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Photoinduced Dilatational Motion in Monolayers of Poly(methyl methacrylate) Having Benzospiropyran Side Groups

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ABSTRACT: The photochemical properties of poly(methyl methacrylate) chains having benzospiropyran side groups have been used for the first time to generate longitudinal motion in Langmuir monolayers. Measurements of the associated surface pressure variations at various distances from the photoexcited region demonstrate the viscoelastic behavior of two-dimensional poly(methyl methacrylate) films. The experimental results are in quantitative agreement with a simple theoretical model taking into account the surface viscoelasticity, the viscosity of the liquid substrate, and the rate constant for the photochemical process.

Introduction

Mechanical response of photochromic polymer materials is a subject of considerable biophysical and technological interest.[1] For instance Van der Veen and Prins have shown that thin films of poly(hydroxyethyl methacrylate) doped with an isomerizable dye can contract and expand reversibly upon visible light irradiation.[2] Similarly, Smets and de Blauwe[3] and Eisenbach[4] have studied the mechanical properties of several poly(ethyl acrylate) dry films containing photosensitive cross-links. Working in solutions, Irie and coworkers[5] have measured the photoinduced viscosity change in several polymer systems containing photoisomerizable groups in the main backbone or in the side chains. In the two cases, the photoinduced isomerization of the chromophores induces conformational changes in the polymer chain, which in turn lead to macroscopic variations in the physical and chemical properties of the films and of the polymer solutions. Such a mechanism is also believed to be operating in biological membranes containing photoexcitable proteins, e.g., the rhodopsin and its retinal chromophore in the rod outer segments of the eye.[6] With this in mind, several groups have started to investigate the photochemical response of polymer monolayers spread at the air–water interface. Photochromic azo polyamides have been used by Blair et al.,[7] while Gruler et al.[8] have investigated statistical copolymers of methacrylate with 5.1% of a spiropyran derivative. Following light excitation in the adsorption band of the chromophore, marked increases of the surface pressure were detectable. In the case of spiropyran chromophores, the effect was unambiguously ascribed to a change in the concentration of the chromophore at the air–water interface.[8] In the dark the spiropyran species, which are hydrophobic, tend to stay away from the water. In contrast, the photogenerated merocyanine species, being zwitterionic and highly polar, try to maximize their interaction with the aqueous substrate and penetrate the monolayer to the maximum possible extent. The effect is fully reversible and the surface pressure will return to its initial value with a time constant directly related to the life time of the photogenerated species. This thermal relaxation is usually very slow, on the order of minutes to hours. Much faster relaxation times are possible by using pulsed optical excitation in the adsorption band of the merocyanine.[6]

In all studies so far, the irradiation was spatially homogeneous and therefore the strain associated to the surface density increase did not induce macroscopic mechanical motion along the monolayer. In the present paper, we show how localized pulsed light excitation can be used to generate nonuniform mechanical strains, thus triggering in-plane dilatational motion. Such dilatational motion is detected by the time dependence of the recorded surface pressure at various distances from the excitation zone. We have constructed a simple theoretical model that is in perfect agreement with the experimental results. This photochemical method seems therefore a worthy substitute for the more macroscopic technique in which oscillatory[9,10] or uniform[11] mechanical strain is created by the displacement of a hydrophobic barrier sweeping the interface.

Materials and Methods

The copolymer of methyl methacrylate with 5.1 mol % of a spiropyran derivative (1-(β-(methacryloyloxy)ethyl)-6′-nitro-DIPS) was obtained from G. Smets at the University of Leuven, Belgium, and used as received. It had a molecular weight of 215 000. The DIPS acronym stands for 3,3-dimethylspiro(2*H*-1-benzopyran-2,2′-indoline). Dilute solutions (0.1 mg·cm^{-1}) were prepared in chromatographic grade benzene and controlled volumes were spread on aqueous substrates contained in various types of Teflon Langmuir troughs. The surface density of chains was calculated, assuming a monolayer has been formed, from the trough surface and the total amount of material deposited. The pH of the water was adjusted to be 1.88, by adding 0.01 N HCl, in order to obtain the same conditions as in ref 8. The surface tension was measured by the Wilhelmy method using a thin platinum plate attached to a electromicrobalance (Beckman, LM600) and a chart recorder (Sefram). All experiments were performed at room temperature (22 ± 0.5 °C).

In order to obtain true equilibrium isotherms the monolayer was compressed in a series of small, well-defined steps by using a Teflon barrier. At each new position the time evolution of the surface pressure was recorded until an equilibrium value was observed over several minutes.

The monolayer was irradiated from the top side with a low-power xenon flash gun (Elgawa N128C, DDR). The duration of a single flash was 1.25 ms. A narrow optical bandwidth, centered at 360 ± 35 nm, was selected by using a Schott UV glass filter of 2-mm thickness. This band corresponds to the absorption maximum of the spiropyran moieties.

The study of the mechanical response of the monolayer was carried out in the following way. At first, the dilatational motion was induced by uniform mechanical strain in the absence of

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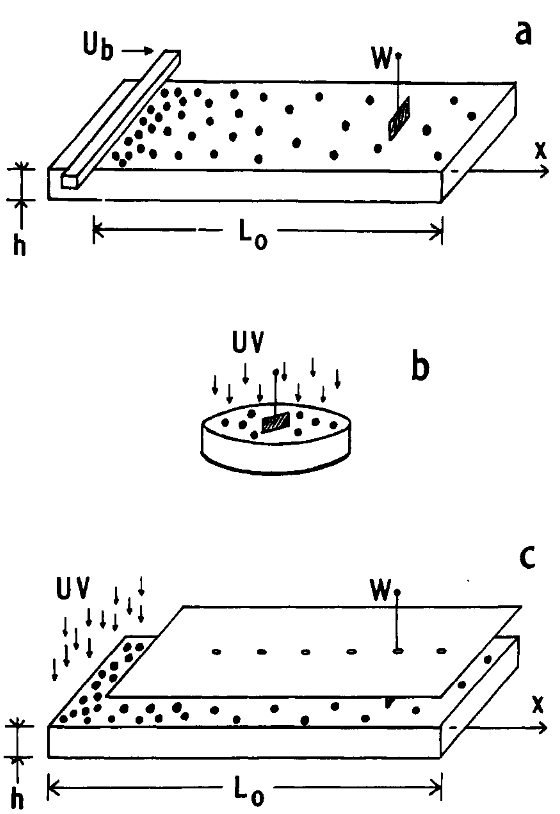

Figure 1. Schematic description of the three experimental setups: W, Wilhelmy plate; L_0, monolayer length; h, thickness of the bulk liquid phase; u_b, barrier velocity; UV, ultraviolet irradiation. For details, see under Materials and Methods.

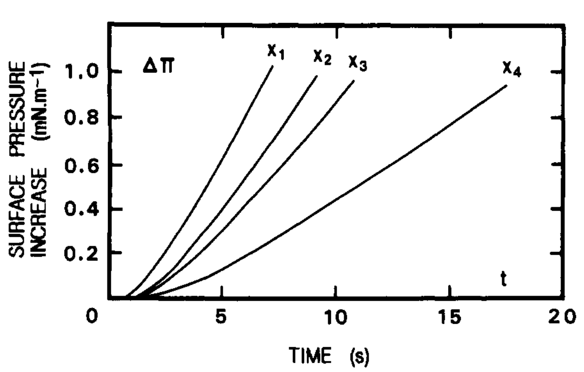

Figure 2. Progressive buildup of the surface pressure, $\Delta\Pi(t)$, as the monolayer of copolymer of methyl methacrylate containing 5.1 mol % of a benzospiropyran derivative is compressed by a mechanical barrier moving at constant velocity $u_b = 0.054$ cm·s^{-1}. The four curves correspond to various distances between the Wilhelmy plate detector and the barrier: $x_1 = 5$ cm; $x_2 = 10$ cm; $x_3 = 15$ cm; $x_4 = 20$ cm. Initial surface pressure Π_0 was 9.75 mN·m^{-1}. Total length of the monolayer was 26.7 cm. $T = 22$ °C; pH = 1.88.

ultraviolet irradiation. In a separate experiment, the kinetics of the photochemical reaction was then measured by using homogeneous illumination of the whole monolayer. Finally, these two experiments were combined to investigate the coupling of the photochemical reaction with the dilatational motion along the monolayer.

Thus, three different measurements were performed:

(i) Mechanical Generation of an Interfacial Dilatational Motion (Figure 1a). The monolayer was spread on an aqueous substrate in a large rectangular Teflon Langmuir trough (40 cm × 10.5 cm × 0.7 cm) and compressed by steps up to an initial equilibrium surface pressure value Π_0. Then, in the dark, a local mechanical stress was applied, by compressing the monolayer with a barrier moving at a constant velocity u_b. This induces a local perturbation of the surface pressure, which propagates along the monolayer. Since the longitudinal motion of the film is accompanied by a simultaneous drag of the liquid substrate, the surface pressure increase $\Delta\Pi$ will not be the same throughout the monolayer. Rather it will depend on the distance x from the moving barrier. The space and time dependence of the change of the surface pressure $\Delta\Pi(x,t)$ was recorded by using a single Wilhelmy plate detector put at various positions x away from the barrier.

(ii) Uniform Photochemical Excitation (Figure 1b). The monolayer was spread on an aqueous substrate in a small cylindrical Teflon dish, 4.8 cm in diameter. The electronic flash was fixed above the monolayer in order to irradiate the air–liquid interface uniformly. A single flash was then fired. The induced surface pressure change ($\Delta\Pi(t)$ was a function of time only and was directly related to the photochemical interfacial reaction kinetics for the chromophores contained in the monolayer. No dilatational interfacial motion was created.

(iii) Localized Photochemical Stress Inducing an Interfacial Dilatational Motion (Figure 1c). The monolayer was spread on an aqueous substrate in a Teflon Langmuir trough (40 cm × 10.5 cm × 0.7 cm) and compressed by steps up to a preset value Π_0 of the surface pressure. A small rectangular area (10.5 cm × 2 cm) of the trough was then irradiated by a single flash of light. The photochemical stress following the irradiation pulse induces a perturbation of the local surface pressure, which propagates along the monolayer. The surface pressure changes $\Delta\Pi(x,t)$ were measured by positioning a Wilhelmy plate at various distances from the irradiated zone. The plate orientation was along the y axis, perpendicular to the direction of propagation of the dilatational wave.

Results

(i) Uniform Mechanical Compression. The change in the local surface pressure $\Delta\Pi(x,t)$ following compression of the monolayer by a mechanical barrier moving at constant velocity u_b has been recorded as a function of time, t, and the distance, x, to the barrier. A typical set of data is shown in Figure 2, corresponding to four positions of the surface pressure detector. The surface pressure rises monotonously in all cases, following an initial time lag, which increases as the detector is moved farther away from the barrier. It has been shown in other systems that this time delay is related to the viscous dissipation in the subphase. At longer times a gradual increase in the local surface pressure is observed. The variation is almost linear, with a characteristic slope that becomes smaller as x increases. This difference in slopes is characteristic of viscoelastic behavior within the monolayer.[11b] Part of the mechanical energy gets dissipated by internal relaxation processes before it can contribute to the increase in surface pressure at the detector level. In contrast, if the monolayer had a purely elastic behavior, the slope would be independent of the detector position.[11a]

(ii) Variation of the Surface Pressure Induced by Homogeneous Ultraviolet Light Excitation of the Whole Monolayer. The time dependence of the change in surface pressure $\Delta\Pi(t)$ following uniform illumination of the whole monolayer by a single flash of ultraviolet light is shown in Figure 3. The surface pressure increases immediately after the 1.25-ms-long light pulse and reaches its asymptotic value in a matter of seconds. We have checked that the measured pressure changes are indeed independent of the detector position within the monolayer. Since the initial surface pressure was 9.75 mN·m^{-1}, the relative pressure change in the case shown is of the order of 4%. This value depends on the actual irradiation light intensity and on the number of excitable chromophores. The basic photochemical process is described in Figure 4. Absorption of light at 350 nm by spirobenzopyran molecules leads to bond breaking between the carbon and the oxygen atoms followed by a marked mo-

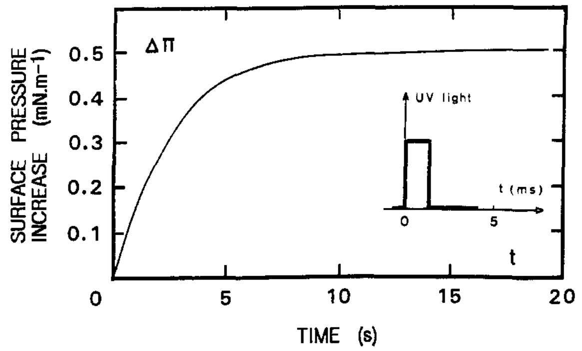

Figure 3. Progressive buildup of the monolayer surface pressure, $\Delta\Pi(t)$, following pulse light excitation over its whole surface with ultraviolet light at 350 nm. The monolayer is formed with a copolymer of methyl methacrylate containing 5.1 mol % of a benzospiropyran derivative. T = 22 °C; pH = 1.88.

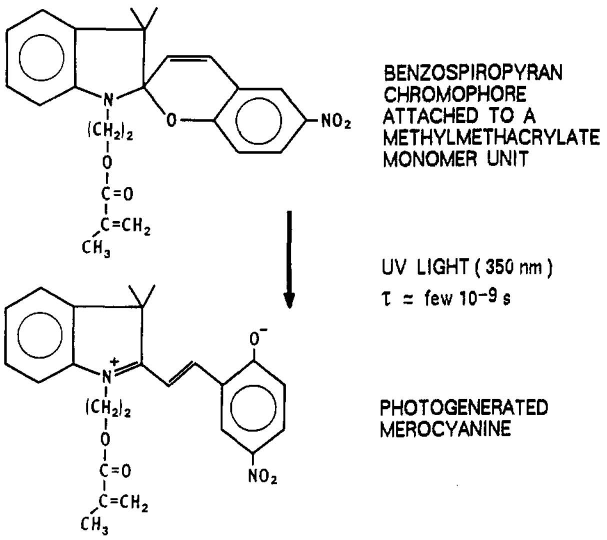

Figure 4. Chemical scheme for the photoconversion of benzospiropyran into merocyanine.

lecular rearrangement. Ultimately a merocyanine moiety is formed.[6] Since the duration of the whole process is very fast and never exceeds a few nanoseconds,[12] the conversion of the spiropyran to the merocyanine form can be considered as instantaneous in the time frame of our experiment. It remains to be explained how this photochemical process can lead to an increase in the monolayer surface pressure. Observation of the merocyanine structure shows that this molecule is highly conjugated and has a strong zwitterionic character (see Figure 4). These two effects combine to make the photogenerated species much more hydrophilic than the initial benzospiropyran molecule. As a consequence, the methyl methacrylate monomers bearing the chromophore groups will tend to move closer to the water subphase. The spatial rearrangement contributes to an increase in the surface pressure by making the monolayer denser.[8] The time necessary for this molecular reorientation is much slower than that necessary for the photochemical conversion. It will therefore constitute the rate-limiting step of the total process.

If we assume first-order kinetics we can derive the reaction rate K from the curve shown in Figure 3. Indeed, we have

$$\Delta\Pi(t) = \Delta\Pi_{\max}(1 - e^{-Kt})$$

if we make the reasonable assumption that the surface pressure change is proportional to the number of photoconverted chromophores that have penetrated the monolayer during the interval of time 0–t.

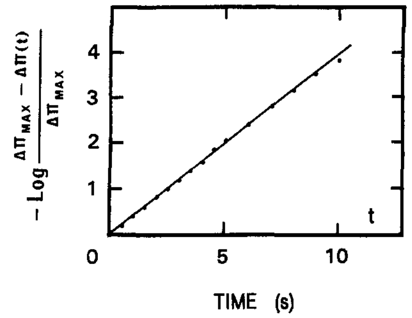

Figure 5. Logarithm of the relative change in surface pressure versus time following a homogeneous UV light pulse excitation of the photochromic methyl methacrylate copolymer monolayer. The points have been calculated from the experimental curve shown in Figure 4. The linear variation evidences first-order rate kinetics.

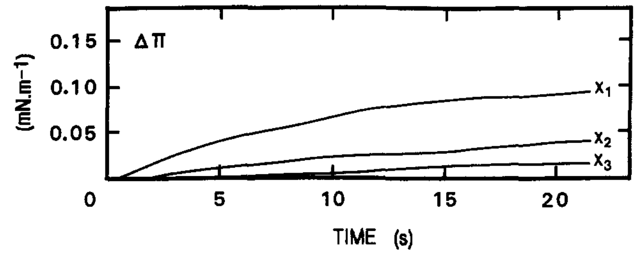

Figure 6. Progressive buildup of the surface pressure, $\Delta\Pi(x,t)$, as a small strip of monolayer is photoexcited by a pulse of ultraviolet light at 350 nm. The three curves correspond to different positions of the Wilhelmy plate detector with respect to the illuminated region: x_1 = 11 cm; x_2 = 14 cm; x_3 = 17 cm. *Initial surface pressure* Π_0 *was* 10 mN·m^{-1} *for all three detector* positions. Total length of the monolayer was 25 cm. T = 22 °C; pH = 1.88.

In Figure 5 we have plotted the logarithm of the surface pressure variation as a function of time. In this representation all data points fall on a straight line. This is good evidence for a first-order rate process. The value of the rate constant is obtained from the slope. For Π_0 = 9.75 mN·m^{-1}, one finds K = 0.39 ± 0.02 s^{-1}.

(iii) Variation of the Surface Pressure Induced by a Localized Photoexcitation of the Monolayer. The time dependence of the change in surface pressure $\Delta\Pi(x,t)$ following localized illumination of the monolayer by a single flash of ultraviolet light is shown in Figure 6. It is immediately apparent that the experimental curves combine some of the features observed during uniform light excitation with some of the features observed during continuous mechanical compression. First, a different response is obtained according to the detector position with respect to the excitation zone. There is also a marked time delay τ_x which increases with detector x position. One observes τ_{x1} = 0.6 s, τ_{x2} = 2.0 s, and τ_{x3} = 5.8 s. Finally, the surface pressure, rather than increasing linearly with time, seems to reach an asymptotic value, which again depends on the detector position.

Discussion

The surface pressure dependence following a continuous mechanical compression by a moving hydrophobic barrier in the case of viscoelastic monolayers has already been analyzed theoretically by one of us (I.P.).[11b] We will therefore only give a short summary of the results that are necessary to understand the localized photochemical excitation case.

Any comprehensive hydrodynamic theory must incorporate the simultaneous motion of the monolayer and that of the bulk liquid substrate. The motion of the incompressible liquid substrate is described by the Navier–Stokes equation simplified to the case of thin liquid layers. On the other hand, the rheological properties of the monolayer can be described in first approximation by a viscoelastic Maxwell two-dimensional constitutive equation with a surface dilatational elasticity $E_0 = \mathrm{d}\Delta\Pi/\mathrm{d}\ln\Gamma$ and a specific relaxation time $\Theta = E_0/\eta$ (Γ is the surface concentration and η the surface dilatational viscosity). The surface dynamic equation is given by the balance of forces acting on the surface

$$\frac{4\mu}{h}u = \frac{\partial\Delta\Pi}{\partial x} \tag{1}$$

where h and μ are the thickness and the viscosity of the bulk liquid phase, respectively, and u is the velocity vector in the plane of the interface. For small amplitudes of deformation, the variation in surface pressure $\Delta\Pi(x,t)$ is related to the variation in surface concentration $\Delta\Gamma(x,t)$ by

$$\frac{\partial\Delta\Pi}{\partial t} = \frac{E_0}{\Gamma_0}\frac{\partial\Delta\Gamma}{\partial t} \tag{2}$$

where Γ_0 is the unperturbed surface density value. The equation expressing the conservation of mass in the insoluble monolayer is simply

$$\frac{\partial\Delta\Gamma}{\partial t} = -\Gamma_0\frac{\partial u}{\partial x} \tag{3}$$

Finally the velocity field $u(x,t)$ parallel to the interface obeys a propagation equation[11b]

$$\frac{\partial u}{\partial t} = D_u\frac{\partial^2 u}{\partial x^2} - \frac{1}{\Theta}u \tag{4}$$

The parameter $D_u = E_0h/4\mu$ is a pseudo surface diffusion coefficient for the surface momentum along x. In the case of an elastic monolayer on a viscous substrate, $\Theta \rightarrow \infty$ and the propagation time is given by $\tau = x^2/D_u$.

It is now possible to calculate the time variation of the surface pressure by solving eq 4, using the proper boundary conditions and the ancillary eqs 2 and 3. In the case of a rectangular trough, one has

$$u = 0 \quad \text{for} \quad t = 0, x = 0 \tag{5a}$$

$$u = u_b \quad \text{for} \quad t \neq 0, x = 0 \tag{5b}$$

$$u = 0 \quad \text{for} \quad t \neq 0, x = L_0 \tag{5c}$$

The final result for $\Delta\Pi(x,t)$ is then

$$\frac{\partial\Delta\Pi}{\partial t} = E_0u_b\alpha\frac{\cosh\alpha(L_0 - x)}{\sinh\alpha L_0} \tag{6}$$

where L_0 is the total length of the trough.

The parameter $\alpha^{-1} = (D_u\Theta)^{1/2}$ has the dimension of a length. It represents the characteristic decay distance for the velocity field in a monolayer obeying Maxwell viscoelasticity. The limits of application of eq 6 are discussed in details in ref 11b.

Equation 6 can be used to fit the experimental data of Figure 2. To restrict the number of floating variables, the value of the surface dilatational elasticity $E_0 = \mathrm{d}\Delta\Pi/\mathrm{d}\ln\Gamma$ was derived independently from the equilibrium surface pressure isotherm of the monolayer, shown in Figure 7. By calculating the derivative of this curve, we obtain $E_0 = 26.5 \pm 0.5$ mN·m^{-1} at $\Pi_0 = 9.75$ mN·m^{-1}. Once E_0 and therefore D_u are known, the value for Θ^{-1} can then be obtained from the least-square fit. In the case of the poly(methyl methacrylate) copolymer monolayer, we find that $\Theta^{-1} = 4.97 \pm 0.20$ s^{-1}. This value is comparable to Θ^{-1} values obtained for monolayers of biopolymers, such as the apoprotein of the Folch-Lee proteolipid from myelin[11b] and the membrane tubulin protein.[13]

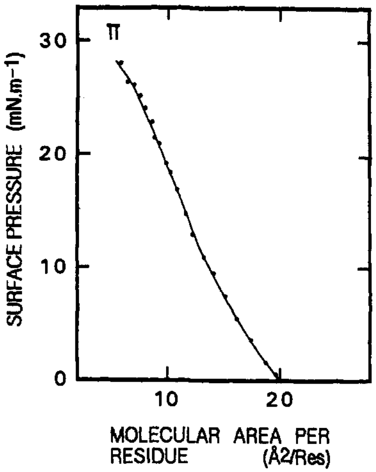

Figure 7. Equilibrium surface pressure isotherm for a monolayer of copolymer of methyl methacrylate containing 5.1 mol % of a benzospiropyran derivative. The surface molecular area is calculated per residue, taking in account the difference in molecular weight between the two types of monomeric units. T = 22 °C; pH = 1.88.

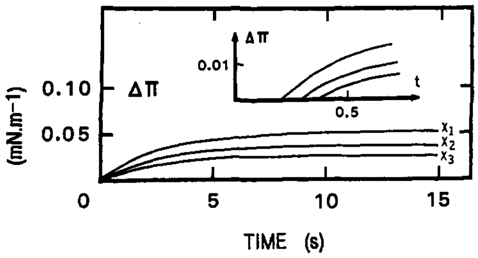

Figure 8. Theoretical curves for the surface pressure variations, $\Delta\Pi(x,t)$, drawn according to eq 9 and following a local photoexcitation of the Langmuir monolayer. The experimental parameters used in the calculation are those derived from the curves shown in Figure 6. The two sets of curves can therefore be directly compared to each other.

We can now turn to the quantitative description of the time dependence of the surface pressure variation following localized photochemical excitation.

In order to describe quantitatively the coupling between the first-order rate photoexcitation of the monolayer and its dilatational motion along the interface, it is necessary to solve again eqs 3 and 4, but with different boundary conditions

$$u = 0 \quad \text{for} \quad t = 0, x = 0 \tag{7a}$$

$$u = u_{\max}e^{-Kt} \quad \text{for} \quad t \neq 0, x = 0 \tag{7b}$$

$$u = 0 \quad \text{for} \quad t \neq 0, x \rightarrow \infty \tag{7c}$$

The second boundary condition is a direct consequence of the first-order kinetics, which describe the reorientation of the macromolecules following light excitation (a value of 0.022 cm·s^{-1} was obtained for $u_{\max}$ in the experimental case discussed in Figure 3). For the last boundary condition we have used $x \rightarrow \infty$ rather than $x = L_0$ in order to simplify the equations. This is permitted if the characteristic length, $(D_u\Theta)^{1/2}$, for the propagation of the velocity $u(x,t)$ is smaller than the length of the trough, L_0. In our case $(D_u\Theta)^{1/2}$ is calculated to be 9.6 cm, which is indeed smaller than L_0 = 25 cm.

The velocity vector $u(x,t)$ is a complicated function of Θ, D_u, and K

$$u(x,t) = \frac{1}{2}u_{\max}e^{-Kt}\left\{e^{-x[(\Theta^{-1}-K)/D_u]^{1/2}}\operatorname{erfc}\left[\frac{x}{2(D_ut)^{1/2}} - [(\Theta^{-1}-K)t]^{1/2}\right] + e^{x[(\Theta^{-1}-K)/D_u]^{1/2}}\operatorname{erfc}\left[\frac{x}{2(D_ut)^{1/2}} + [(\Theta^{-1}-K)t]^{1/2}\right]\right\} \quad (8)$$

Similarly, the surface pressure variation $\Delta\Pi(x,t)$ is shown to obey

$$\frac{\partial\Delta\Pi}{\partial t} = \frac{E_0}{2}u_{\max}e^{-Kt}\left\{\frac{2}{(D_u\pi t)^{1/2}}e^{-[x^2/(4D_ut)]-(\Theta^{-1}-K)t} + \left(\frac{\Theta^{-1}-K}{D_u}\right)^{1/2}e^{-x[(\Theta^{-1}-K)/D_u]^{1/2}}\operatorname{erfc}\left[\frac{x}{2(D_ut)^{1/2}} - [(\Theta^{-1}-K)t]^{1/2}\right] - \left(\frac{\Theta^{-1}-K}{D_u}\right)^{1/2}e^{x[(\Theta^{-1}-K)/D_u]^{1/2}} \times \operatorname{erfc}\left[\frac{x}{2(D_ut)^{1/2}} + [(\Theta^{-1}-K)t]^{1/2}\right]\right\} \quad (9)$$

The predicted variation for $\Delta\Pi$ as a function of time has been plotted in Figure 8 using the previously determined values for the kinetic (K) constant and the rheological (E_0 and Θ) constants.

The similarity between these calculated curves and the experimental ones is striking, especially in view of the fact that no adjustable parameters were used. All the characteristic features shown in Figure 6 are retained: (i) there is an initial time lag, followed by a monotonous increase of the surface pressure; (ii) saturation is eventually reached at long times, with a plateau value depending strongly on the detector position; (iii) the theoretical values of the time lag τ_x ($\tau_{x1} = 0.20$ s, $\tau_{x2} = 0.28$ s, $\tau_{x3} = 0.35$ s) are in qualitative agreement with the experimental ones (Figure 6). Another slight discrepancy that remains is the difference between the relative surface pressures at saturation, especially for the x_1 position. It is probable that the two-dimensional Maxwell model of viscoelasticity that has been used to describe the photochromic polymer monolayer constitutes only a first approximation and needs further refinements.

The present discussion may also explain some earlier results by Mobius et al.[14,15] on the propagation of in-plane compressional waves in elastic monolayers of low molecular weight amphiphiles. In their experiments they use the isomerization of spiropyran derivatives containing one long hydrocarbon chain to excite local surface density perturbation in fatty acid and phospholipid monolayers. The characteristic time of propagation, τ, as detected by microphone sensors[14] or optical detection[15] was claimed to be proportional to the distance x. Our theoretical approach suggests that τ should rather scale as the square of the distance. This hypothesis is apparently confirmed by the data of ref 15 since one observes in Figure 4 that the propagation pulse velocity indeed decreases with the distance to the detector.

Conclusion

The present experiments demonstrate the possibility of using photochemical reactions to excite longitudinal surface pressure waves in monolayers. From the time dependence of the surface pressure it is possible to extract the same viscoelasticity parameters as measured by the barrier compression mechanical method. Moreover, the present method is contact free and is therefore less prone to experimental artifacts.

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