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## Enhanced photoinduced birefringence in polymer-dye complexes: Hydrogen bonding makes a difference

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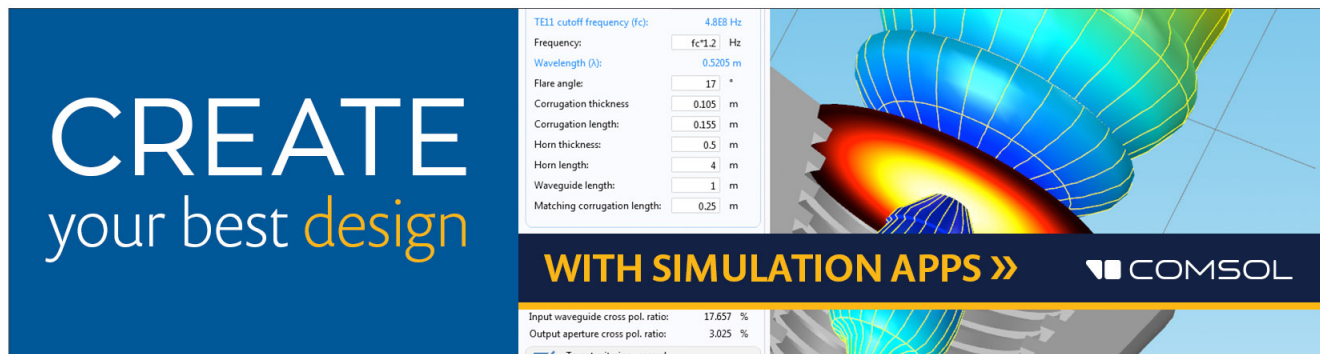
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## Enhanced photoinduced birefringence in polymer-dye complexes: Hydrogen bonding makes a difference

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The authors demonstrate that photoinduced birefringence in azo-dye-doped polymers is strongly enhanced by hydrogen bonding between the guest molecules and the polymer host. The primary mechanism behind the enhancement is the possibility to use high dye doping levels compared to conventional guest-host systems because dye aggregation is restrained by hydrogen bonding. Moreover, hydrogen bonding reduces the mobility of the guest molecules in the polymer host leading to a larger fraction of the induced birefringence to be preserved after the excitation light has been turned off. © 2007 American Institute of Physics. [DOI: 10.1063/1.2714292]

Photoinduced optical anisotropy of amorphous azobenzene-containing polymers has emerged as a source of exciting optical phenomena,<sup>1,2</sup> which are of potential use in applications ranging from optical data storage<sup>3</sup> and switching<sup>4</sup> to waveguiding<sup>5</sup> and diffractive optical elements.<sup>6,7</sup> The photoactive properties of such materials arise from the photoisomerization of the N=N double bond of the azo molecules. Upon excitation with linearly polarized light, the molecules with sufficient dipolar component in the polarization direction undergo successive isomerization cycles and change their orientation. Due to the selective excitation, the molecules tend to line up perpendicularly to the polarization of the writing beam, thus becoming insensitive to the excitation light. The anisotropic molecular orientation results in stable photoinduced birefringence or dichroism, which can be optically erased, for instance, by randomizing the alignment with circularly polarized light.<sup>8</sup>

In the simplest form of amorphous photoactive polymers, the azo dyes are dissolved in a passive polymer matrix. Such guest-host systems are flexible and cost effective as they only require mixing of the constituents to produce a desired compound. However, their applicability is restricted by aggregation of the dye molecules due to intermolecular dipole-dipole interactions, which limits the dye concentration to moderate levels. The aggregation changes the spectroscopic properties of the material, and also affects the photoinduced reorientation process.<sup>9–12</sup> Furthermore, the temporal and thermal stabilities of the induced anisotropy in guest-host systems are typically poor. The photoalignment and the subsequent relaxation process is strongly influenced by the local environment provided by the polymer matrix.<sup>13</sup> In particular, by using polymers with high glass-transition temperature ( $T_g$ ), the stability of the photoinduced orientation can be increased.<sup>14</sup>

The drawbacks of guest-host systems have been addressed by covalently bonding the photoactive moieties to the polymer backbone to form side-chain systems. In such systems, the dye concentration can be significantly increased, and efficient photoalignment can be induced even when an

azo molecule is attached to each repeating unit of the polymer.<sup>5,9</sup> By combining the high dye concentration with optimized molecular design, copolymers with exceptionally large photoinduced birefringence have been synthesized.<sup>15–17</sup> Dye aggregation takes place also in side-chain polymers, but the onset of the dipole-dipole interactions is delayed to higher concentrations. A further advantage of side-chain polymers is the long-term stability of the induced anisotropy, which is significantly higher than in corresponding guest-host systems.<sup>14</sup> From a practical point of view, however, covalently linked polymers are considerably less attractive than guest-host systems, as organic synthesis is required for each combination of a polymer and an active molecule, which makes the sample preparation slower and more expensive.

We have previously reported that dye aggregation in a polymer host can be suppressed by forming hydrogen-bonded or protonated polymer-dye complexes.<sup>18</sup> Although weak, spontaneous noncovalent interactions enable high dye concentrations to be incorporated into the host polymer without sacrificing the ease of processing of conventional guest-host systems. Moreover, Banach *et al.* have reported that such specific noncovalent interactions can be used to enhance the electro-optic response of poled guest-host polymers.<sup>19</sup> In this letter, we show that hydrogen bonding between the dyes and the polymer host and the subsequent delay in the onset of dye aggregation can be used to obtain significantly higher photoinduced birefringence values compared to similar guest-host systems where no such interactions occur. Furthermore, the stability of the induced birefringence is enhanced in hydrogen-bonded guest-host systems, reaching a level comparable to the one traditionally obtained in covalently linked polymers.

We study the photoalignment of a common azo dye, Disperse Red 1 (DR1), doped in different polymers that are structurally similar but contain different functional groups (Fig. 1). As polymer hosts we used polystyrene (PS), ( $M_n = 50\,000$ ,  $T_g \approx 100^\circ\text{C}$ ), poly(4-vinylphenol) (PVPh), ( $M_n = 1100\text{--}5200$ ,  $T_g \approx 120^\circ\text{C}$ ), and poly(4-vinylpyridine) (P4VP) ( $M_n = 50\,000$ ,  $T_g \approx 140^\circ\text{C}$ ). PS is a nonpolar polymer that acts as an inert reference with no significant interactions with the polar DR1 molecules. PVPh and P4VP are polar

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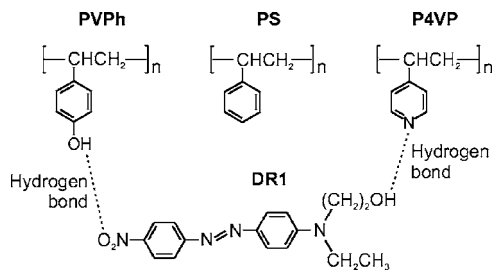


FIG. 1. Chemical structures of the materials used.

polymers containing functional groups that enable specific intermolecular interactions between the polymer host and the DR1 molecules. More precisely, the phenol and pyridine groups of PVPPh and P4VP can form hydrogen bonds with the nitrobenzene and hydroxyl groups of DR1, respectively.<sup>19,20</sup>

Thin films with different doping levels of DR1 in the polymer hosts were prepared by spin coating the constituents from dimethylformamide (DR1 in PVPPh/P4VP) or tetrahydrofuran (DR1 in PS) onto clean glass substrates. The film thicknesses were measured with a DEKTAK 3 surface profiler, and they ranged from 70 to 700 nm. The thicknesses were varied from sample to sample to maintain constant optical density at the writing wavelength (532 nm), which is necessary for meaningful comparison of the photoinduced anisotropy in different samples.<sup>21</sup> UV-vis absorption spectra were taken with a Perkin-Elmer Lambda 950 spectrophotometer.

The photoalignment was performed by using an *s*-polarized (normal to the plane of incidence) beam from a continuous-wave Nd:YVO laser (532 nm) with an angle of incidence of approximately 10°. The process was monitored with a diode laser (850 nm), normally incident on the sample. The transmitted intensity of the monitoring beam through a polarizer-sample-analyzer combination was measured with a photodiode to probe the photoinduced anisotropy. The orientation of the polarizer/analyzer was set to ±45° with respect to the polarization direction of the writing beam. The birefringence  $|\Delta n|$  can be obtained from the transmission data as

$$I = I_0 \sin^2\left(\frac{\pi|\Delta n|d}{\lambda}\right), \quad (1)$$

where  $I_0$  is the photodiode signal for parallel polarizer/analyzer orientation (in the absence of the sample),  $d$  is the film thickness, and  $\lambda$  is the wavelength of the monitoring beam.

The absorption spectra of the samples containing different concentrations (5–30 wt %) of DR1 doped in PS, PVPPh,

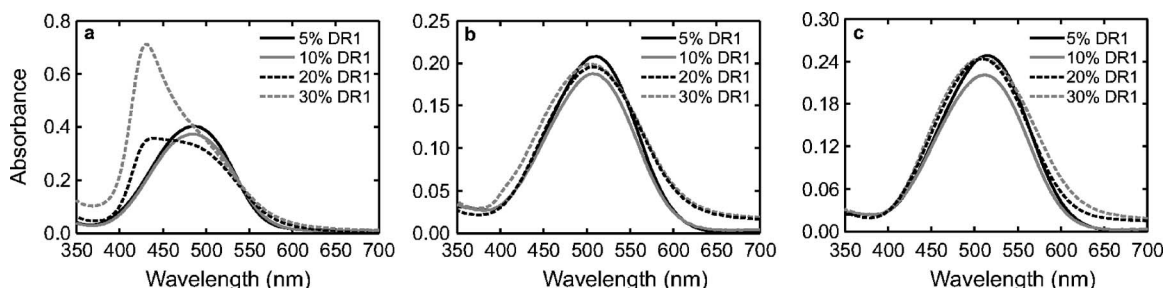


FIG. 2. Absorption spectra of thin films of (a) DR1 in PS, (b) DR1 in PVPPh, and (c) DR1 in P4VP.

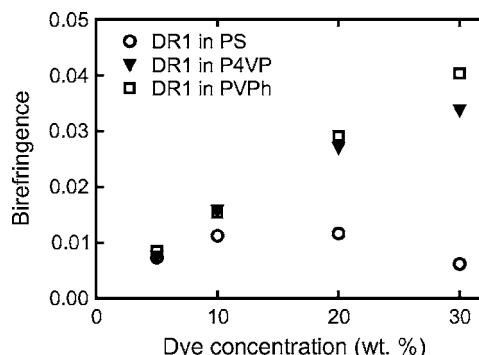


FIG. 3. Photoinduced birefringence as a function of dye concentration for DR1 in PS, P4VP, and PVPPh. The reported values are the saturation values of the birefringence while the writing beam is applied on the sample. The writing beam intensity was 150 mW/cm<sup>2</sup>.

and P4VP are presented in Fig. 2. In PS, DR1 aggregation results in a significant blueshift of the absorption maximum at concentrations exceeding 10 wt %. In PVPPh and P4VP this behavior is absent, indicating that most of the dye molecules remain isolated in the investigated concentration range. The reduced aggregation in the active host polymers is attributed to the coupling of DR1 to the polymer chains through specific noncovalent interactions, providing a more favorable environment for the dye molecules.<sup>18,19</sup>

Figure 3 shows the photoinduced birefringence of DR1 in PS, PVPPh, and P4VP as a function of dye concentration. At 5 wt % DR1 concentration, the birefringence is essentially the same in each matrix. However, at higher concentrations the difference between the polymers is significant. In PS the maximum birefringence (approximately 0.01) is achieved at 10–20 wt % after which it decreases to 0.005 at 30 wt %. In PVPPh birefringence increases approximately linearly, reaching a value >0.04 at the 30 wt % DR1 concentration. In P4VP the behavior is similar, aside from the slight saturation observed at high concentrations. This result correlates well with the absorption spectra of Fig. 2 and addresses the destructive impact of dye aggregation on the photoinduced anisotropy. We also remark that the 30 wt % DR1 concentration corresponds approximately to a molar ratio of 0.15:1 of DR1:polymer unit. We have shown earlier that by exploiting stronger noncovalent interactions such as proton transfer, the onset of aggregation can be delayed until essentially all functional groups of the polymer are occupied (1:1 molar ratio).<sup>18</sup> Thus we expect that by optimizing the functional groups of the material system, the range of linear growth of the birefringence can be extended to even higher concentrations.

Apart from providing the possibility to use higher dye concentrations, specific noncovalent interactions can de-

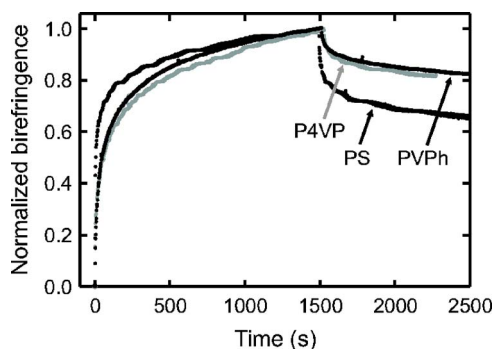


FIG. 4. Writing/relaxation curves for samples containing 5 wt % of DR1 in PS, PVPh, and P4VP. The irradiation period was 0–1500 s and the writing beam intensity was 30 mW/cm<sup>2</sup>.

crease the mobility of the dyes, thus improving the temporal stability of their net alignment.<sup>19</sup> In our case, dye concentration played no essential role in relaxation, implying that plasticization effects due to addition of the dye are insignificant. Hence, we only consider the samples containing 5 wt % of DR1 (each having essentially the same birefringence) in more detail. Figure 4 shows the normalized writing/relaxation curves for these samples. The writing process is seen to be slower in PVPh and P4VP than in PS, which could be due to the lower mobility of the DR1 molecules in the interacting polymers. However, our preliminary results on other polymer-dye complexes suggest that this limitation could be overcome simply by choosing a proper pair of materials. The most notable difference between the polymers is in the stability of the birefringence. The fitting of the normalized decay curves with a biexponential function yields a remnant birefringence of 64% from the saturation value in PS, while in PVPh and P4VP this value exceeds 80%. Such a high stability is comparable to the values of DR1-containing side-chain polymers.<sup>9</sup> This result emphasizes that *spontaneous* noncovalent interactions provide a promising alternative to the more traditional approach based on covalent interactions. Note also that the difference in the long-term stability probably cannot be accounted for by the small differences in the glass-transition temperatures; for PS and PVPh this difference is only approximately 20 °C.

In conclusion, we have shown that hydrogen bonding between azo dyes and polymer chains can be used to enhance the photoinduced anisotropy in guest-host polymers. Such specific interactions allow the dye concentration to be increased without aggregation, resulting in birefringence value of 0.04 at 30 wt % DR1 in PVPh. Moreover, the long-term

stability is comparable to the stability of similar side-chain polymers—more than 80% of the birefringence is conserved after the excitation beam is turned off. The concept provides a particularly simple method to obtain high and stable photoinduced birefringence by using guest-host polymers and is potentially useful in various applications where dye aggregation can be a limiting factor for the system performance.

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