Large Photo-induced Thickness Change in Evaporated Spiropyran Films

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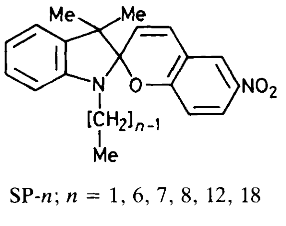
Evaporated spiropyran films exhibit a large photo-induced thickness change, which is caused by the change in molecular size associated with ring-opening.

A number of studies have been carried out to cause changes in material size by photochemical procedures. Representative materials reported so far are systems containing spiropyran, azobenzene, or photo-sensitive dyestuff units. Spiropyran polymers have been found to display a 3% photoinduced shrinkage.[1] Azo-aromatic polyimides show a reversible photo-contraction of about 0.6%, which seems to be associated with *trans–cis*-isomerization.[2] Cross-linked poly-(2-hydroxyethyl methacrylate) gel containing chrysophenin contracts about 1.2% after being irradiated.[3] These deformations are too small to be of practical use. A large deformation has been found in cross-linked poly-4-(*N*,*N*-dimethylamino)-*N*-γ-D-glutamanilide film.[4] When it was in contact with carbon tetrabromide, a photo-induced dilation of 35±2% was obtained in each dimension, representing a volume change of 146%. However, the deformation occurred only under wet conditions. In this communication, we describe a new system for realizing a several-fold deformation under completely dry conditions. Our system uses evaporated spiropyran films with long *N*-alkyl chains.

6-Nitro-*N*-alkyl-3′,3′-dimethylspiro(2*H*-l-benzopyran-2,2′-indoline) derivatives with different *N*-alkyl chain lengths, which we designate SP-1, -6, -7, -8, -12, and -18, were used in this study. SP films of thickness 2μm were prepared on glass plates by evaporation under reduced pressure. Photo-irradiation was carried out at room temperature using a 500 W high-pressure Hg lamp with a coloured glass filter ($240 < \lambda < 410$ nm). The intensity of the u.v. light was about 20 mW/cm^2. Except for SP-1, these evaporated films became strongly coloured immediately on exposure to u.v. light. The optical density measured at $\lambda_{max.}$ (580 nm) was almost saturated after u.v. irradiation for 60 s. At the same time, some films showed a change in thickness. Figure 1 shows the ratios of thickness before (d_0) and after (d) u.v. irradiation for 60 s; a large change was seen for the SP-6, -7, and -8 films, whereas there was almost none for the SP-1, -12, and -18 films. The SP-7 film showed the most change, its thickness increasing almost 3-fold. The films were decolourized on exposure to visible light or to heat, and regained their initial thickness. However, the smoothness of the film surface was reduced. It has been reported that ring opening of SP molecules involves an increase in molecular size and that the change in the area occupied by one molecule is 2- to 3-fold for SP monolayers at the air–water interface.[5] Taking this fact into consideration, the 3-fold thickness change is reasonable.



SP-*n*; *n* = 1, 6, 7, 8, 12, 18

The fact that SP-6, -7, and -8 films alone exhibited a large deformation suggests that there is a specific limit for the *N*-alkyl chain length within which a large deformation can occur. Two opposing mechanisms are involved in this. One is the ease by which the ring-opening of the SP molecule takes

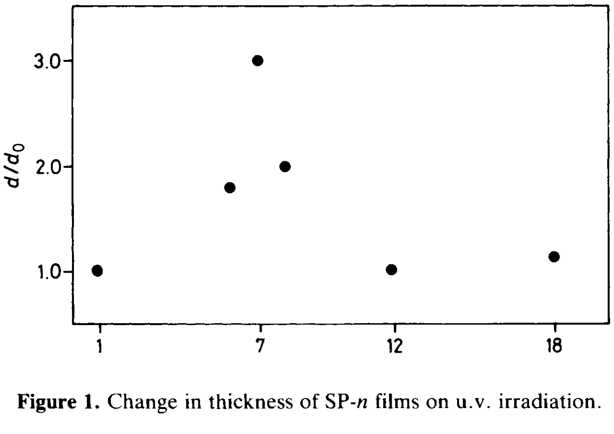


Figure 1. Change in thickness of SP-*n* films on u.v. irradiation.

place, and the other is the stress-absorbing effect of the alkyl chains.

With regard to the ease of ring-opening, the SP-1 film crystallizes immediately after evaporation and shows slight colour formation; its stiffness prevents the SP molecule from isomerizing which would involve a size increase. On the other hand, SP films with longer alkyl chains do not crystallize immediately and easily show colour formation because they are relatively soft; ring opening involving size increase takes place more easily in the SP films with longer alkyl chains.

With regard to the stress-absorbing effect of the alkyl chains, SP-12 or -18 has a flexible alkyl chain long enough to be distorted by isomerization-induced stress in the evaporated films, leading to little distortion at the macroscopic level. On the other hand, since shorter alkyl chains have less capacity to absorb the stress caused by the ring opening, distortion that cannot thus be accomodated is apparent as a macroscopic distortion. This means that SP films with shorter alkyl chains are more easily deformed.

The specific limit of the chain length is the result of a trade-off between the two factors mentioned above. This conclusion is in good agreement with the result obtained for cross-linked poly-4-(*N*,*N*-dimethylamino)-*N*-γ-D-glutamanilide film[4] in which a trade-off between the mechanical rigidity and deformability is observed.

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