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Photochromism of Monolayers of Poly(methyl methacrylate) Having Spirobenzopyran Side Groups

R. Vilanove, H. Hervet, H. Gruler, and F. Rondelez*

Physique de la Matière Condensée, Collège de France, 75231 Paris Cedex 05, France.
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ABSTRACT: Monolayers of photochromic indolinospiropyran groups covalently attached to a polymer backbone of poly(methyl methacrylate) have been investigated as a function of pH at an air-water interface. All measurements have been performed at room temperature by using the Wilhelmy hanging plate technique to detect the surface pressure changes induced in the monolayer by the photochromic processes. Ultraviolet light excitation induces an heterolytic cleavage of the closed spiropyran structure. At low pH (<3), the chromophore is transformed into a conjugated *o*-hydroxystyrylic salt absorbing at 410–460 nm. At high pH (>4), it is converted into a highly conjugated merocyanine form absorbing at 520–560 nm. The quantum yield of the photoreaction is large, of the order of 0.5 at low pH. Its value depends on the surface concentration, typically by a factor of 2. The photogenerated species can be returned to their original forms by dark thermal processes and/or by subsequent light irradiation in their visible absorption bands. In the dark, the *o*-hydroxystyrylic salt formed at low pH decays spontaneously back to the original spiropyran molecule with a long time constant of about 50 min. In contrast, the zwitterionic merocyanine structure formed at high pH seems indefinitely stable. These decay times are markedly lowered by visible light excitation. At low pH, the photoconversion to the spiropyran form occurs almost instantaneously (in the limit of our 0.1-s detector response). At high pH, the merocyanine is momentarily converted to a different isomer, which can then undergo a dark transformation to the spiropyran form. The positions of the chromophores relative to the air-water interface can also be assessed, at least qualitatively. The polar merocyanines are close enough to the aqueous subphase to be sensitive to changes in the hydrogen concentration. In contrast, the apolar spiropyrans are so little buried in the monolayer that they do not even contribute to the film surface pressure.

Introduction

The possibility of inducing mechanical changes in photochromic polymer materials is a subject of considerable industrial interest.[1] Although it can by no means be considered a new field, it has been revitalized recently by several research groups working with polymer solutions. In all these experiments, the photoactive units are covalently attached to the polymeric backbone, either into the main chain or as pendant groups. This permits amplification of the mechanical variations under illumination and/or dissolution of the chromophores into solvents that would otherwise be considered nonsuitable for the unmodified materials. Both monolayers and bulk solutions have been investigated. Blair et al.[2] and Gruler et al.[3] have studied Langmuir monolayers of azo and spiropyran chromophores spread at an air-water interface, while Irie et al.[4] and Eisenbach[5] have worked with bulk solutions and rubbery networks. In all cases, reversible photoinduced conformational changes of the polymer chains have been observed. The most obvious interpretation of these macroscopic changes is that they reflect the molecular volume changes of the chromophores. However, it has been observed in solutions that the sign of the photoinduced effect is sometimes opposite to what could have been expected. This apparent discrepancy has been resolved by Irie[4a] only recently. Working on a single photoresponsive polymeric system dissolved in various organic solvents, he has showed the necessity of taking into account the solvation mechanisms. Intramolecular solvation of the chromophores can indeed compete with solvation by the solvent, especially when strongly polar compounds are photogenerated. In the case of the merocyanines, the net effect is a shrinkage of the chain, corresponding to a decrease in the thermodynamic quality of the solvent. It is clear that similar solvation problems can occur in Langmuir monolayers since the photogenerated polar groups will experience considerable attraction from the water subphase.

In bulk solutions, these changes are best followed by monitoring the viscosity under on-off light conditions,[4] while in monolayers, one measures the film surface pressure in the concentration regime where the two-dimensional chains are slightly interacting.[6] Classical surface tension techniques are then applicable,[7] and 1% changes in the area occupied by each chain become easily measurable.[3] Such monolayer studies are of course particularly interesting if one wants to use these photoresponsive polymers as model photoreceptors to explain photoregulated processes in biological membranes.[8] They are also important technically in the ever-growing field of colloidal photochemistry, for instance, to control drug release from vesicles.[9]

This paper represents the continuation of our previous work[3] on monolayers of poly(methyl methacrylate) having spirobenzopyran side groups and spread at an air-water interface. A systematic investigation of the photoinduced surface pressure changes is described for several values of the pH of the water substrate. Special attention is paid here to the optical reversibility of the pressure changes and to their dynamical behavior.

Materials and Methods

The polymer poly(methyl methacrylate) (unlabeled PMMA) had a molecular weight of 150 000. The copolymer of methyl methacrylate with 5.1 mol % of a spiropyran derivative [1-(β-(methacryloxy)ethyl)-6′-nitro-DIPS] had a molecular weight of 215 000. The DIPS acronym stands for 3,3-dimethylspiro(2*H*-1-benzopyran-2,2′-indoline). The polymer was prepared by methods already reported.[10] A 0.04 mg/cm^3 benzene solution (Merck analytical grade) was spread in a cylindrical glass container (6.24 cm diameter, 0.5 cm height) filled with ultrapure water (Millipore Q-TM) of controlled pH. The pH was adjusted by using 0.1 N HCl (Prolabo). The surface tension was measured by the Wilhelmy technique with a platinum foil (2 × 0.9 × 0.01 cm^3) attached to a force transducer (Model FTAI-I, Sanborn, Waltham, MA) fed into an amplifier (Hewlett-Packard HP 8805B). The monolayer was irradiated from the water side either with an expanded laser beam (Model 171, Spectra Physics) or with a low-power xenon flash gun (Soligor MK-6A). The wavelength distribution of the light pulse was generally selected by optical wide-band filters. UV light around 330 ± 35 nm was obtained through an UG-11 Schott glass filter. Visible light in different wavelengh regions was produced by using a number of Wratten Kodak plastic filters. In these cases a 1-cm-thick plexiglass plate was also used to cut out all ultraviolet light below 390 nm. Filter no. 36 gave light centered around 430 ± 30 nm. Filters no. 15,

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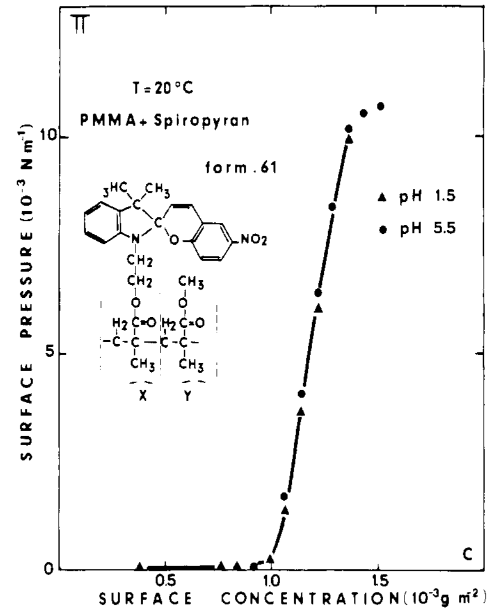


Figure 1. Surface pressure vs. concentration for monolayers of spirobenzopyran molecules attached to a PMMA polymeric backbone, molecular weight 215 000. pH of the water subphase is 1.5 (▲) and 5.5 (●).

22, and 25 transmitted only light above 510, 560, and 600 nm, respectively. Filter no. 58 gave light centered around 530 ± 30 nm. A series of sharp-cut high-pass filters (Schott KV, GG and OG) was also used in the measurement of the photoaction spectra at pH 1.5 and 5.5. They allowed improvement of the wavelength resolution down to $\simeq$20 nm. The argon laser has several UV lines, but only the 351 nm one was selected by using a dispersing fused-silica prism. Since its power can be accurately measured with a thermopile (Model 210, Coherent Radiation, Palo Alto, CA), the laser beam was used in all the quantum yield experiments. A diverging lens permitted expansion of the 1-mm laser beam to roughly the size of the trough. The incident power was measured directly after crossing the air-water interface. The molar absorption coefficient of the polymer was obtained separately by using an UV-visible spectrophotometer (Model 219, Varian Associates, Palo Alto, CA). For this purpose, the optical densities of polymer solutions dissolved in concentrations of 10^{-3} g/cm^3 in two solvents, namely benzene and chloroform, were measured in quartz cuvettes of 2-mm optical path length.

Results

To characterize the static properties of our polymer monolayers, a first series of experiments was performed in the absence of light excitation. The surface pressure π exerted by the monolayer is shown in Figure 1 as a function of the total copolymer surface concentration C expressed in g/m^2. The results have been plotted for two very different pH values. They show readily that, in the dark, π is independent of the hydrogen ion concentration in the water subphase. Figure 2 shows a comparison of the π values between a homopolymer of poly(methyl methacrylate) and the copolymer of poly(methyl methacrylate) labeled with pendant spiropyran groups. Here the abscissa scale has been modified to only count in the surface concentration the fraction of the methyl methacrylate monomers C_{MMA}. For the homopolymer, C_{MMA} is obviously identical with the total surface concentration C. For the copolymer,

$$C_{\mathrm{MMA}} = C\left[1 + \left(\frac{m}{1-m}\right)\left(\frac{M_{\mathrm{sp}}}{M_{\mathrm{MMA}}}\right)\right]^{-1}$$

where m is the molar content in spirobenzopyran and M_{MMA} and M_{sp} are the methyl methacrylate and the

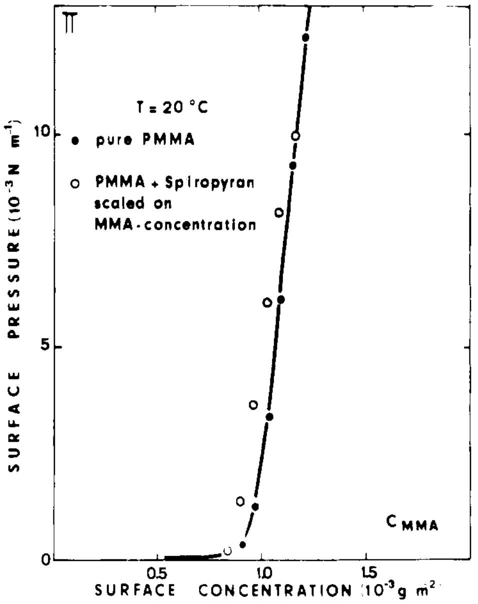


Figure 2. Surface pressure vs. concentration for monolayers of poly(methyl methacrylate) homopolymers (●) and copolymers (○). The homopolymer has a molecular weight of 150 000. The surface pressure data for the copolymer are the same as in Figure 1, but the corresponding surface concentrations have been recalculated to only count their methyl methacrylate content in the plotted surface concentration. Water subphase is at pH 5.5.

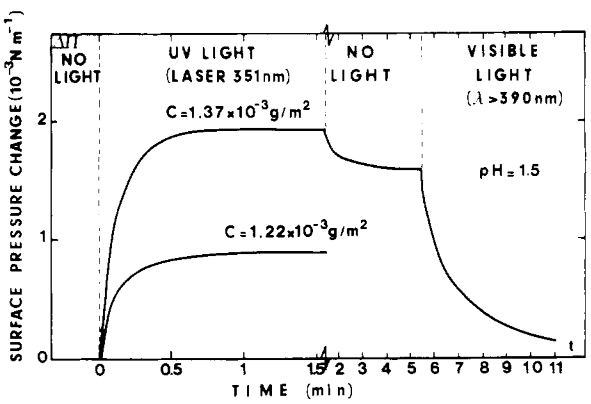


Figure 3. Surface pressure variation upon irradiation with 6 mW/cm^2 of laser light at 351 nm. Copolymer surface concentration = 1.22×10^{-3} g m^{-2} and 1.37×10^{-3} g m^{-2}. Water subphase is at pH 1.5. The dark relaxation of the surface pressure is also observed between 1.5 and 6 min. The photodecrease produced by illuminating the film with visible light pulses (>390 nm) is observed at times longer than 6 min.

(methacryloxy)ethyl spirobenzopyran monomer molecular weights, respectively. $M_{\mathrm{MMA}} = 100$ while $M_{\mathrm{sp}} = 333$. With this transformation of scale, the two surface pressure isotherms are practically superimposed. This indicates that the spiropyran content for a nonphotoexcited copolymer film gives only a small contribution, if any, to the total surface pressure.

When these monolayers are submitted to various types of light excitation, large changes in the surface pressure are observed, as already reported in ref 3. Here we present more detailed results on the pH dependence, the reversibility under visible light excitation, and the dynamics of such changes.

Figure 3 shows the gradual increase in the surface pressure of the film after continuous ultraviolet laser light excitation has been turned on. Two different surface concentrations, 1.22×10^{-3} and 1.37×10^{-3} g/m^2, have been investigated at pH 1.5. The average incident laser power density was 6 mW/cm^2. In both cases, a plateau is reached

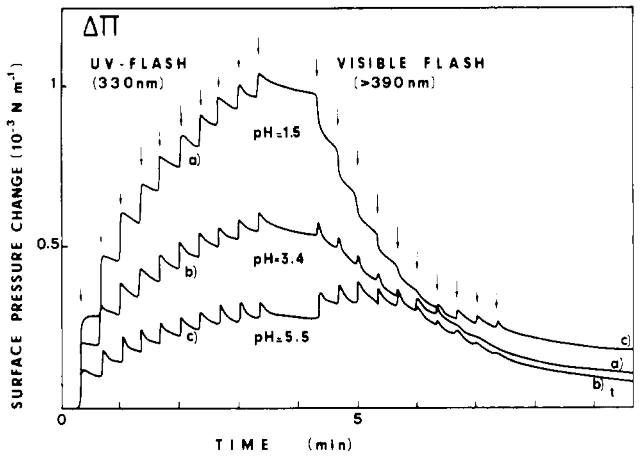


Figure 4. Surface pressure variations upon irradiation, first with a series of UV (330 nm) flash pulses and then with a series of visible pulses (>390 nm). Copolymer surface concentration is 1.37 × 10^{-3} g m^{-2}. Water subphase is at pH 1.5 for curve a, pH 3.4 for curve b, and pH 5.5 for curve c.

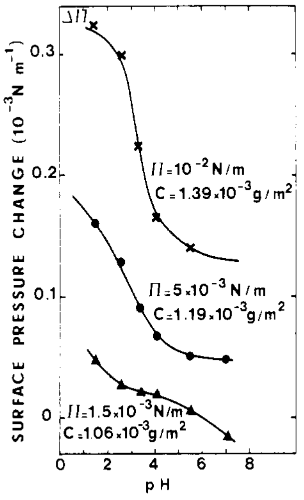


Figure 5. Surface pressure increase upon irradiation with a *single* UV pulse as a function of pH and for three different concentrations. Copolymer surface concentration is 1.39 × 10^{-3} g m^{-2} (×), 1.19 × 10^{-3} g m^{-2} (●), and 1.06 × 10^{-3} g m^{-2} (▲). The starting pressures before irradiation are 10 × 10^{-3}, 5 × 10^{-3}, and 1.5 × 10^{-3} N m^{-1}, respectively.

after about 1 min. The actual saturation level is independent of the irradiating power at least in the range 1.7-10 mW/cm². On the other hand, it differs with surface concentration, being higher for the larger concentrations. After 1.5 min, the laser was turned off and the thermal relaxation is observed. Its time decay can be markedly accelerated by firing visible light flashes of wavelengths greater than 390 nm.

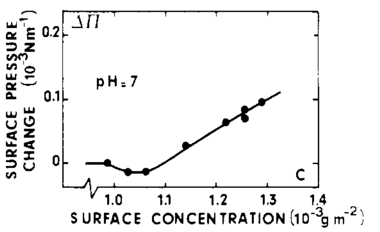


Figure 6. Surface pressure variations upon irradiation with a *single* UV pulse vs. copolymer surface concentrations for pH 7.

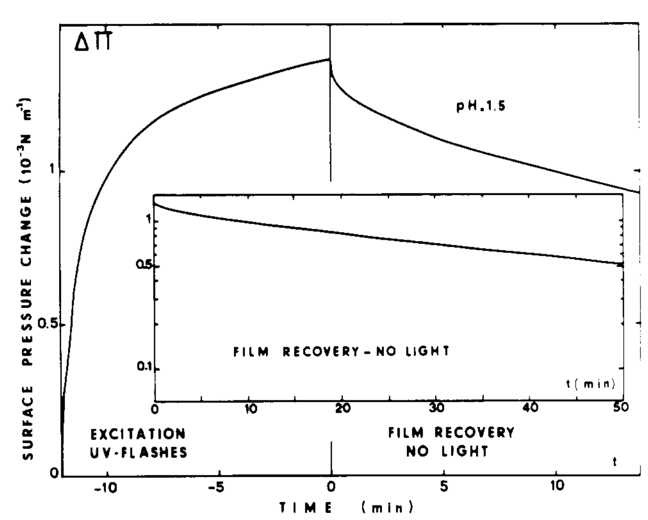


Figure 7. Thermal recovery (positive time scale) of the surface pressure following a UV light excitation of the monolayer up to its saturation state (negative time scale). Copolymer surface concentration is 1.37 × 10^{-3} g m^{-2}, water subphase is at pH 1.5. Inset: Semilogarithmic representation of the time dependence of the surface pressure.

Similar experiments can be repeated by using pulsed, instead of continuous, ultraviolet light excitation. Successive flashes of 2 × 10^{-3} s duration were fired at 30-s intervals until surface pressure of the film was observed to level off. This is displayed in Figure 4a–c, for the three different pH values 1.5, 3.4, and 5.5. We observe here the additional feature that the maximum pressure increase is a strong function of the pH of the subphase. There is nearly a factor of 3 between the data obtained at pH 1.5 and 5.5. This important observation is also apparent in the response to each individual flash. Figure 5, in which the single flash response has been plotted as a function of pH for three different surface concentrations, demonstrates this point in more detail. For any given concentration the plot resembles a titration curve. This is most clearly seen with the highest concentration for which it is possible to separate two different regimes, respectively above and below a characteristic pH value of 3.5 (called pH* thereafter). It is also interesting to note that, for the lowest concentration, the photoinduced surface pressure change becomes negative at pH 7. This effect is not an artifact and has been confirmed by many experiments. Figure 6 shows that this negative variation is only observed in a certain range of concentrations. At large surface concentrations ($C > 1.1 \times 10^{-3}$ g/m²) the single flash response is positive while at very low surface concentrations ($C < 10^{-3}$ g/m²) the single flash response is strictly zero. This latter result is not surprising since we know that, in the dilute regime, the polymer chains do not interact. In that "gaseous" state, the surface pressure depends on the number of chains in the monolayer but is independent of their dimensions.

We have already mentioned several times the existence of a dark reaction that tends to relax the photoinduced surface pressure change. A typical relaxation curve following a UV-flash excitation is displayed in Figure 7 for a pH value of 1.5. It is clear, from the inspection of the semilogarithmic plot shown in the inset, that the curve exhibits considerable deviation from a single-relaxation (first-order) process. Over the time scale accessible to the experiment, we can detect at least two different relaxations, one with a time constant of 2 ± 1 min, the other with a time constant of 50 ± 10 min. Moreover we cannot be certain that there are not other relaxation processes involved, since we have never been able to perform the experiment over a half-day period, which is probably required to observe the complete relaxation of the surface pressure back to its initial value. Indeed, over long time scales, our detection system is plagued by drift problems. Within that

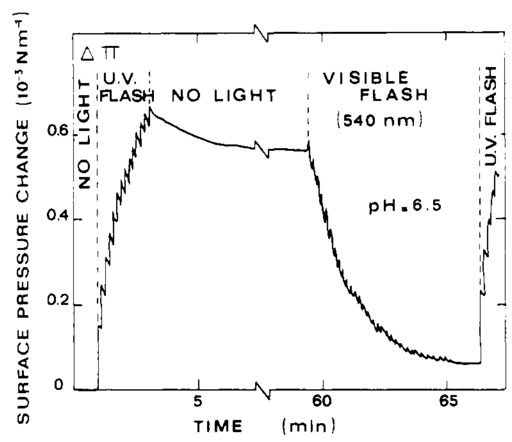


Figure 8. Surface pressure variation upon irradiation, first with UV light pulses and then with visible (540 nm) light pulses. Water subphase is at pH 6.5. Note that, contrary to the case of pH 1.5, the visible pulses induce first an increase and then a decrease in the surface pressure. Copolymer surface concentration is 1.37 $\times 10^{-3}$ g m^{-2}.

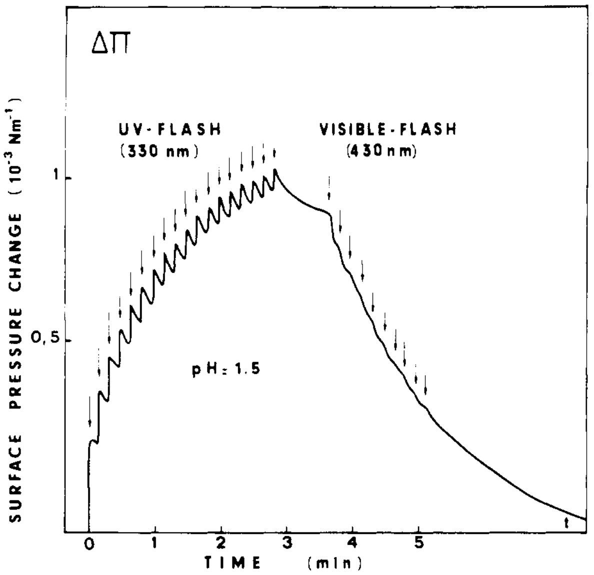


Figure 9. Surface pressure variation upon irradiating first with UV light pulses then with visible (430 nm) light pulses. Copolymer surface concentration is 1.37 $\times 10^{-3}$ g m^{-2}. Water subphase at pH 1.5.

restriction, we have checked that the slow relaxation seems independent of surface pressure or surface concentration, at least in the investigated range of 1 $\times 10^{-3}$ to 12 $\times 10^{-3}$ N/m. The possibility of a thermal dark relaxation is more problematic at high pH. The curve displayed in Figure 8 shows no evidence for such a relaxation after a series of ultraviolet flashes has been fired if we except for a small initial decay, which probably corresponds to a structural rearrangement of the monolayer.

The long-term drift problems do not exist when the relaxation rates are increased by illuminating the monolayer with visible light, and the photoinduced relaxations are therefore much easier to observe. Figure 4 shows the curves obtained for three pH values of the water subphase. It is noticeable that the results are quite different depending on pH. For pH <3, each visible flash induces a large, instantaneous decrease in the surface pressure. Consequently, the monolayer can be returned rapidly to its low initial surface pressure. The system is therefore fully reversible (see also Figure 9). Alternate ultraviolet–visible light excitation cycles can be repeated many times with no apparent fatigue. For pH >3, the behavior

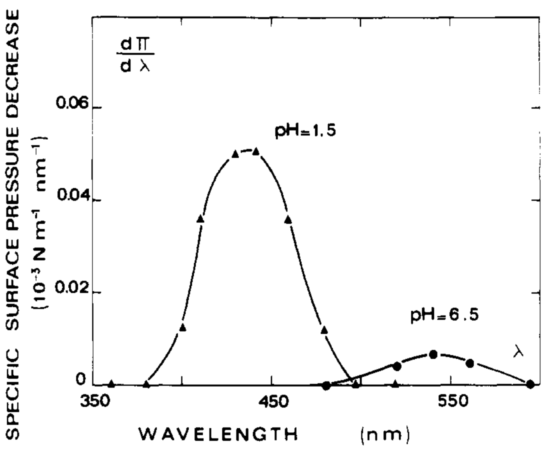


Figure 10. Photoaction spectra of the photoinduced 62 molecular form (pH = 6.5) and the 114 molecular form (pH = 1.5). The ordinate scale is proportional to the surface pressure decrease induced in the monolayer following a *single* pulse of visible light. The optical bandwidth is 20 nm. The surface concentration in both experiments was 1.37 $\times 10^{-3}$ g m^{-2}.

is more complex. Each visible flash induces a sharp rise, instead of a decrease, in the monolayer surface pressure. However, it is immediately followed by a decrease. On the whole, the final surface pressure is lower than the original one. This new value is indefinitely stable, in the absence of further visible excitation. On the other hand, if a sufficient number of visible flashes are fired in succession (Figure 8), it is possible to slowly return the monolayer surface pressure to its low initial value, prior to the ultraviolet excitation. Then, the whole process can be repeated again. Therefore, in this case also, the photoinduced mechanical strain variations can be considered reversible.

The detailed photoaction spectra of these visible-light-induced relaxation processes have been investigated by using well-characterized optical filters (Figure 10). At pH 1.5, the surface-pressure changes are maximum for light centered around 435 ± 35 nm. At pH 5.5, the maximum response is shifted to longer wavelengths, namely 540 ± 40 nm. In both cases, illumination outside these optical bands has no detectable effect. These photoaction spectra can be considered, in a first approximation, the optical absorption spectra of the photoinduced forms. Such information would be inaccessible with direct optical density measurements because of the low molar concentration of spirobenzopyran chromophores in the monolayer. It proves unambiguously that, depending on the pH of the aqueous subphase, various molecular states are reached following an ultraviolet irradiation.

Discussion

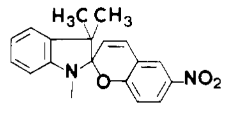
We shall start the discussion with the case of nonphotoexcited indolino–spiropyran copolymer monolayers.

Since their surface pressure isotherms are independent of pH and are almost identical with those of the homopolymer, the repartition of the spiropyran chromophores at the air–water interface can be assigned unambiguously. Indeed, were the spiropyran molecules in intimate contact with the water subphase, one should have observed at least some pH dependence of the film surface pressure. For instance, the results on three-dimensional solutions show a change of the molecular state of the spiropyran with the proton concentration.[11] Also, were the spiropyran chromophores residing inside the monolayer, they should give a significant contribution to the film surface pressure since they represent 5.1 mol % of the copolymer chain. Since our present observations allow us to answer negatively to these two points, we are led to conclude that, in the dark, the spiropyran chromophores tend to stay away from the water. This is in good accord with the common observation[12] that individual spiropyran molecules do not spread spontaneously at an air-water interface.

We shall now examine the case where the spiropyran-methyl methacrylate copolymer film is submitted to a continuous ultraviolet irradiation in the absorption band of the chromophore. It is well-known from experiments on bulk solutions that, under these conditions, the photochromic spiropyrans are converted to merocyanines through intermediate photoexcited states involving the heterolytic cleavage of the C–O bond.[11] These new forms, being highly polar, should experience strong attraction from the water. Detailed experiments on this last point have been reported by Polymeropoulos and Möbius[12] on mixed monolayers of spiropyran covalently bonded to a C_{18} hydrocarbon chain with tripalmitin, a surface-active molecule. In the absence of light, the spiropyrans contribute only weakly to the surface pressure. Upon illumination, a large increase is observed, which can be correlated with a surface occupancy of about 0.6 nm^2 per merocyanine. This value is in fair agreement with estimations from molecular models that give 0.7–0.9 nm^2, depending on the orientation of the chromene ring. In our copolymer monolayer experiments, the photoexcited chromophores will also tend to move closer to the aqueous subphase, therefore inducing a spatial rearrangement inside each macromolecular chain. This will in turn be responsible for the observed increase in the film surface pressure.

The observation that this increase is strongly dependent on the initial surface concentration C_i correlates well with what is known of the surface pressure isotherms of pure poly(methyl methacrylate) monolayers. In ref 3, we have shown that, in the high-pressure regime where the chains are strongly interacting, π scales with concentration as C^{10}. Therefore identical surface concentration changes δC will induce different surface pressure changes $\delta\pi$ according to C_i. In the case of Figure 3, where C_i = 1.37 mg m^{-2} and C_i = 1.22 mg m^{-2}, the $\delta\pi$s reached at saturation differ by a factor of 2. This is in good agreement with the calculations, which predict a factor of 2.8.

The fact that the photoexcited species are attracted toward the water subphase is further demonstrated by the strong pH dependence of the surface pressure change induced by the UV light. The photogenerated species are indeed highly sensitive to protonation. Therefore various molecular states can be reached depending on the actual pH of the subphase. This explains the differences in the single flash response observed in Figure 5. It also explains why the maximum of the optical absorption of the monolayer in the visible light region is shifted from 435 nm at low pH to 540 nm at high pH (pH >3.5). Two different forms referred to as **62** and **114** in the Bertelson nomenclature[11] have been identified from experiments on bulk solutions. We can tentatively assume that these two forms also play a role in our two-dimensional experiments. Their respective molecular structures are given below, where **61** represents the initial spirobenzopyran molecule, **62** is the classical merocyanine open structure, and **114** corresponds to the salt of the open merocyanine and is formed by the attachment of one proton to the oxygen of the pyran ring. It is this addition that is responsible for the strong hypsochromic shift of the absorption band down to ≃430–440 nm.[11]



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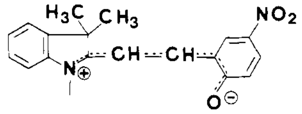

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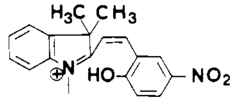
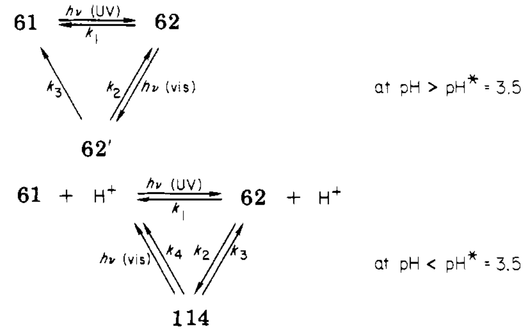


114

Using the photochemical scheme established for three-dimensional solutions, we will, in the following, try to interpret our observations on monolayers as follows:



(**62′** has a yet unknown molecular structure.) The k_i's represent first-order rate constants for thermal kinetics. The $h\nu$'s indicate photoinduced reactions, either with visible (vis) or with ultraviolet (UV) light.

Let us start with the high-pH case. Illumination of the copolymer with UV light leads to a pressure increase due to the apparition of the new **62** merocyanine form. From Figure 9, it appears that this new state of the chromophore is quite stable. Therefore, k_1 is very small. This is not surprising since ionic species are highly stabilized in polar media. Flannery[13] has also observed this effect in three-dimensional solutions. The fading rate of the merocyanines decreases from hours to weeks when the solvent polarity is increased up to aqueous solutions. Working with spiropyran-containing polyvinyl alcohol polymeric matrices, Smets, Brecken, and Irie[1] have reported values as low as 10^{-7} s^{-1} for k_1 at room temperature. Here we can only estimate k_1 to be less than 10^{-4} s^{-1}. A more accurate measurement is not possible with our present apparatus because of the interference of instrumental drift with the slow surface-pressure decay.

The photoaction spectrum of the UV-excited monolayer is characteristic of the **62** form, with a maximum response around 520–560 nm (Figure 10). Illumination of the copolymer monolayer in this wavelength range leads to a temporary pressure increase (Figures 4 and 8). This is an indication that **62** is converted to a new **62′** form. This form, however, is highly metastable, as evidenced by the rapid relaxation of the surface pressure when the visible light is turned off. The time decay is ~50 s. Since it is well-known that open-ring merocyanines can exist in the form of different isomers, it is most probable that the action of the visible light is to shift the equilibrium distribution between the various isomers. The most stable isomer is photoconverted to a less stable one. Very similar conclusions have been reported by Smets, Brecken, and Irie.[1] In their investigation of the photocontraction of polymer networks cross-linked with indolino benzospiropyrans, they also concluded that the changes in the mechanical stress induced by visible light illumination were due primarily to the interconversion between different merocyanine isomers. There is, however, an important difference between the two sets of experiments. In ref 1b, the original stereoisomer equilibrium was fully restored when the visible light was cut off. This does not seem to be the case in the monolayer example. Indeed, it appears that, in the dark, the **62′** merocyanine is not returned to the **62** open-ring merocyanine but rather to the closed-ring benzospiropyran, **61**. Proofs of this assertion are several (Figure 8): (1) The surface pressure of the monolayer following the excitation with a single visible flash does not return to its original value but to a lower value. (2) After a sufficient number of visible flashes are fired, it is possible to recover a surface pressure identical with that of a fresh, nonirradiated, monolayer. (3) The UV–visible cycle can be repeated over and over again, with responses absolutely reproducible. For all these reasons, it therefore appears that, at high pH, the **62** merocyanine molecules photogenerated by ultraviolet excitation can be returned by visible light excitation to the spiropyran **61** form, via a **62′** merocyanine intermediate. It can also be added that the **62′** → **61** thermal reaction rate, k_3, is much faster that the **62′** → **62** back-reaction rate, k_2.

At low pH, the reaction scheme is also very complex. The first observation is that we are not able to detect, in the visible light region, the photoaction spectrum characteristic of the **62** form after exciting the monolayer with UV light. Rather, the photoaction spectrum of the UV-excited monolayer is characteristic of the **114** form, with a maximum response around 435 nm (Figure 10). Therefore, it appears that **62** is only a fast transient state of the monolayer and is readily converted to **114**. The reaction rate k_2 from **62** to **114** is very large, at least 1 s^{-1}, and the corresponding back-reaction rate, k_3, is small.

The effect of the visible light excitation in the 410–460-nm range is to quickly convert this **114** *o*-hydroxystyrylic salt form into the **61** spiropyran form (Figure 9). That the open salt **114** can be photochemically converted to the closed spiropyran has already been mentioned in the literature.[11] A dark thermal reaction is also possible. This is shown in Figure 7, which displays the decrease of surface pressure of the monolayer under dark conditions. The monolayer can then be reirradiated with ultraviolet light and the whole cycle repeated over and over again. Most of the relaxation curve can be described with a decay rate k_4 of about 3×10^{-4} s^{-1}. There is some evidence for a faster initial decay, which is not included in our simplified scheme but should be considered for a more refined analysis.[14] These two decays are observed to be independent of polymer concentration inside the film. This indicates that they are not due to a structural relaxation, where at least part of the elastic stresses could be released by local rearrangements of the polymeric chains.

Our data, obtained with the 351-nm laser light illumination, can be used to determine the quantum yield ϕ of the ultraviolet photoreaction **61** → **114**. This quantity is defined as the ratio of the number of molecules that contributes to the surface pressure change to the number of absorbed photons. The number of photons absorbed per unit time is

$$\mathrm{d}n/\mathrm{d}t = (P/h\nu)(1 - e^{-\alpha C}) \qquad (1)$$

where α is the molar absorption coefficient, C is the concentration of spiropyran molecules in the monolayer in mol L^{-1}, P is the laser power, ν is the frequency of the laser light, and h is Planck's constant.

The number N^* of spiropyrans that are photoconverted per unit time is such that

$$\frac{\partial N^*}{\partial t} = \left(\frac{N_0}{\Delta\pi_s}\right)\left(\frac{\mathrm{d}\pi}{\mathrm{d}t}\right) \qquad (2)$$

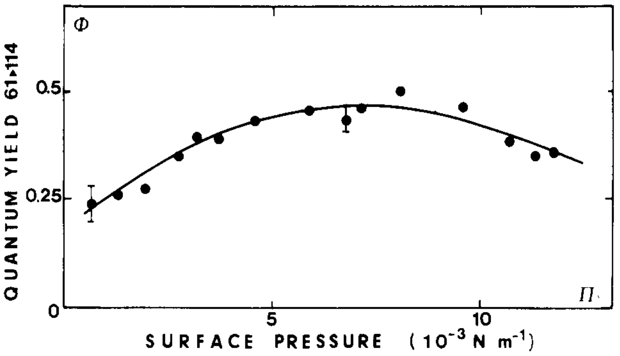


Figure 11. Quantum yield of the photoconversion **61** → **114** (see text) vs. initial surface pressure at pH 1.5.

where N_0 is the total number of excitable spiropyrans and $\Delta\pi_s$ is the pressure change at saturation.

For $\alpha C \ll 1$, we get for the quantum yield:

$$\phi = \left(\frac{h\nu \mathcal{N} V}{P\alpha}\right)\left(\frac{1}{\Delta\pi_s}\right)\left(\frac{\mathrm{d}\pi}{\mathrm{d}t}\right) \qquad (3)$$

where V is the equivalent volume occupied by the monolayer (total area A times the monolayer thickness L) and $\mathcal{N}$ is Avogadro's number.

The molar absorption coefficient α of spiropyran was measured in a separate experiment on dilute bulk solutions. Two solvents were used, namely, benzene and chloroform. The α values were slightly different, reflecting the slight differences in the solvent polarities. α was found to be 1.33×10^4 L mol^{-1} in one case and 1.63×10^4 L mol^{-1} in the other.

Putting together all the numerical values for the different parameters in eq 3, we finally get the quantum yield ϕ of ~0.45 for average monolayer concentration values. The experimental accuracy is not better than 5–10%. We can, however, observe a small, but definite, dependence of the quantum yield on the surface concentration. This is shown in Figure 11, which gives ϕ vs. the initial film surface pressure as measured in the dark. At low pressures ϕ is of the order of 0.24 ± 0.05, while it is of the order of 0.35 at large pressures. These drops can be explained by the fact that the pressure measurements may underestimate the actual quantum yield whenever photoexcited chromophores do not couple to an elastic response of the film. This can indeed be the case at both ends of the surface pressure range: (i) at low surface concentrations (pressures) they can find enough empty space within the monolayer to penetrate the film without inducing spatial rearrangements; (ii) at high surface concentrations they can find it too difficult to enter the compact monolayer when trying to move closer to the aqueous substrate.

Conclusion

We have first shown that nonphotoexcited indolinospiropyran chromophores covalently attached as side groups to a polymeric methyl methacrylate chain interact only weakly with the water subphase and do not contribute significantly to the film surface pressure. On the other hand, we have observed that an ultraviolet light excitation of the film induces drastic modifications in the monolayer. Our interpretation is that the photogenerated species are strongly attracted by the water and penetrate the monolayer more deeply, resulting in the apparition of a photochemical strain. The maximum photoinduced surface pressure change represents about 10% of the initial surface pressure. This value is markedly dependent on the pH of the water subphase, being larger the lower the pH. Using photoaction spectroscopy, we have been able to identify, at low pH, the formation of a nonionic, *o*-quinoidal structure, also called an *o*-hydroxystyrylic salt, absorbing at 435 nm. At high pH, the ultraviolet photogenerated species is a zwitterionic merocyanine, absorbing at 520–560 nm.

We have detected an initially unexpected pressure dependence of the quantum yield of the photoreaction at low pH which would deserve more investigations. Indeed it may have some interesting applications in biologically related experiments. For example, the light detection capabilities of the rod outer segments over an enormous dynamic range of 8 decades is still an unraveled puzzle.[8] In view of our results, it would be worth checking if the elastic coupling between the photoexcitable rhodopsin proteins imbedded in the disk membranes does not affect the quantum yield of the cis–trans photoisomerization of the retinal chromophore.

We have also studied the reversibility of these ultraviolet photoinduced surface pressure changes. At low pH, a spontaneous return of the *o*-hydroxystyrylic salt to the spiropyran form is observed under dark conditions. At high pH, there is no such dark thermal relaxation and the photoexcitation of the monolayer in the visible is required. The photoconversion of the merocyanine molecules to the spiropyran molecules takes place through at least one different merocyanine stereoisomer.

The dynamics of the light-induced changes have been investigated in the time domain from 1 s to 1 h. Although our experiments are still not very detailed, it is worth pointing out that they represent a new approach to flash photolysis. Here the transient photoexcited species are not detected through their optical spectrum changes with a spectrophotometer but rather through their molecular configuration changes with a mechanical force transducer. Such a two-dimensional method may be important when the scarcity of the material to be investigated is a premium parameter. A drawback is, however, that investigation of short-lived species seems precluded because of the slow detector response. Other measuring devices, which would allow faster reaction rates to be followed, typically down into the 10^{-3}-s range, have been described recently in the literature.[15,16]

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References and Notes

(1) (a) Aviram, A. *Macromolecules* **1978**, *11*, 1275. (b) Smets, G.; Brecken, J.; Irie, M. *Pure Appl. Chem.* **1978**, *50*, 845.
(2) Blair, H. S.; Pogue, H. I.; Riordan, J. E. *Polymer* **1980**, *21*, 1195.
(3) Gruler, H.; Vilanove, R.; Rondelez, F. *Phys. Rev. Lett.* **1980**, *44*, 590.
(4) (a) Irie, M.; Menju, A.; Hayashi, K. *Macromolecules* **1979**, *12*, 1176. (b) Irie, M.; Hirano, Y.; Hashimoto, S.; Hayashi, K. *Ibid.* **1981**, *14*, 262.
(5) Eisenbach, C. D. *Polymer* **1980**, *21*, 1175.
(6) Vilanove, R.; Rondelez, F. *Phys. Rev. Lett.* **1980**, *45*, 1502.
(7) Gaines, G. L. "Insoluble monolayers at liquid-gas interfaces"; Wiley: New York, 1966.
(8) See, for example: "Biophysik"; Hoppe, W., Ed.; Springer-Verlag: Berlin, 1977.
(9) Ringsdorf, H.; Holden, D. A. "Proceedings of the E.S.F. workshop on monolayers, multilayers and liposomes"; Mainz: West Germany, 1981.
(10) Smets, G. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 2223.
(11) Photochromism: In "Techniques of Chemistry"; Brown, G. H., Ed.; Wiley: New York, 1971; Vol. 3.
(12) Polymeropoulos, E. E.; Möbius, D. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 1215.
(13) Flannery, J. B., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 5660.
(14) Chaudê, O. *Cah. Phys.* **1954**, *50*, 37.
(15) Albrecht, O.; Sackmann, E. *J. Phys. E* **1980**, *13*, 512.
(16) Stenberg, M.; Löfgren, H. *Rev. Sci. Instrum.* **1979**, *50*, 1098.

Asymmetric Bonding of Identical Units: A General A_gRB_{f-g} Polymer Model

John L. Spouge

Trinity College, Oxford OX1 3BH, England. Received September 28, 1982

ABSTRACT: Flory's A_gRB_{f-g} model describes the polymerization of identical structural units, each having g functional groups of type A and $(f - g)$ groups of type B. In this model, the units react subject to three conditions: (a) Functional groups of type A react only with those of type B and vice versa (thereby forming asymmetrical A–B bonds between the units). (b) Intramolecular reactions do not occur (and therefore only branched-chain (noncyclic) polymers are formed). (c) *Flory's principle of equireactivity*, all functional groups are equally reactive, is followed. This paper uses the theory of branching processes to relax the equireactivity condition. Let the probability that a unit has k reacted A's and l reacted B's be p_{kl}. Using $P(a,b) = \sum p_{kl}a^kb^l$, the generating function of $\{p_{kl}\}$, we give the average molecular weights and size distribution of the sol before gelation and derive the gel point. Using the corresponding *conditional* probabilities $\{\tilde{p}_{kl}\}$ for units in the postgelation sol, we give postgelation results as well. We derive the $\{\tilde{p}_{kl}\}$ by the method of extinction probabilities. Our results agree with known results for the equireactive case. Although we refer to chemical bonding between groups, our results apply to asymmetric bonding in general.

Introduction

In 1941, Flory[1] introduced the RA_f (f functional random polycondensation) model of polymerization. In the RA_f model, each structural unit of a polymer has f functional groups of type A. The units react subject to three conditions: (a) Functional groups of the type A react with one

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