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Reversible Photochemical Strain in Langmuir Monolayers

H. Gruler,[a] R. Vilanove,[b] and F. Rondelez
Collège de France, Physique de la Matière Condensée, 75231 Paris Cédex 05, France

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This paper reports investigation of the photoinduced mechanical response of a monolayer consisting of the copolymer poly(methyl methacrylate)-spiropyran (molecular weight 215 000, 5.1 mole% spiropyran) at an air-water interface. Irradiation with uv-light pulses isomerizes the spiropyran chromophore and leads to a relative surface-pressure increase up to 10% at saturation. The photoexcited state has a typical decay time constant of 20 min. Irradiation with visible light returns the chromophore to the initial state making the mechanical process fully reversible.

Mechanical response of monolayers following light excitation plays an important role in many biophysical systems[1] and also in applied fields such as printing technology.[2] Light receptors for photoregulated biological processes consist of photoisomerizable molecules covalently attached to membrane proteins. Two well-known examples are the rhodopsin with the retinal, and the phytochrome with the tetrapyran, chromophores. They undergo a *cis*-to-*trans* photoisomerization which then triggers the optical nerve excitation in one case and the growth of the cell(s) in the other.[3] Photoinduced conformational changes of synthetic polymers have also been observed in dilute solutions and in the bulk.[3] Again, the changes are due to the presence of chromophores either attached covalently to the chain[4,5] or simply dissolved into the macromolecules.[6] This distinction is important in monolayer studies since a recent experiment[7] seems to have been plagued by the change of solubility of the free chromophore following light excitation.[8] In this Letter, we report on the first experimental evidence of a reversible mechanical response in monolayers of synthetic polymers covalently bonded to photoexcitable chromophores.

We used a copolymer of methyl methacrylate A with 5.1 mole% of a spiropyran derivative B [1-(β-methacryloxyethyl)-6′-nitro-di-isopropyl sulfate]. The molecular weight was 215 000.[9] Unlabeled poly(methylmethacrylate) (PMMA) of molecular weight 150 000 was also used in some experiments. A 0.04-mg/ml benzene solution (Merck analytical grade) was then spread in a cylindrical glass container (6.24 cm diam, 0.5 cm height) filled with ultrapure water (Millipore Q-TM) of controlled pH. The surface tension was measured by the Wilhemy technique with a platinum foil ($2\times0.9\times0.01$ cm^3) attached to a force transducer (Model FTAI-I, Sanborn, Waltham, Mass.) fed into an amplifier (Hewlett Packard HP 8805B). The monolayer was irradiated by a low-power xenon flash gun (Soligor M K-6A). The wavelength distribution of the light pulse was selected to be either in the ultraviolet (uv, 370 ± 35 nm) or in the visible region (> 390 nm) by additional Schott filters. The measurements of surface pressure versus area were performed with a Langmuir film balance (Messgeräte Werk, Lauda, Germany).

We first irradiated the monolayer at fixed concentrations of macromolecular chains. Large changes in the surface pressure Π were observed with spiropyran-labeled PMMA while the unlabeled species showed no effect. This is displayed in Fig. 1. Several flashes were successively fired. The pressure increases after each uv shot; however, saturation effects start to appear as the excitable chromophores are progressively exhausted. The relative change $\Delta\Pi/\Pi$ is then of the order of 10%. We estimate that the amplitude for the first flash corresponds to 10–15% of excited molecules. There is a slight decrease in $\Delta\Pi$ between two successive flashes. This is bet-

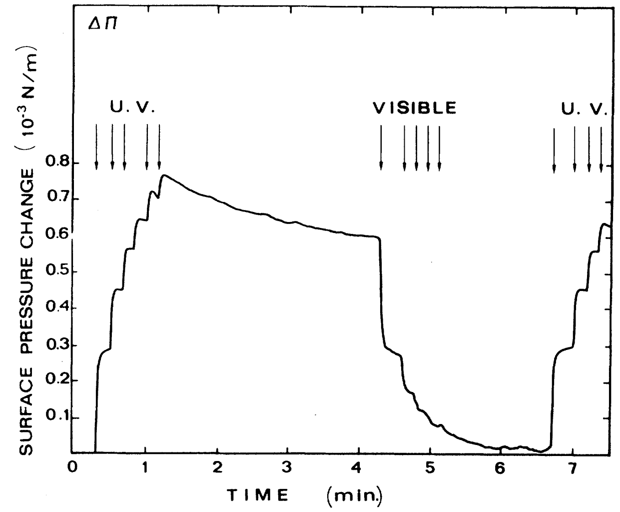

FIG. 1. Surface pressure of a spirobenzopyran-methylmethacrylate copolymer monolayer vs time upon irradiation with sucessive uv and visible light pulses. Surface concentration $=0.875$ mg/m^2, water subphase at pH$=1.0$.

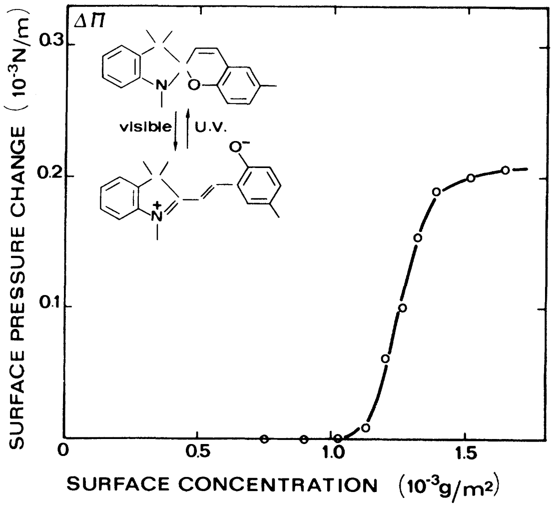

FIG. 2. Surface pressure variation induced by a single uv light pulse vs concentration of the copolymer. Water subphase at pH$=7.0$.

ter observed after the last uv light pulse where one can estimate a typical decay time of 20 min. It is possible to make that decay considerably faster by use of visible light pulses. After 5 pulses, the pressure has returned to its original value. The whole process can be repeated over and over, showing the reversibility of the photoinduced mechanical response.

Next we varied the chain concentration at the air-water interface. In Fig. 2, we have plotted the pressure variation $\Delta\Pi$ following one single uv-light pulse for concentrations ranging from 0.5 to 1.6 mg/m^2. $\Delta\Pi$ is nearly zero up to a concentration of 1.1 mg/m^2 and then increases rapidly up to a maximum of about 0.21 mN/m. The relative variation $\Delta\Pi/\Pi$ is of the order of 2% after one pulse over the whole concentration range. The absolute Π values were obtained separately with a Langmuir film balance and are given in Fig. 3 for both labeled and unlabeled PMMA in the nonphotoexcited state.

In a last experiment, we used mixed monolayers of unlabeled and labeled PMMA. The partial molar concentration C of the labeled species was varied from 0 to 100% while the total surface concentration was simultaneously adjusted to hold the surface pressure of the film always constant in the absence of optical excitation. The $\Delta\Pi$ changes induced by a single uv light pulse are plotted in Fig. 4 for two different total pressures of 5.0 and 10.0 mN/m. $\Delta\Pi$ increases linearly with C in both cases, with a larger slope for the highest total pressure. For $C=0$, $\Delta\Pi=0$.

Spirobenzopyrans are well-known photochromic molecules.[3] Under uv excitation (< 350 nm) they isomerize by heterolytic cleavage to the strongly colored, open-ring, merocyanin form (see inset of Fig. 2). The merocyanin form then returns to the colorless spiropyran form by either thermal or visible-light excitation. Once incorporated as side groups into polymer chains,[9] their properties are not qualitatively changed. On the other

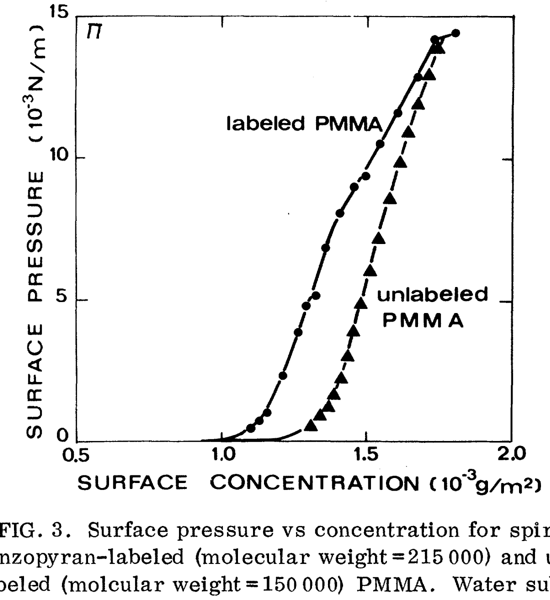

FIG. 3. Surface pressure vs concentration for spirobenzopyran-labeled (molecular weight$=215\,000$) and unlabeled (molcular weight$=150\,000$) PMMA. Water subphase at pH$=7.0$.

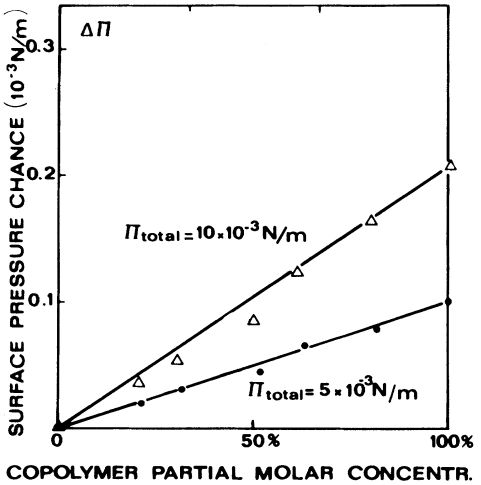

FIG. 4. Surface pressure variation induced by a single uv light pulse vs partial molar concentration of labeled chains in a mixed monolayer with unlabeled PMMA. Total surface pressures are $\pi = 5$ mN/m and $\pi = 10$ mN/m. Water subphase at $p\mathrm{H} = 7.0$.

hand, their large conformational changes from a twisted to a planar form upon isomerization react on the chain configuration.

In our experiments, this effect shows up as a pressure increase at fixed surface area, evidencing an expansion of the copolymer chain under light excitation. For one uv pulse, $\Delta\Pi/\Pi = 2\%$ which corresponds to a relative surface change of 0.4% as derived from Fig. 3. Our data show also that the pressure variation exists only at high concentrations. Indeed, at low concentrations, the chains are no longer touching each other and are in a more "gaseous" state. The pressure is then proportional to the number of chains but independent of their actual dimensions. From the crossover concentration, it is possible to estimate the radius of gyration of the copolymer chain spread at the air-water interface. For our molecular-weight-215 000 compound, we get $R_G \approx$ Å. This value is in reasonable agreement with a direct calculation assuming that a PMMA chain is close to the θ state at an air-water interface,[10] $R_G = N^{1/2} a \approx 120$ Å,[11] where N is the degree of polymerization and a is the monomer length.

Up to now we have only discussed the pressure increase in terms of mechanical forces induced by steric interactions. The photoexcited state of the spirobenzopyran chromophores has a strong dipole moment. Other types of interactions, e.g., dipole-dipole, could then be expected. However, our dilution experiment (Fig. 4) seems to rule out that possibility since ΔΠ goes linearly with the partial molar concentration of labeled chains.

To conclude, we have shown that it is possible to build photochromic monolayers by covalently bonding the chromophores to a polymer chain backbone. The two-dimensional film is then stable over long periods of time. Large pressure changes up to 10% are induced by low-power light excitation. The mechanical response is quasi instantaneous and can be made reversible. This two-dimensional photomechanical engine strongly reminds us of the Katchalsky isothermal chemical engine.[12] Our preliminary results already open a field for new experiments, namely (i) photochromism in two dimensions, (ii) dynamical response of polymer films, and (iii) model systems for photoregulated biological processes.

This work was initiated from a helpful discussion with C. Casagrande, A. Dubault, and M. Veyssié who had obtained preliminary results on spiropyrans attached to C-16 chains. This experiment was made possible by the generous loan of spiropyran-PMMA copolymer by G. Smets, Leuven Universiteit, Belgium. We also gratefully acknowledge the support of the Centre National de la Recherche Scientifique under one contract "ATP surfaces," and of the Naturalia and Biologia Association.

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[a] On leave from Experimentelle Physik III, Universität Ulm, D-7900 Ulm, West Germany.

[b] Permanent address: Université Paris VII, 2 Place Jussieu, 75005 Paris, France.

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