

ELASTICITY OF MONOLAYER OF LINOLEIC ACID AND ITS POLYMER*

HE Pingsheng (何平笙)

(*Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China*)

PELTONEN J.P.K. and ROSENHOLM J.B.

(*Department of Physical Chemistry, Abo Akademi University, Abo, Finland*)

Abstract The dynamic elasticity of linoleic acid monolayer on a subphase of 10^{-4} mol/L TbCl_3 at various surface pressure has been measured by means of dynamic oscillation method in measuring the change of surface pressure caused by periodic compression-expansion cycles of the barrier. The elasticity of monolayer increases with increasing of surface pressure linearly. The linoleic acid polymer monolayer has been obtained under UV-irradiation in situ when keeping a constant surface pressure. But the elasticity of the resulting polymerized monolayer is even smaller than that of its corresponding monomer monolayer. The elasticity of the polymerized linoleic acid monolayer decreases with increasing polymerization time. The explanation based on entropy has been presented.

Keywords Elasticity, Monolayer, Linoleic acid

INTRODUCTION

The mechanical properties of materials are of importance for application purposes. The materials without certain strength are useless. It is also true for monolayer and Langmuir-Blodgett (LB) films^[1]. Due to the difficulty of measurement, there are comparatively few reports concerning mechanical properties of monolayer and LB films^[2,3]. To our knowledge, there is no report concerning elasticity comparison of monomer monolayer with its resulting polymerized monolayer. In this paper a dynamic oscillation method was used to measure the elasticity of linoleic acid monolayer on a subphase of 10^{-4} mol/L TbCl_3 , and its resulting polymer monolayer polymerized in situ under UV-irradiation.

The elasticity of a monolayer, $E = \delta\pi/(\delta A/A)$ (where π is the surface pressure and A the surface area covered by monolayer), is generally determined from the

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slope of surface pressure-area isotherm. The dynamic method measures the elasticity directly by determining the changes in surface pressure caused by sinusoidal compression-expansion cycles with small amplitude. M. Blank et al.^[4] has used this method to measure the elasticity of protein monolayers.

Dynamic properties of monolayer are more close to the practical use than the "equilibrium" compression isotherm to such systems. Dynamic technique generally provides more information on intermolecular interaction. Additionally, relaxation behavior of monolayer can also be obtained from the difference in phase between the surface pressure changing and the oscillating barrier if the monolayer is viscoelastic.

EXPERIMENTAL

Materials

Linoleic acid of reagent grade was purchased from FLUKA and used without further purification. It was dissolved in *n*-hexane to form solution with a concentration of 1 mg/ml. Until spreading the solution was kept away from the light and stored in a refrigerator. Terbium chloride TbCl_3 was also obtained from the same manufacturer.

Monolayer formation and polymerization

A KSV LB-5000 balance system with Wilhelmy balance was used. The monolayer was obtained by spreading the solution on a subphase of 10^{-4} mol/L TbCl_3 with the water of resistance above 18 $\text{M}\Omega\text{cm}$ purified by Milli-Q system. The polymerization of the monolayer was carried out at a constant surface pressure of 15 mN/m using a 30 W low pressure mercury lamp hanging 15 cm above the monolayer. The Langmuir trough was protected against normal UV-light from space by covering the front window with a yellow semitransparent plastics.

Measurement of elasticity

The dynamic elasticity measurements were performed with the VISCOS mode in KSV LB-5000 which could vary the frequency and amplitude of the barrier movement in a sinusoidal pattern by a special designed program. Waiting for 10 min. after spreading, the barrier was moved forward. When the surface pressure reached the designed value, the computer turned the barrier movement into VISCOS mode automatically, and a periodic compression-expansion cycles started. The change of surface pressure caused by the periodic barrier movement was recorded by the computer. All measurements were performed under a constant temperature of $20 \pm 0.3^\circ\text{C}$.

RESULTS AND DISCUSSION

Isotherm of linoleic acid monolayer

The surface pressure-area isotherms of linoleic acid monolayer on the subphase of 10^{-4} mol/L TbCl_3 are shown in Fig. 1. Due to the presence of *cis* form in double bond in linoleic acid and it is in the middle position instead of the end of the chain, the molecular configuration makes them impossible to be arranged tightly on the water surface. The compression isotherm rises slowly and the collapse pressure is reached at the mean molecular area which is far away from the area should be occupied by one- CH_2 group, indicating that linoleic acid molecules in monolayer occupy a relatively large area even in the case of their possible tight arrangement, there are enough spaces between the molecules for their further closing, and the intermolecular force is not so strong.

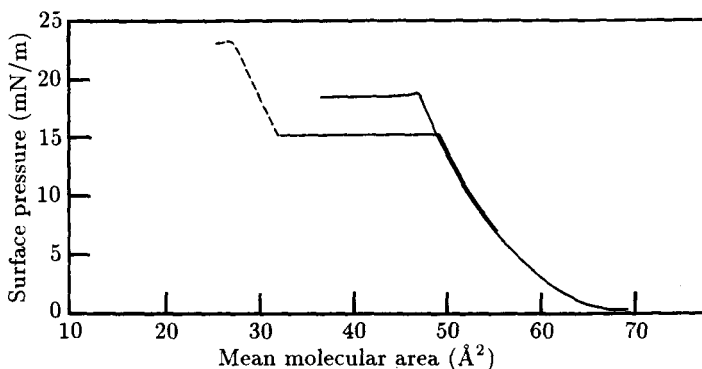


Fig. 1 The surface pressure-area isotherms of linoleic acid monolayer on a subphase of 10^{-4} mol/L TbCl_3 , 20°C . The dotted line is that after 100 min. UV-irradiation

Elasticity of linoleic acid monolayer

The experimental curve of surface pressure oscillation of linoleic acid monolayer on a subphase of 10^{-4} mol/L TbCl_3 caused by periodic compression-expansion cycles at a surface pressure of 10 mN/m with the frequency of 40 mHz and amplitude of 1.5 mm is shown in Fig. 2. The VISCOS mode in KSV LB-5000 is a specially designed program to measure the elasticity of monolayer on liquid surface. The amplitude of barrier oscillation can be changed from 0.1 mm to any value principally. Although the larger amplitude is, the more change of surface pressure is, the large amplitude will be favor for the measurement. However, if the amplitude is too large, the result will be incorrect for the points where the phase transitions occur. The amplitude of 1~2 mm would be suitable for most experiments. The oscillation frequency in VISCOS mode is between 0.1 mHz and 150 mHz. At lower frequency

the gradual change in surface pressure with time is considerable with respect to the periodic change, and higher frequency is not allowed for the movement of mechanical device like the barrier in Langmuir trough. In the range of frequency and amplitude mentioned above the results is no measurable change. All experiments were performed at a frequency of 40 mHz and amplitude of 1.5 mm.

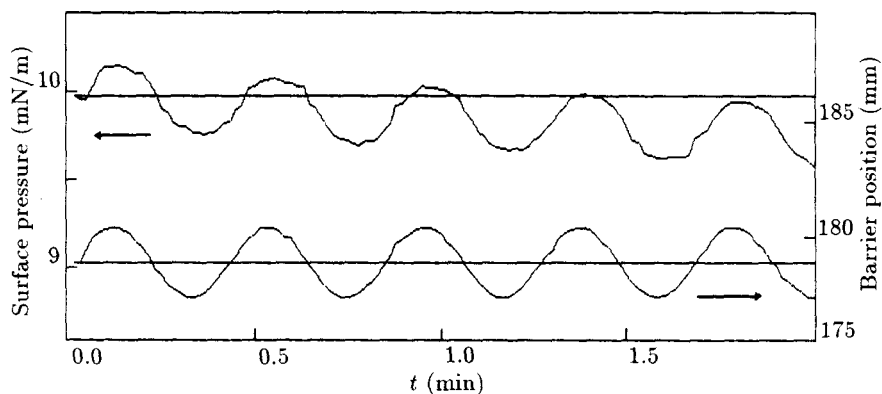


Fig. 2 The oscillation of surface pressure of linoleic acid monolayer caused by periodic compression-expansion cycles of barrier around surface pressure of 10 mN/m

The elasticity of linoleic acid monolayer increases from 36 to 106 mN/m when the surface pressure increases from 2 to 17 mN/m linearly. The fact that the elasticity increases with increasing surface pressure is in agreement with its pressure-area isotherm from which the elasticity is obtained usually. Actually, the elasticity-surface pressure curve is the differential form of the change of surface pressure during compression and would be better to response to the surface state of the monolayer than its integral form of pressure-area isotherm. The linear relationship between elasticity and surface pressure implies that the intermolecular interaction in linoleic acid monolayer increases gradually and no jump at all when compression. Therefore, there is no phase transition in the monolayer during compression process in the measured range of surface pressure, not like stearic acid monolayer which has phase transitions and shows peaks in its elasticity-surface pressure curve^[5].

Polymerization of linoleic acid monolayer

There were many reports about the polymerization of unsaturated fatty acid derivations which usually had double bond(s) in the end position of the molecular chain. It was thought generally that the unsaturated fatty acids with double bond(s) in their middle position of chain would be difficult to polymerize. But the polymerization of monolayer of linoleic acid with the double bonds in its 9, 12-positions in the chain has been carried out successfully^[6].

The polymerization of monolayer was performed in KINETIC mode in KSV LB-5000. The linoleic acid monolayer on a subphase of 10^{-4} mol/L TbCl_3 was compressed to a surface pressure of 15 mN/m which was kept constant throughout the whole experiment. The polymerization was started after 10 min. Stabilization period which was enough to minimize the barrier speed regulating the surface pressure.

Switching on the UV-light, the barrier moved forward due to the contraction of area occupied by molecules arising from the changing of Van der Waals' distances into chemical bonds. The barrier speed and mean molecular area were used to monitor the polymerization kinetics. The typical polymerization kinetic curve is shown in Fig. 4. The following facts indicated the polymerization of linoleic acid monolayer has occurred indeed on the subphase surface: firstly, the barrier speed increased to a clear maximum

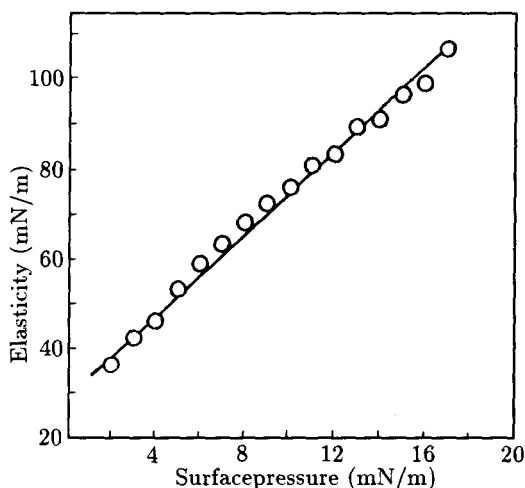


Fig. 3 The dependence of elasticities of linoleic acid monolayer on surface pressure

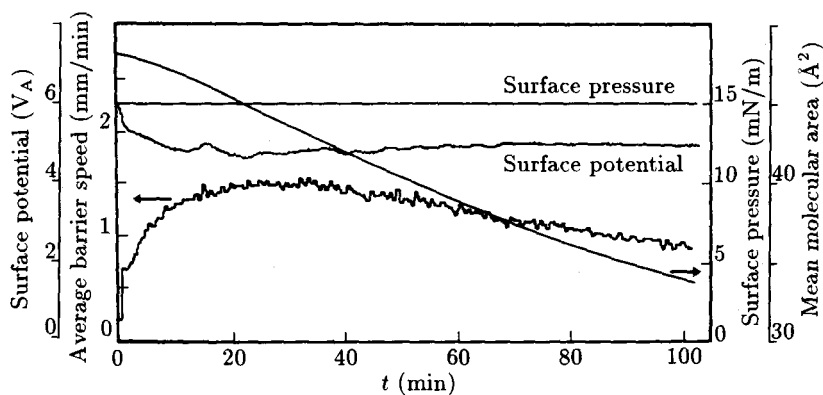


Fig. 4 The kinetic curves of the barrier speed and mean molecular area of a linoleic acid monolayer on a subphase of 10^{-4} mol/L TbCl_3 under a constant surface pressure of 15 mN/m and UV-irradiation.

The zero-time corresponds to the switching on of UV-light. The surface potential is also shown as a function of UV-irradiation time.

when irradiating the monolayer with UV-light (see Fig. 4); secondly, as the monolayer compression was continued after the irradiation, a collapse pressure of 22 mN/m

was reached. That is clearly higher than that of monomer monolayer of 18 mN/m (also see Fig. 1, the dotted line); finally, after a 100 min. polymerization, by sweeping the surface carefully, a milk-white solid residue was collected. A typical amorphous resin-like material could be observed by optical microscopy. However, the monomer *cis*-9, 12-linoleic acid with the melting point between $-1 \sim -5^{\circ}\text{C}$ is a liquid at the test temperature.

Attempt to measure the molecular weight of the polymer product by GPC failed because it did not dissolve in the GPC solvent tetrahydrofuran (and other ordinary solvents) during a period as long as 3 months. However, the insolubility of the product implies the cross-linking structure of the polymer.

Elasticity of polymerized linoleic acid monolayer

The linoleic acid monolayer on the subphase of 10^{-4} mol/L TbCl_3 was compressed until the surface pressure of 15 mN/m was attained and kept it constant under UV-irradiation. After 100 min. UV-irradiation the polymerization was almost completed, then elasticity measurement of the resulting polymerized linoleic acid monolayer was followed. Surprisingly, elasticity of the resulting polymerized monolayer is only 40.4 mN/m which is lower than that of its monomer monolayer of 96.3 mN/m. This fact can also be seen in Fig. 1 in which surface pressure-area isotherm (dotted curve) of 100 min. UV-irradiated monolayer rises slightly slower than that of unirradiated monolayer, indicating that the change of surface pressure caused by changing area will be smaller and the elasticity is smaller.

During polymerization, the volume contraction will occur, because the monomer molecules which are in a Van der Waals' distance become combined with each other by chemical bonds. In the case of monolayer the surface area occupied by film-forming compound will contract and monomer molecules will come closer each other. Linoleic acid monolayer on subphase of 10^{-4} mol/L TbCl_3 had its mean molecular area (MMA) of 0.48 nm^2 at constant surface pressure of 15 mN/m. The MMA was getting smaller under UV-irradiation and reduced to about 0.33 nm^2 after 100 min. UV-irradiation.

Under UV-irradiation the linoleic acid monomer molecules are excited and reacted each other, the molecules located at a Van der Waals' distance from one another move to within a covalent distance, which lead to the reduction of the area covered by monolayer. The point is that some linoleic acid monomer molecules have turned into macromolecules, while the unreacted molecules are still located in Van der Waal's distance, and the distances between resulting macromolecules are still in Van der Walls' distance. Nevertheless, when the MW of macromolecules is large

enough the entropy will play a more important role in the mechanical properties. The macromolecules of polymerized linoleic acid can vary their conformation instead of changing bond length and bond angle to suit the change of applied force in compression-expansion cycles of barrier. The elasticity should be lower than that of monomer monolayer with molecules arranged very regularly. The surface potential has almost no change during polymerization (also see Fig.4), indicating that the arrangement of polymerized linoleic acid monolayer is not, at least, so tighter than that of its monomer in the monolayer.

In order to proof the above idea, experiments with different UV-irradiation time were performed. The elasticity of linoleic acid monolayer as a function of polymerization time is shown in the Fig.5. The elasticity decreases with increasing polymerization time. The longer UV-irradiation time is, the more macromolecules are formed, and more important the role of entropy is.

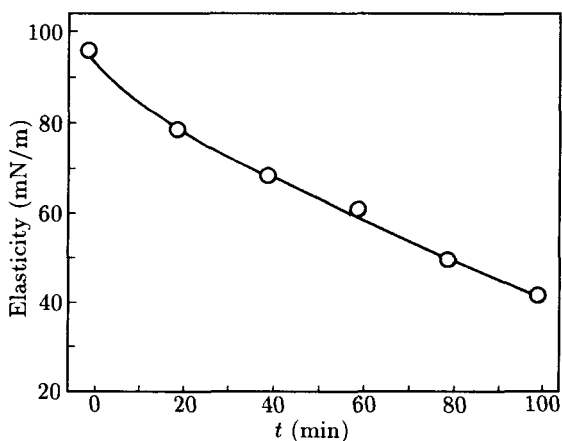


Fig. 5 The elasticities of linoleic acid monolayer as a function of UV-irradiation time

The study of condensed state of polymer is one of the basic problems in polymer physics. In general, there are crystalline and amorphous states in polymer and three mechanical states i.e. glassy, rubbery and viscous flow states for amorphous polymers, which are well known fact. The question is that are there still the same condensed and mechanical states in some special situations of polymers as in normal polymers? The special situations should include single chain macromolecule^[7], two-dimensional molecular film, i.e. polymeric monolayer and LB films^[8], super drawing polymer^[9] and macroscopic single crystal of polymer with 100% degree of crystallinity^[10]. For example. The existence of single-chain glasses or single crystal is a characteristic for flexible chain polymers^[7], and there is no glass transition in the macroscopic single crystal of polydiacethylene with 100% degree of crystallinity^[10].

The elasticity of the polymerized linoleic acid monolayer is lower than its monomer monolayer implies that there may exist a rubbery state in two-dimensional cross-linking monolayer.

The phase angle between the surface pressure oscillation and the compression-expansion cycles was not observed for the polymerized linoleic acid monolayer, which may support the existence of rubbery state in the polymerized linoleic acid monolayer.

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