Hysteresis cycles were obtained by first compressing the films followed by decompressing them and by successive compressions between two fixed areas. The reported surface pressure-area isotherms are mean contours from at least four isotherms. The results were reproductible within experimental error which did not exceed ± 3% of the mean.

A vertical phase Langmuir-Blodgett technique was used to transfer spread films from the water surface to hydrophilic glass slides (2 cm × 3 cm) freshly cleaned with sulfochromic acid and abundantly rinsed with ultra pure water (Millipore appratus) and then dried in an oven. The transfer was realized with a single upward stroke of the slide and at a constant rate of 3 mm. min^{-1} under a constant surface pressure (10 mN/m), *i.e.* the compressing barrier was automatically moved so that the pressure remained constant. In contrast to the sampling of poly (lactic acid) monolayers which was done at a given constant area, the sampling of derivatives of hyaluronic acid was performed at a constant pressure. In the latter case the polymers differ in the chemical composition and only the LB transfer at a constant pressure enables their characterization in comparable conditions.

Contact angles on these transferred films were measured with the reference liquids. Alpha-bromonaphthalene instead of diiodomethane was used as an apolar liquid, as the latter appeared to interact with the polymer monolayer. The angles were recorded with a Kruss G40 automatic contact angle meter, using independent image analysis of a liquid drop. Average drop volume in these measurements was 15 μl and the measuring accuracy for angles higher than 30°C was ± 1° and for angles lower than 30° was ± 2°.

Figure 3 shows the surface pressure-area curves for the ethyl and benzyl ester derivatives of hyaluronic acid. Clearly, there is a difference in behavior between these two monolayers.

The lateral compressibility data, τ, of the monolayers, calculated for each π/A isotherm from: $\tau = -1 dA/A\, d\Pi$, provide a certain insight in this regard (Fig. 4). Although both HYAFF 7 and HYAFF 11 films are incompressible, the ethyl derivative's compressibility appears to be higher compared with that of the benzyl ester, indicating possible rearrangements of the ethyl derivative segments of hyaluronic acid on compression.

What is not clear is why HYAFF 7 displays higher pressures than HYAFF 11 and why its adhesion to the aqueous substrate is lower than that of HYAFF 11 at large areas. The wettabilities of the LB films sampled from these monolayers lead one to derive certain inferences regarding the interfacial adhesion of these LB films.

The analysis of the data reported in Table III would suggest that HYAFF 11 is more hydrophobic than HYAFF 7. This appears to be quite surprising as one would expect benzyl groups to be less hydro-

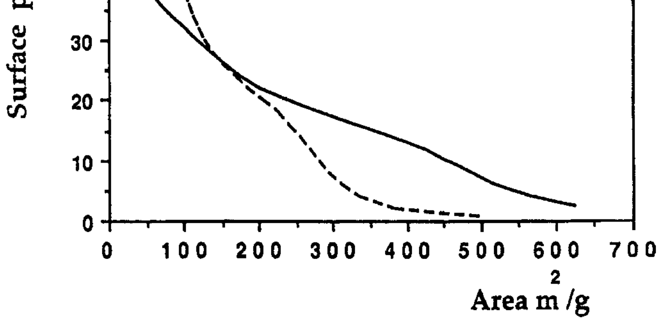


FIGURE 3 Surface pressure (π)-area (A) isotherms of hyaluronic acid derivative monolayers.

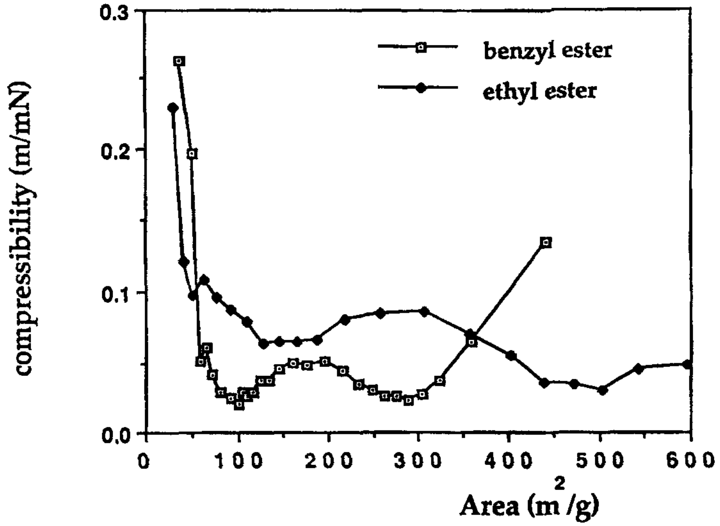


FIGURE 4 Compressibility *vs* area curves of hyaluronic acid derivative monolayers.

TABLE III Advancing contact angles ($\theta°$) on HYAFF 7 and HYAFF 11 LB films

	water	*ethylene glycol*	*α-bromonaphtalene*
HYAFF 7	60	33	32
HYAFF 11	71	34	24

phobic than ethyl ones. However, the calculated thermodynamic quantities using the van Oss-Chaudhury-Good approach throw a new light on the problem.

In Table IV are presented the calculated Lifshitz-van-der-Waals (γ_S^{LW}) electron acceptor (γ_S^+) and electron donor (γ_S^-) components together with interfacial free energies (ΔG_{SW}) of HYAFF 7 and HYAFF 11 LB films with water.

From the data recorded in Table IV it is apparent that whereas for HYAFF 11 γ_S^{LW}, as expected, is higher than for HYAFF 7, *i.e.*, that HYAFF 11 is more hydrophilic than HYAFF 7, the γ_S^{AB} and ΔG_{SW}^{AB} values are higher for HYAFF 7. Based on the criterion that acid-base free energy of interaction acts as a driving force in adhesion pro-

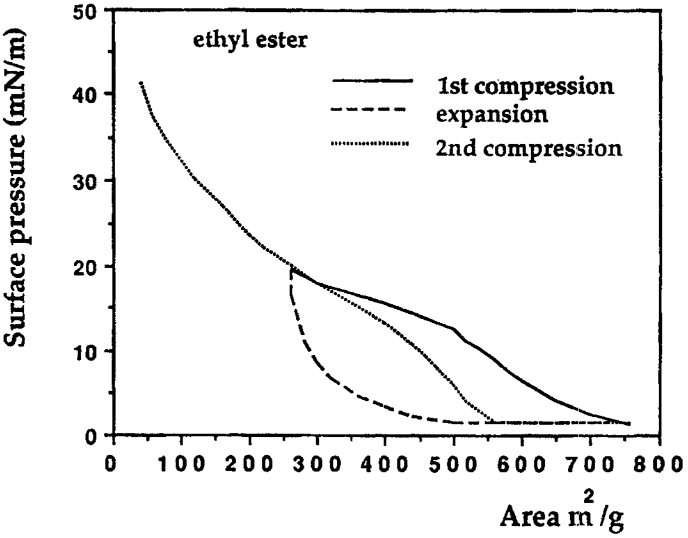
TABLE IV Lifshitz-van der Waals (γ_S^{LW}), electron-acceptor (γ_S^+) and electron-donor (γ_S^-) components of the free energies of ethyl and benzyl derivatives of hyaluronic acid LB films (in mJ/m^2)

LB films	γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	ΔG_{SW}^{LW}	ΔG_{SW}^{AB}	$\Delta G_{SW}^{LW}/\Delta G_{SW}^{AB}$
HYAFF 7	37.7	0.5	19.9	6.3	−57.3	−52.4	1.1
HYAFF 11	40.8	0.7	7.9	4.7	−59.6	−35.9	1.6

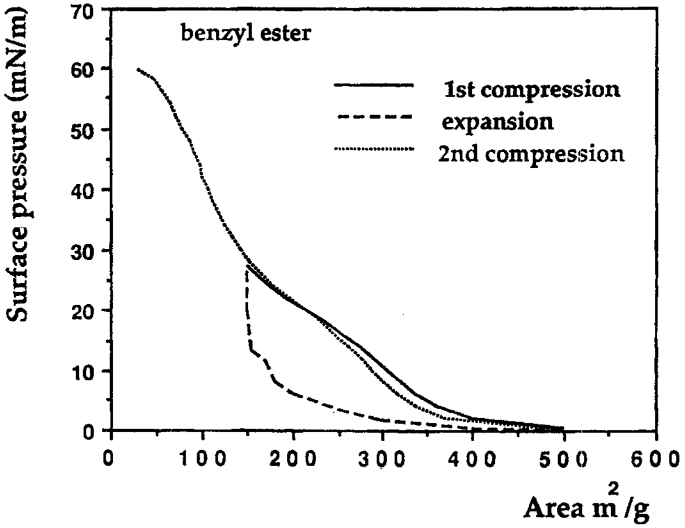
cesses [60], one would expect adhesion of HYAFF 7 to the water subphase to be favored. However, the reverse effect (Fig. 3) is observed and HYAFF 7 displays lower adhesion to water within surface areas ranging from 150 to 600 m^2/g. All seems to indicate that the energy balance, as expressed by the ratio of $\Delta G_{SW}^{LW}/\Delta G_{SW}^{AB}$, plays an important role in adhesion of the films to water. As previously suggested for processes of adsorption of proteins from aqueous solutions onto polymer solid films [63], a higher $\Delta G_{SW}^{LW}/\Delta G_{SW}^{AB}$ ratio would favor polymer film adhesion to the aqueous phase.

This analysis lends less support to the occurence of increased surface pressure on further compression of HYAFF monolayers. The surface pressure of HYAFF 7 film monotonically increases over the whole range of areas. This would be indicative of the occurence of intersegment interactions between ethyl groups in polymer segments localized in highly concentrated domains. At areas smaller than 150 m^2/g HYAFF 11 exhibits surface pressures higher than HYAFF 7. What might possibly occur is that benzyl groups of HYAFF 11 are forced to positions oriented outward to the air phase.

The evidence for highly cohesive structures produced on compression of HYAFF 7 film is indirectly reinforced by compression-expansion cycles depicted in Figure 5. Thus, if HYAFF 7 exhibits a considerable hysteresis, respreading over the whole available area of the trough on decompression of the film occurs only with HYAFF 11. This leads us to believe that the intersegment interactions in which benzyl groups are involved are not enough strong to prevent totally the redeployment of the polymer at the air/water interface after its decompression. A reverse trend is observed for the ethyl ester derivative (HYAFF 7) of hyaluronic acid. Like the monolayers of poly (D, L-lactic acid) spread from good solvents (chloroform for example),



(a)



(b)

FIGURE 5 Compression/expansion cycles of hyaluronic acid derivative monolayers. Influence of the chemical group substituted on glucuronic acid moieties of the polymer: ethyl ester in Figure 5 (a); benzyl ester in Figure 5 (b).

HYAFF 7 films exhibit only a partial redeployment of the polymer as documented by an important hysteresis between the curves of the first and the second compression.

It may be inferred from this work that the van Oss-Chaudhury-Good approach makes it possible to predict the strength of adhesion of polymer monolayers toward the aqueous subphase by measurement and analysis of contact angle data on LB films transferred from these monolayers.

Dedication

One of us (A.B.) is graceful to Dr. Robert J. Good for his continuous interest in the author's research and for its theoretical contribution to the understanding of intermolecular forces involved in adhesion processes that made possible the interpretation of the results reported in this paper.

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