Extraordinarily Thermostable Photodichroism of Poly(4-cyano-4'-methacryloyloxyazobenzene) Films

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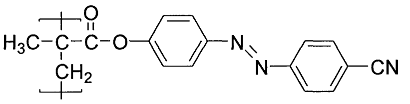
Linearly-polarized-light-induced optical anisotropy of a thin film of polymethacrylate with *p*-cyanoazobenzenes side-chains is enhanced at elevated temperatures to display anomalously high stability toward heat and light.

It has been well known that the exposure of thin films of polymers incorporating azobenzene moieties to linearly polarized light generates optical anisotropy such as photodichroism as a result of the repetition of *E/Z* photoisomerization of the chromophores to lead to the reorientation of their molecular axis.[1,2] Our recent reports have described that this sort of dichroism is also induced by slantwise illumination of films of azobenzene polymers with non-polarized light.[3,4] The level and thermal stability of the azobenzene dichroism induced by linearly polarized light are influenced crucially by some factors including whether azobenzene molecules are embedded in polymer matrices chemically or physically and the thermal properties of polymers.[1] Usually, the relaxation of photo-oriented azobenzenes in polymer films is suppressed efficiently by tethering the chromophores to polymer backbones covalently and disappears thoroughly at temperatures above glass temperatures for amorphous polymers[5,6] and above transition temperatures leading to isotropic phase for liquid crystalline polymers.[7] Taking notice of the current situation that the photogeneration of optical anisotropy of polymer thin films has been of great significance because of the versatile practical applicability,[1,2] our efforts have been focused in particular to reveal the structural effects of azobenzenes as well as polymers on the level and thermostability of photodichroism of the chromophores. During our systematic studies on polarization photochemistry of azobenzenes, we have found anomalously thermostable photogenerated dichroism of *p*-cyanoazobenzene residues tethered to polymethacrylate backbones directly. We report here the considerable enhancement of photogenerated dichroism of the azobenzene by heating films of the polymer at elevated temperatures and its thermostability.

Poly(4-cyano-4'-methacryloyloxyazobenzene) (**1**) (Mw = 4.3 x 10^4, Mw/Mn = 3.3, Tg = 185 °C) was prepared by the radical polymerization of the corresponding monomer in tetrahydrofurane and purified by repeated precipitation in methanol from a tetrahydrofurane solution.



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A 1 wt% solution of the polymer in cyclohexanone was spin-cast on a silica plate to give a thin film of ca. 30 nm thickness. It was found that the *E-to-Z* photoisomerization upon exposure of the film to 365 nm light takes place in an extremely slow rate when compared with that of the corresponding unsubstituted azobenzene polymer, poly(4-methacryloyloxyazobenzene) (**2**).[8] The suppression of the photoisomerizability arises evidently from strong dipole-dipole interactions among highly polar azobenzene chromophores.

When a spin-cast film of **1** was illuminated with linearly polarized 365 nm light of a 0.1 J/cm^2 dose at room temperature leading to a ca. 9% *E-to-Z* conversion (Figure 1), the film exhibited a small dichroism of DR= -0.037 in a manner similar to that of **2**; DR is defined here as $(A_{//} - A_{\perp})/(A_{//} + A_{\perp})$ whereas $A_{//}$ and $A_{\perp}$ stand for absorbances at λ_{max} monitored by probe light with the electric vectors parallel to and perpendicular to the polarization plane of the linearly polarized UV light, respectively. Quite different behavior between **1** and **2** was observed when their films exposed to linearly polarized UV light was heated at elevated temperatures to recover *E*-isomers thermally. Whereas a photoinduced dichroism of **2** disappeared thoroughly after annealing, DR of the film of **1** was rather enhanced to become -0.20 after heating at 240 °C for 10 min. Note that the heating temperature is much higher than Tg of **1**. Thermal enhancement of photodichroism was also reported with regard to several liquid crystalline polymers having azobenzene side chains in their mesophase.[6] Further study revealed that the presence of cyclohexanone as a residual solvent in an as-cast film plays an essential role in the thermal enhancement of the photodichroism. When a spin-coated film of **1** was heated at 100 °C for 1 h to remove the solvent thoroughly before the photoirradiation, DR = -0.036 of the film, generated by the polarized light irradiation, was considerably reduced to be -0.0026 after heating at 240 °C for 10 min. These results can be interpreted as follows. As suggested in our previous papers,[9] the generation of photodichroism upon

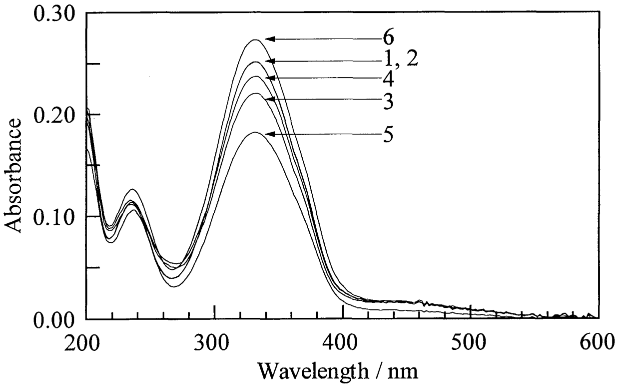

Figure 1. Polarized absorption spectra of a film of **1** before (1, 2) and after irradiation with linearly polarized 365 nm light at an exposure dose of 0.1 J cm^{-2} (3, 4), and annealed at 240 °C for 5 min (5, 6). The polarization plane of the probing light is parallel (1, 3, 5) and perpendicular (2, 4, 6) to that of the actinic light.

linearly polarized light irradiation stems from the axis-selective bleaching of molecules with a transition moment in parallel with the electric vector of the light and the consequent reorientation of molecular axis as a result of the repetition of *E/Z* photoisomerization. The presence of the residual solvent in a film leads favorably to the molecular photo-reorientation, while the photoinduced reorientation process, which requires a relatively large sweep volume, is essentially suppressed in a dried film owing to strong dipole-dipole interactions among the polar chromophores.

In order to obtain further information of the thermal enhancement of the photodichroism, an as-cast film of **1** was subjected to exposure to linearly polarized 436 nm light, which preferably forms *E*-isomer at a photostationary state. An exposure dose of 0.1 J/cm^2 gave rise to the emergence of DR = -0.037, which was followed by a marked increase of DR = -0.18. As seen in Figure 2, polarized IR spectra of the annealed film support the perpendicular reorientation of the CN groups. Note here that C=O groups are arranged anisotropically, indicating that polymer backbones suffer also from the uniaxial reorientation induced by annealing. The thermal enhancement of photodichroism was followed by monitoring DR values of a photoirradiated film after intermittent heat treatment for 3 min with gradual temperature rises. The results are shown in Figure 3. DR increases gradually at ca. 200 °C, slightly higher than the Tg, followed by an abrupt increase at ca. 250 °C or higher, and levels off at 300 °C. UV-visible absorption spectra of the heated film suggested that gradual decomposition of the azobenzene moieties takes place at 300 °C. However, the dichroism of **1** was maintained without decomposition at 240 °C for 5 h. It should be stressed that the dichroism is extremely stable at very high temperatures. This kind of extraordinary thermostability of photoinduced dichroism may result from the semi-crystalline nature of **1**, as suggested by Natansohn who employed an unsaturated polyester with azobenzene side chains.[10] Though detailed studies on thermal properties of **1** is needed, preliminary observation by a polarized microscope showed that an annealed film of **1** displays in fact optical anisotropy while the film is completely amorphous before heating. Consequently, the irradiation with linearly polarized light of an amorphous film of **1** generates dichroism in a relatively lower level, which is amplified by heat treatment above its Tg owing to the effective intermolecular interactions of the *p*-cyanoazobenzene units as a result of command effect of the photoaligned chromophoric residues.

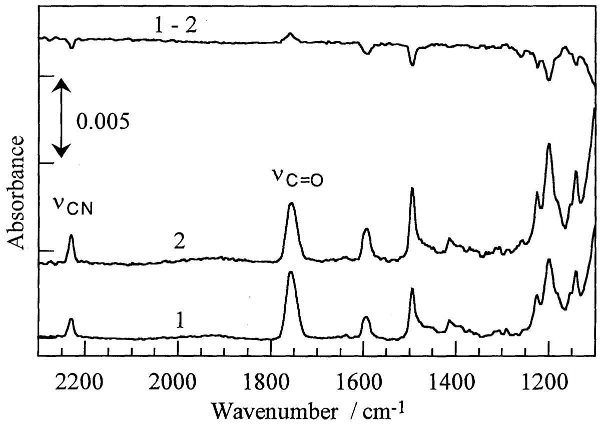

Figure 2. Polarized FT-IR spectra (1; parallel probing, 2; perpendicular probing, 1 - 2; difference of 1 from 2) of a film of 1 irradiated with linearly polarized 436 nm light at an exposure dose of 1 J cm^{-2} and annealed at 240 °C for 5 min.

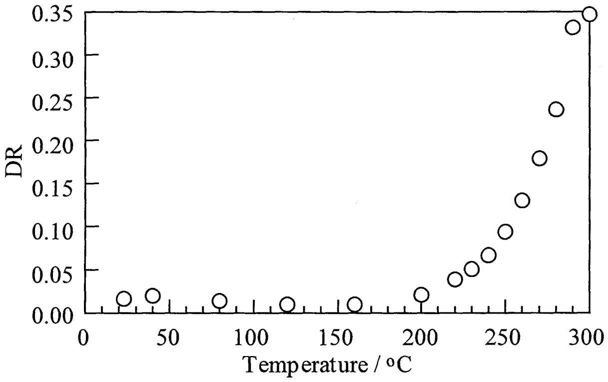

Figure 3. Thermally amplified photoinduced dichroism (DR) of a film of 1 irradiated with linearly polarized 436 nm light at an exposure dose of 0.2 J cm^{-2} as a function of annealing temperatures. The spectra were taken at room temperature after annealing at each temperature for 3 min.

In summary, photoinduced dichroism of thin films of **1** is considerably enhanced by heat treatment at elevated temperatures because of the semi-crystalline nature of the polymer. The enhanced optical anisotropy is quite thermally stable even at 240 °C so that this type of films is of practical significance in application to achieve the alignment control of nematic liquid crystals exhibiting thermal stability.[11]

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