High and stable photoinduced anisotropy in guest–host polymer mediated by chromophore aggregation

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We present a novel materials concept for optical inscription of stable birefringent optical elements into guest–host type polymers by making use of chromophore aggregation. The method is based on photoalignment of azobenzene chromophores, the aggregation of which leads to significant enhancement and stabilization of the photoinduced birefringence. The obtained order parameter of the molecular alignment (0.3) in combination with the exceptional thermal stability of the anisotropy renders the material system unique among amorphous azobenzene-containing polymers and provides a route toward designing efficient photoresponsive optical elements through the guest–host type approach.

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Photoinduced modifications of azobenzene-containing polymers have attracted significant research interest in the past decades [1,2]. The photoalignment of the azobenzene chromophores with polarized light can give rise to strong birefringence and refractive-index modulation, showing potential for rewritable optical storage, holographic recording, and inscription of diffractive optical elements [3,4]. Furthermore, the photomechanical effects driven by the photoisomerization reaction extend the applicability of the azobenzene-containing polymers toward light-driven micromachines and actuators [5–7]. The mobility of the azobenzene chromophores, and hence the response of the material system to optical fields, is highly sensitive to the local chromophore environment. Therefore, it is important to study the role of intermolecular interactions on the photoresponsive behavior of the material system. The control over such interactions may provide novel routes for the design of photoresponsive optical elements and devices for a variety of applications.

The optical response of conventional guest–host polymers, where the guest chromophores are dissolved in a passive polymer matrix, generally suffers from excessive aggregation at high chromophore concentrations (which is required for strong optical anisotropy) and low temporal stability of the chromophore alignment [8]. One way to address these problems is to covalently attach the chromophores to the polymer backbone [3]. However, if feasible, the guest–host type approach would be highly desirable because of the simple and cost-effective sample preparation compared to the covalently functionalized polymers. It has recently been shown that efficient photoresponsive polymers can be designed through supramolecular concepts [9], that is, by exploiting spontaneous noncovalent interactions to attach the chromophores to the polymer backbone [10–14].

In this Letter, we reveal an unexpected beneficial property of guest–host polymers. We show that chromophore aggregation can be exploited in a controlled manner to obtain high and thermally stable photoinduced anisotropy. Hence, the proposed concept provides a pathway toward using guest–host systems for the inscription of stable birefringent optical elements and also provides a new insight into the role of chromophore aggregation on the optical response of polymeric materials.

Our system consists of Disperse Red 1 chromophores (DR1; see the inset of Fig. 1) dissolved in a nonpolar polystyrene (PS) host. DR1 is a highly dipolar chromophore, exhibiting strong optical response and fast thermal cis–trans isomerization [15,16]. Because of its large ground-state dipole moment, DR1 is prone to aggregation even at moderate chromophore concentration, especially in nonpolar hosts [17]. We used two different DR1 concentrations: 7 wt. % (Sample 1) and 40 wt. % (Sample 2). In Sample 1, the chromophore content is sufficiently low so that the majority of the DR1 molecules are isolated [18]. By contrast, the DR1 concentration in Sample 2 is well above the aggregation threshold (which is below 20 wt. % for DR1 in PS) [18], and the absorption

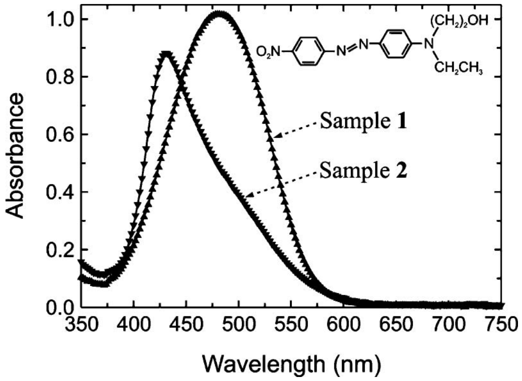

Fig. 1. Absorption spectra of the thin films of 7 wt. % (unaggregated; Sample 1, thickness 1630 nm) and 40 wt. % (aggregated; Sample 2, thickness 380 nm) of Disperse Red 1 in a PS host. The thicknesses of the samples were chosen to yield comparable optical densities at the writing wavelength. The chemical structure of Disperse Red 1 is shown in the inset.

maximum is blue shifted from approximately 480 nm (isolated DR1 molecules) to 430 nm (aggregated DR1 molecules), as illustrated in Fig. 1. Such a spectral shift follows from antiparallel stacking of the chromophores, often referred to as *H*-type aggregation [19,20]. Even if the exact supramolecular architecture of the DR1 aggregates cannot be deduced from simple spectral studies, the aggregate size is sufficiently small not to cause significant scattering at optical wavelengths. Thus, provided that the aggregates can be efficiently photoaligned, the polymeric thin films behave as optically homogeneous birefringent materials.

The photoalignment was performed by exciting the chromophores with a vertically polarized beam from a 457 nm continuous-wave diode-pumped solid state laser, and probed with a normally incident 820 nm diode laser beam (power approximately 1 mW) by measuring its transmission through a polarizer–sample–analyzer combination. The orientation of the polarizer/analyzer was set to ±45° with respect to the polarization of the excitation beam. The induced birefringence Δn is obtained from the transmission data using the equation $I = I_0 \sin^2(\pi \Delta n d/\lambda)$, where I_0 is the signal for parallel polarizer/analyzer orientation, d is the film thickness, and λ is the wavelength of the probe beam. The polarized absorption spectra ($A_\parallel$ and $A_\perp$ denote the absorbances parallel and perpendicular to the excitation beam polarization, respectively) of the samples were measured in real time with a fiber-optic spectrometer by using a fiber-coupled xenon lamp as a light source. The spectra were used to determine the order parameter $S = (A_\perp - A_\parallel)/(2A_\perp + A_\parallel)$ of the samples, which characterizes the in-plane alignment of the chromophores within the polymer matrix.

Figures 2(a) and 2(b) present the photoinduced birefringence of the samples upon irradiation with an intensity of 30 and 300 $\mathrm{mW/cm^2}$, respectively. Upon low-power irradiation, the obtained birefringence values are 4.7×10^{-3} (Sample 1) and 3.2×10^{-3} (Sample 2). That is, for low irradiation intensities the increased chromophore content in Sample 2 does not show up as a more efficient optical response. This can be attributed to hampered photoisomerization due to chromophore aggregation [21].

When the irradiation intensity is increased from 30 to 300 $\mathrm{mW/cm^2}$ [Fig. 2(b)], the induced birefringence remains essentially unchanged for Sample 1, whereas for Sample 2 the birefringence reaches a value of 0.06, being enhanced almost by a factor of 20 compared to the low-intensity irradiation. Furthermore, the induced birefringence is temporally stable (except for the 1% drop once the irradiation is ceased). No thermal relaxation was observed even when the sample was heated to 50°C for a period of 15 h. The birefringence can be erased with circularly polarized light, and subsequent irradiation with linearly polarized light restores approximately 80% of the birefringence. The rewritability suggests that the high and stable optical anisotropy encoded in Sample 2 is not driven by selective photodecomposition of the chromophores.

The polarized absorption spectra of Sample 2 for low- and high-intensity irradiation are shown in Figs. 3(a) and 3(b), respectively. The spectral order parameter deduced from Fig. 3(b) for the 300 $\mathrm{mW/cm^2}$ case attains a value of 0.30 (cf. $S < 0.02$ for 30 $\mathrm{mW/cm^2}$ irradiation), which, to the best of our knowledge, is the highest value reported in amorphous polymers containing dipolar chromophores. Note that irradiation with linearly polarized light does not break the aggregates in our material, unlike what has been reported to occur for some liquid-crystalline side-chain polymers [22–24]. The spectrum is slightly broadened upon irradiation, but the absorption maximum is not shifted [see the inset of Fig. 3(b)], indicating that the majority of the chromophores also remain aggregated in the birefringent state.

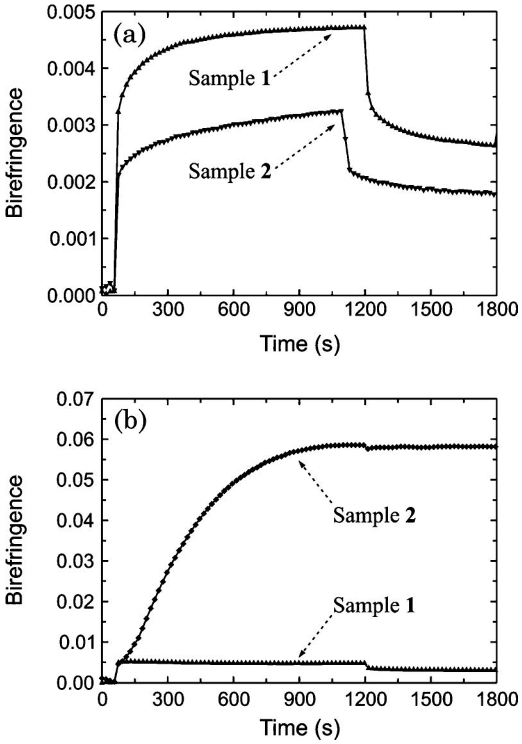

Fig. 2. Photoinduced birefringence for Samples 1 and 2 upon irradiation with linearly polarized light at 457 nm with a power density of (a) 30 $\mathrm{mW/cm^2}$ and (b) 300 $\mathrm{mW/cm^2}$. The irradiation period is from 60 to 1200 s.

The main conclusion of the above results is that chromophore aggregates can provide high and stable optical anisotropy to the material system under sufficiently intense irradiation, which opens up the possibility to produce stable birefringent optical materials through the conventional guest–host approach. The high value of the obtained order parameter of the molecular alignment (0.3) together with the lack of thermal randomization makes the material system very attractive in view of potential applications in optics and photonics. In fact, the magnitude and the stability of the photoinduced anisotropy in the aggregated guest–host system studied here surpasses the values reported in covalently-functionalized side-chain polymers containing the same DR1 weight fraction [25].

A detailed study on the photoresponsive behavior of the DR1/PS guest–host systems, now underway, should provide us with a more accurate picture of the nature of the photoinduced modification of the chromophore aggregates and allow us to optimize the materials composition and the writing parameters to further increase the photoinduced anisotropy. Most of all, we consider the present study to be an important step toward a fundamental

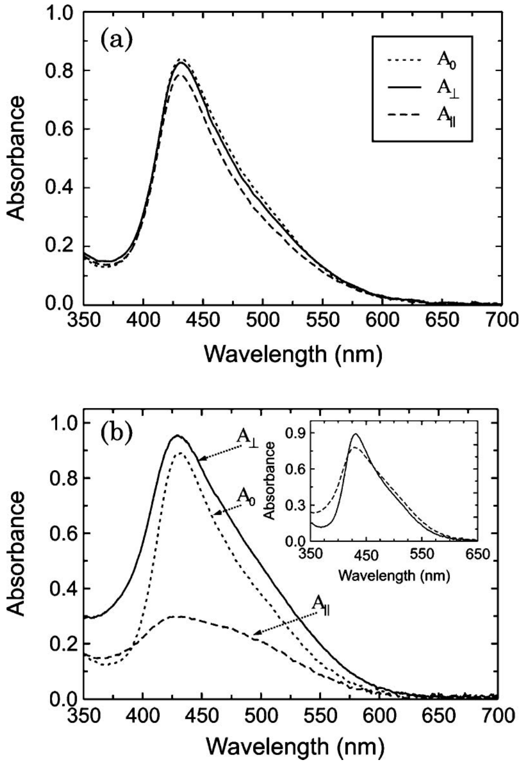

Fig. 3. (a), (b) Polarized absorption spectra, measured at normal incidence, for Sample 2 upon irradiation with 30 and 300 $\mathrm{mW/cm^2}$ intensity, respectively. The inset of (b) displays the unpolarized absorption spectrum of Sample 2 before (solid curve) and after (dashed curve) irradiation (457 nm, 300 $\mathrm{mW/cm^2}$, 20 min). A_0 denotes the absorption spectrum prior to irradiation.

understanding of the role of intermolecular interactions on the photoinduced motions and physical processes occurring in amorphous azobenzene-containing polymers. This will be an essential prerequisite for the design of future photoresponsive materials for photonic applications.

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