

Photoinduced bending of a coumarin-containing supramolecular polymer†

Jie He, Yi Zhao and Yue Zhao*

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An amorphous polymer bearing a number of H-bonded coumarin groups can display large bending towards incident UV light. Imbalanced surface stresses generated by the photocrosslinking of polymer chains occurring on the side of the film receiving the UV light are believed to cause the photoinduced deformation.

Materials that change shape or volume in response to light irradiation are among smart materials of growing interest. Although a few small-molecule photochromic crystals were reported to display photoinduced shape change,^{1,2} most of such materials are polymer-based systems. Generally, to achieve photodeformation with a polymer, a photochromic molecule is incorporated into the polymer structure, and the photoreaction should result in a structural and/or conformational change of the polymer leading to a macroscopic shape or volume change. In this regard, azobenzene has been the most explored chromophore to date and the combined use with liquid crystalline (LC) networks has generated large-scale photoinduced deformations including contraction, elongation and bending, triggered by the trans-cis photoisomerization of azobenzene in all cases.^{3–12} Of particular interest and importance is the large bending of azobenzene LC network films, controllable with either the orientation of mesogens or the polarization of the irradiation, as recently demonstrated by Ikeda's group.^{6–10} Depending on the orientational state of azobenzene mesogens, being homogeneous or homeotropic, the side of the film absorbing UV light can undergo a contraction or expansion only in a region close to the surface and result in bending of the film towards or away from the irradiation light, respectively. Like other systems based on LC networks,^{3–5} the cooperative movement of mesogens is believed to play a key role since no comparable large-scale photoinduced deformations were achieved using amorphous polymers. In view of the potential of photo-deformable polymers for such applications as artificial muscles, actuators, shape-memory materials and remotely photocontrollable devices,^{3–12} it is of interest to explore chromophores other than azobenzene,¹³ and to discover new mechanisms. Here we report a study of poly(4-vinyl pyridine) (P4VP) hydrogen-bonded to a photochromic coumarin group, referred to as a supramolecular polymer due to the non-covalent association. We found that films of this amorphous polymer could exhibit large-scale photoinduced bending similar to azobenzene LC networks. The likely mechanism is discussed in terms of the photodimerization of coumarin pendant groups occurring on one side of the film, which creates imbalanced surface stresses leading to the bending. To our knowledge, this is the

first report of large-scale photoinduced deformation displayed by an amorphous polymer.

The photosensitive polymer shown in Fig. 1, P4VP-CMC, was prepared by partially functionalizing P4VP ($M_w = 160\,000$) with 7-(carboxymethoxy)-4-methylcoumarin (CMC) through H-bonding between the pyridyl and carboxylic acid groups. The preparation method^{14–16} consisted of dissolving weighed coumarin acid and P4VP in DMF (polymer concentration: 10 wt%), followed by slow evaporation of the solvent, while the formed H-bonds could readily be confirmed with infrared spectra (ESI†). Samples of various complexation degrees were prepared (from 4 to 12 mol% of CMC). In contrast to azobenzene LC networks, large films of this amorphous polymer could easily be obtained by solution-casting. Those used in the present study have a thickness of about 50 μm . Since they have a glass transition temperature (T_g) of ~ 90 – 113 °C (lower T_g with more H-bonded CMC), their bending behaviors were investigated at 110–115 °C, slightly above T_g . Also depicted in Fig. 1 is the photoinduced dimerization of coumarin pendant groups upon UV irradiation at $\lambda > 310$ nm, which is responsible for the polymer crosslinking, as well as the cleavage of the cyclobutane bridge upon UV irradiation at $\lambda < 260$ nm. The occurrence of this reversible photoreaction in the films of P4VP-CMC was confirmed with UV-Vis spectra (ESI†). We note that the photocrosslinking of coumarins and, similarly, cinnamic acids were used in a variety of photo-responsive materials.^{17–21}

Fig. 2a shows two photographs for a film (~ 15 mm in length and 4 mm in width) of P4VP-CMC (10 mol% of CMC) before and after 15 min UV irradiation (>310 nm, light intensity 750 mW cm^{-2}) at 115 °C; one end of the film was fixed on a glass slide by a tape. The UV exposure caused a 90° bending of the film towards the light source (the angle is that between the substrate surface and the direction that the straight end of the film is pointing). Fig. 2b shows the plot of bending angle vs. irradiation time for this sample. The

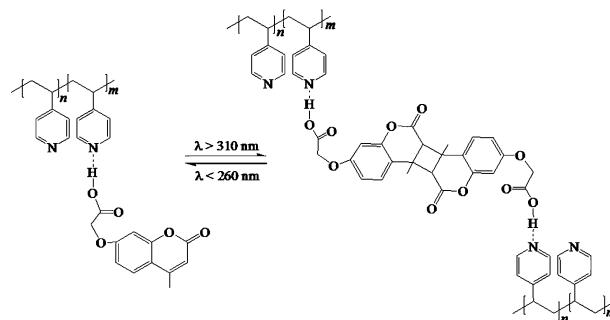


Fig. 1 Chemical structure and the reversible photocrosslinking of poly(4-vinyl pyridine) partially complexed with 7-(carboxymethoxy)-4-methylcoumarin through hydrogen-bonding.

Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1. E-mail: yue.zhao@usherbrooke.ca

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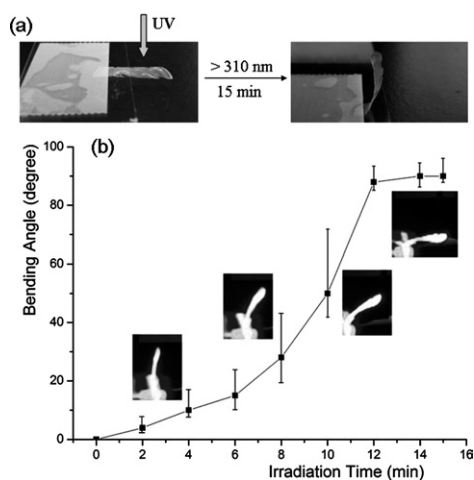


Fig. 2 (a) Photographs for a film of P4VP-CMC (10 mol% of CMC) showing the photoinduced bending towards the UV light (750 mW cm^{-2}), and (b) the increase in the bending angle as a function of UV irradiation time. The error bar indicates the maximum and minimum bending angles observed in five separate experiments.

photographs showing the development of bending over time were taken from a video recording the process (the film was in a nearly vertical position before UV irradiation coming from the right side). The speed of bending becomes greater when the film temperature is higher. For instance, at 120°C , 90° bending was achieved within 5 min. Under the same conditions, the magnitude of bending was found to depend on the content of H-bonded coumarin moieties. Fig. 3 shows the plot of achievable bending angle as a function of coumarin content, accompanied by the corresponding photographs. The bending is more prominent as the amount of pendant coumarin groups increases, reaching $\sim 90^\circ$ bending with 10 mol% or more of CMC. Further increasing the coumarin concentration renders the polymer film more fragile and thus more difficult to prepare. In all cases, after turning off the UV light, the bending deformation is stable at the experimental or lower temperature.

The photoinduced large bending of P4VP-CMC films should originate from imbalanced surface stresses generated by the photo-reaction of coumarin moieties. Similar to azobenzene-based

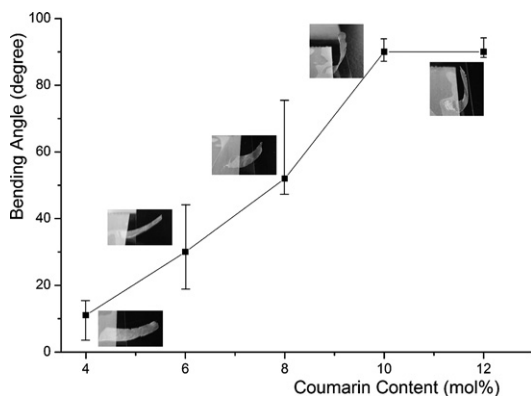


Fig. 3 Achievable bending angle vs. coumarin content for P4VP-CMC films exposed to UV irradiation ($\lambda > 310 \text{ nm}$, 750 mW cm^{-2}). The error bar indicates the maximum and minimum bending angles observed in five separate experiments.

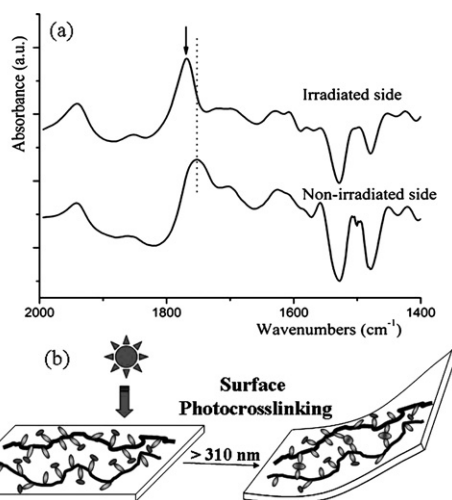


Fig. 4 (a) Reflectance infrared spectra recorded for the two sides of the film shown in Fig. 2. The spectral changes revealing the photodimerization of coumarin moieties which occurred on the side receiving the UV light are marked by arrows. (b) Schematic illustration of the mechanism underlying the photoinduced bending of the film.

polymers,^{6–10} this occurs if the photoinduced crosslinking (Fig. 1) takes place only in a region nearby the surface receiving the UV light. Reflectance infrared spectra were recorded for the two sides of the film in Fig. 2a, *i. e.*, irradiated and non-irradiated sides. The result in Fig. 4a provides evidence that indeed the photoinduced dimerization of coumarin groups occurs only on the side exposed to the UV light. The significant shift of the C=O stretching vibration band, from 1750 cm^{-1} for the non-irradiated side to 1768 cm^{-1} for the irradiated side, is an indication of the photodimerization of coumarin groups.¹⁷ No shift was observed for the non-irradiated side as compared to the film prior to irradiation (spectrum not shown). Even though the actual depth of the photocrosslinked region is unknown, it is reasonable to assume that a crosslinking density gradient could be formed along the film thickness direction as the incident photons propagate through the film. On the basis of this result, the likely mechanism for the photoinduced bending is schematically illustrated in Fig. 4b. The dimerization of two coumarin groups could bring P4VP chains closer to each other and result in an increase in density only on the side exposed to UV light, which exerts a surface volume contraction effect leading to the macroscopic bending of the film. During the UV irradiation, the imbalanced surface stresses should mount as the anisotropic dimerization increases. And the result in Fig. 3 is understandable since such a photoinduced surface contraction effect should be greater with increasing amounts of photocrosslinkable coumarin groups.

To further confirm the mechanism, other experiments were performed (more details in the ESI†). First, P4VP was partially functionalized with 7-(carboxydecyloxy)-4-methylcoumarin (CDC) that has a much longer flexible spacer separating the carboxylic acid and coumarin units than CMC. It could be expected that the greater decoupling of the chain backbone from coumarin groups might reduce the effect of photodimerization on the conformation of the supramolecular polymer chains. Indeed, no meaningful photoinduced bending for the films of P4VP-CDC was observed (only a few degrees). Second, poly(2-vinyl pyridine) (P2VP) was complexed with CMC. The linking of CMC to P2VP through H-bonding would be

less efficient than with P4VP due to an additional steric hindrance affecting the self-assembly.²² This could diminish the photoinduced bending since the transfer of stresses to the chain backbone, arising from the coumarin dimerization, should be less efficient. Indeed, the achievable bending angle for P2VP-CMC (10 mol% of CMC) is about 30°. Third, if the photocrosslinking on one side of the film is what creates the imbalanced surface stresses leading to the bending, the use of other chromophores could reveal the same phenomenon. A preliminary test was conducted by partially functionalizing P4VP with 9-anthracene carboxylic acid (ACA) that is known to undergo a [4 + 4] cycloaddition reaction under 365 nm UV irradiation.² Though less prominent, photoinduced bending was observed for films of P4VP-ACA (bending angle of about 20° for a sample with 10 mol% of ACA).

Back to the bent film of P4VP-CMC in Fig. 2, subsequent exposure of the same side to UV light of $\lambda < 260$ nm could give rise to partial cleavage of the cyclobutane bridges, but this could not unbend the film. By contrast, exposing the opposite side of the bent film to UV light of $\lambda > 310$ nm for photocrosslinking, which results in an inverted contraction effect, could unbend the film by $\sim 10^\circ$ – 20° . Complete unbending of the film was observed upon heating the film to 150 °C. The incomplete photodecrosslinking with coumarin chromophores²¹ may account for the behavior as the remaining crosslinks could prevent the relaxation of the bending-created stresses by increasing the T_g of the crosslinked surface region to above the experiment temperature. That the film is unbent at elevated temperature can be explained by two possibilities: (1) the photodeformed, crosslinked film is heated to above the “surface” T_g so that the elastic deformation of chains is relaxed; and (2) the dissociation of H-bonds becomes important due to the dynamic nature, which effectively decrosslinks polymer chains and release the stresses. What happens may be a combination of both. The reversibility issue can be addressed and improved through polymer design (for example, polymers of low T_g and LC polymers are worth being studied). The role of H-bonding in generating the photoinduced bending is unclear at this time. Our preliminary investigations found that covalently linking coumarin moieties to polystyrene resulted in brittle films that could not be used for the photobending test requiring free-standing films. More studies are underway.

In summary, we found that the amorphous supramolecular polymer of P4VP-CMC can display a large-scale photoinduced bending deformation comparable to that known for azobenzene LC networks. The plausible mechanism is based on a surface volume contraction effect generated by photocrosslinking of polymer chains on one side of the film, and it appears to be general. This finding opens a new avenue in designing and developing photodeformable amorphous polymers. The robust processing possibilities of

amorphous polymers are an important advantage for possible applications.

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