Photochemistry Determined by Light Propagation. Part 1 Three-dimensional Photomanipulation of Self-organized Azobenzenes in Liquid-Crystalline Polymers

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Clear-cut observation of the reorientation and self-organization of azobenzene chromophores to the propagation direction of actinic light is described, using spin-cast thin films of a liquid crystalline azobenzene polymer.

Light absorption by molecules is achieved under exclusive requirements including the coincidence of the electric vector of actinic light with the direction of a transition moment of the corresponding ground state chromophores.[1] When actinic light is linearly polarized, photoinduced dichroism is generated through the angular-selective photoisomerization of the chromophores embedded in polymer films[2-4] or attached to a silica surface.[5] On the other hand, when the propagation direction of light is just in parallel with the transition moment of the chromophore molecule, no light absorption takes place, being irrespective of the electric vector of the light. Our recent work has revealed that the three-dimensional control of orientational direction of azobenzene moieties is in fact attained by slantwise photoirradiation of a polymer film with non-polarized light.[6] But a level of photoinduced optical anisotropy was very small. We report here the unequivocal three-dimensional photomanipulation of molecular orientation by slantwise photoirradiation of spin-cast films of a liquid-crystalline polymer with azobenzene side chains.

Linearly polarized light irradiation of spin-cast thin films of liquid-crystalline polymers substituted with azobenzenes results in the emergence of dichroism, the level of which is much larger than that of amorphous polymers.[7-9] This fact led us to employ a liquid-crystalline poly[6-{4-(4'-methoxyphenyl)azophenyloxy}-hexyl methacrylate] (G 76 S 95 N 137 I, Mw = 1.25 x 10^5, Mw/Mn = 2.8).[10] It was found that prolonged irradiation of a spin-cast film of the polymer (thickness = ca. 70 nm) on a fused silica with 436 nm light of exposure doses of 10 J cm^{-2} or more at ca. 23 °C results in the marked reduction of the π,π^*-absorption band. Note that the formation of a photostationary state containing *E*-isomer as a major component requires exposure doses of 0.1 J cm^{-2} or less. This implies that the decrease of the π,π^*-absorption intensity upon irradiation with the light of a perpendicular incidence (θ_a = 0°) is evidently due to the physical reorientation of the *E*-isomer. In order to obtain further insight into the photoreorientation of the chromophore, absorption spectra of a film exposed to 436 nm light of a 10 J cm^{-2} dose were taken at various incident angles (θ_m) of monitoring light, which is defined as an angle contained by the propagation direction of the light and the surface normal. The results shown in Figure 1 reveal that the monomeric band at λ_{max} = 360 nm due to π,π^*-absorption display a marked blue-shift upto 320 nm as θ_m increases, accompanied by the increase in absorbances. This indicates consequently that the prolonged blue light irradiation leads to the perpendicular reorientation of *E*-isomer, which forms supramolecular H-aggregates.[7-9,11-13]

We define here A_{320}/A_{360} as the measure of a level of H-aggregation, whereas A_{320} and A_{360} are absorbances corresponding to monomeric and aggregated species, respectively. Figure 2 shows changes of A_{320}/A_{360} and absorbances at λ_{max} of the photoirradiated film as a function of θ_m of linearly polarized probe light to bring our observation into relief.[14] Crucially different results were obtained, depending on whether probe light was *p*-polarized or *s*-polarized. When the probe light is *p*-polarized, A_{320}/A_{360} values increase as θ_m increases, while the minimum of monomeric π,π^*-absorbances appears at θ_m = 0°. These facts indicates that the aggregated chromophores align in the direction in parallel with the incident direction of the probe light. On the other hand, both of the absorbance and A_{320}/A_{360} are not much altered by the changes in θ_m of *s*-polarized probe light, the electric vector of which is perpendicular to the incident plane. The latter results arises clearly from the fact that the electric vector of the *s*-polarized light and the transition moment of the perpendicularly photoaligned chromophores exist in a crossed position so that no light absorption takes place under these conditions. In other words, the monitoring with *s*-polarized light is inert to the perpendicular orientation of the azobenzene while *p*-polarized light gives specifically information concerning the perpendicular orientation of the chromophores.

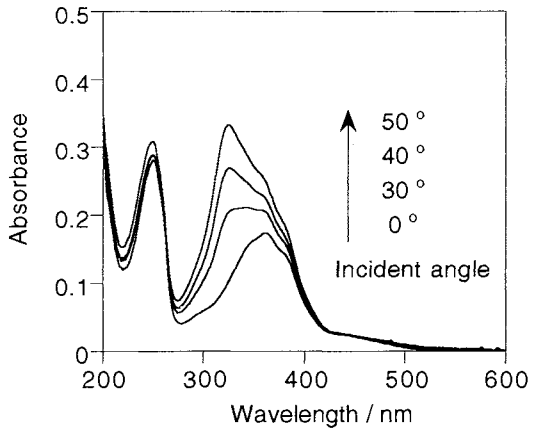

Figure 1. Absorption spectra of a film of the liquid-crystalline polymer exposed to 436 nm light of an exposure dose of 10 J cm^{-2} at various incident angles (θ_m) of probe light.

Encouraged by the results, films of the same polymer were subjected to the irradiation with 436 nm light for *Z-to-E* photoisomerization with various incident angles, θ_a. One of the representative results at θ_a = + 20° is given in Figure 3. θ_m = + 20° of *p*-polarized probe light to give the minimum absorbance is essentially consistent with the θ_a of the 436 nm light. The

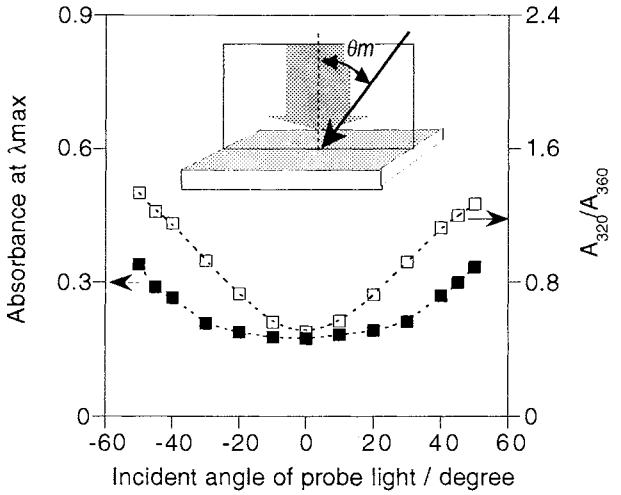

Figure 2. A_{320}/A_{360} and absorbances at λ_{max} of a film of the liquid-crystalline polymer irradiated with 436 nm light perpendicularly to a film surface (θ_a = 0°) as a function of θ_m of *p*-polarized probe light.[14] The thin and broad arrows correspond to monitoring and actinic light, respectively.

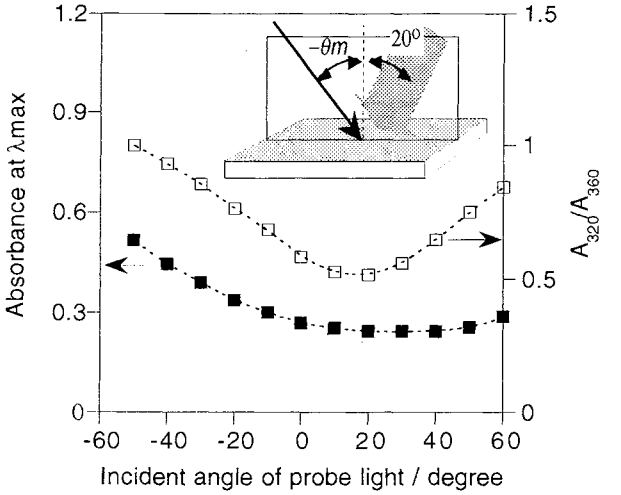

Figure 3. A_{320}/A_{360} and absorbances at λ_{max} of a film of the polymer irradiated with 436 nm light at an incident angle θ_a = 20° as a function of θ_m of *p*-polarized probe light.[14]

appearance of the minimum of A_{320}/A_{360} centered at θ_m = + 20° supports that the molecular axis of aggregated azobenzenes is just parallel to the propagation direction of the actinic light. By using this spectral analysis techniques, it was revealed that the orientational direction is decisively controlled by the propagation direction of non-polarized light for *Z-to-E* photoisomerization.

The present observation can be interpreted as follows. A spin-cast film of the liquid-crystalline polymer shows an amorphous nature which is thermodynamically less stable.[10,11] Irradiation with 436 nm light causes the repetition of *E/Z* photoisomerization of the chromophores to result in the molecular reorientation in such a way that the π, π^*-transition moment of the chromophores lies in parallel with the propagation direction of the light to minimize the light absorption. The three-dimensional optical anisotropy is enhanced by the supramolecular aggregation of the azobenzene side chains owing to the liquid crystallinity.[12,13]

In summary, the prominent photocontrol of three-dimensional orientation of azobenzene chromophores in films of a liquid-crystalline polymer has been realized by irradiation with non-polarized light. The orientational direction of the chromophores exhibiting phototriggered aggregation is in line with the propagation direction of actinic light.

References and Notes

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14 As seen in Figure 1, there is no modification of absorption spectra in a transparent region from 500 nm to 600nm despite the changes in optical path length as a function of incident angles, indicating that the contribution of multiple reflection can be neglected in the present spectroscopic analysis. Absorbances at various θm were corrected by taking into account both of θm and a refractive index of the polymer (n = 1.64).