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Different chromophore concentration dependence of photoinduced birefringence and second-order susceptibility in all-optical poling

Matti Virkki,[1,a)] Martti Kauranen,[1] and Arri Priimagi[2,3]

[1]*Department of Physics, Tampere University of Technology, P.O. Box 692, FI-33101 Tampere, Finland*
[2]*Department of Applied Physics, Aalto University, P.O. Box 13500, FI-00076 Aalto, Finland*
[3]*Chemical Resources Laboratory, Tokyo Institute of Technology, Japan*

We study photoinduced axial and polar ordering in Disperse Red 1 azobenzene–poly(4-vinylpyridine) polymer systems by monitoring both birefringence and second-harmonic generation during all-optical poling. The two responses are found to exhibit very distinct dependences on chromophore concentration: the photoinduced birefringence increasing up to 51 wt. % concentration and the second-order response reaching its peak already at 23 wt. %. The results show that the polar order required for second-order response is highly sensitive to chromophore-chromophore intermolecular interactions, whereas the birefringence is much more robust against such effects. © *2011 American Institute of Physics*. [doi:10.1063/1.3657829]

The linear and nonlinear optical properties of azobenzene-containing polymeric materials arise from the reversible photoisomerization of the azobenzene derivatives.[1] The isomerization process provides the possibility to photo-orient the chromophores with polarized light[2] and to induce macroscopic mass transport in the material.[3] Such photoinduced motions render azo-polymers promising for optical data storage, switching, diffractive optics, and nanotechnology.[3–6]

The light-induced molecular ordering in azo-polymers is greatly affected by the properties of the exciting light. Excitation with a single linearly polarized beam orients the molecules perpendicular to the polarization direction, and the resulting anisotropic ordering gives rise to birefringence.[2] On the other hand, excitation with a superposition of beams at a fundamental frequency and its second-harmonic gives rise to two- and one-photon excitation of the chromophores redistributing the molecules into a noncentrosymmetric polar ordering (Fig. 1). This process is known as *all-optical poling*.[7,8]

The polar ordering depends delicately on electrostatic interactions between the chromophores. Such interactions account for the fact that the second-order nonlinear optical response of azo-polymers does not increase linearly with chromophore concentration, but exhibits a maximum at a concentration value dictated by the dipole moment of the chromophores.[9,10] This optimal concentration has been studied in noncovalently[11] and covalently[12,13] coupled azo-polymer systems using electric field poling. On the other hand, we have shown that, as long as chromophore aggregation can be suppressed, the photoinduced birefringence increases linearly with concentration[14] and that intermolecular interactions can even enhance the photo-orientation process when efficient packing of the molecules is possible.[15,16] Hence, chromophore-chromophore interactions seem to play a distinct role in the axial and polar molecular alignment. All-optical poling leads to polar as well as axial molecular ordering.[8] Hence, it is important to understand whether the

same or different mechanisms constrain the birefringence and second-order response that can be achieved by all-optical poling.

In this letter, we simultaneously monitor the photoinduced birefringence and second-harmonic generation (SHG) during all-optical poling and show that the two processes exhibit distinct concentration dependences. The photoinduced birefringence levels off only at very high azobenzene concentrations. The photoinduced noncentrosymmetry, on the other hand, reaches its maximum at much lower concentration. This result provides important information about the molecular-level interactions that take place in azo-polymer systems during photoinduced chromophore redistribution, and highlights the different role of electrostatic interactions in photoinduced birefringence and all-optical poling.

In order to access a wide concentration range, we take advantage of the selective hydrogen bonding between the chromophores and the polymer matrix, which allows high chromophore concentration without deteriorating sample quality.[17,18] Thin film samples were fabricated from Disperse Red 1 (DR1) and poly(4-vinylpyridine) (P4VP, $M_w = 22\,000$ g/mol), which were used as received. Their molecular structures are show in
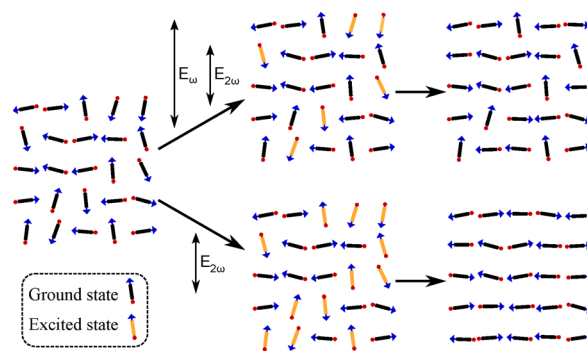

FIG. 1. (Color online) Redistribution of the in-plane molecular alignment of an isotropic structure (left) into a noncentrosymmetric structure (upper right) through selective excitation with a dual-frequency beam and into a birefringent structure (lower right) through excitation with a single linearly polarized beam.

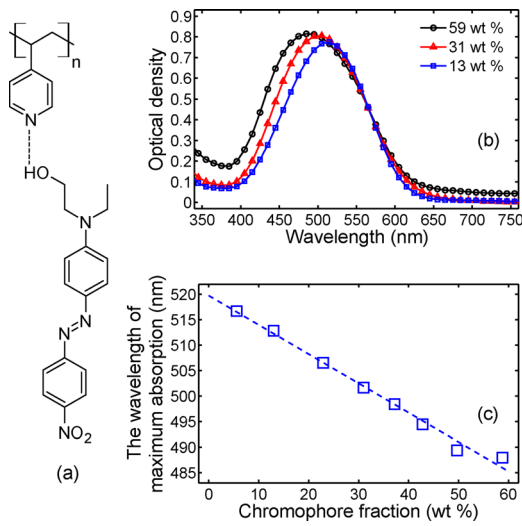a)Electronic mail: matti.virkki@tut.fi.

FIG. 2. (Color online) (a) Molecular structure of Disperse Red 1 hydrogen bonded to poly(4-vinylpyridine). (b) Absorption spectra for samples with low (13 wt. %), medium (31 wt. %), and high (59 wt. %) chromophore mass fraction. (c) Wavelength of the absorption maximum as a function of chromophore concentration. The dashed line is a linear fit to the data.

Fig. 2(a). The chromophore and polymer were separately dissolved in dimethylformamide and filtered through a syringe filter with 200 nm pore size. The solutions were mixed in different proportions to form eight complex solutions with chromophore mass fraction ranging from 5.6 to 59 wt. %. The solutions were spin-coated on glass substrates. The absorbance of the samples at 532 nm was fixed to ca. 0.7 by controlling the film thickness.

All-optical poling was performed with a similar setup as in Ref. 8. The dual-frequency poling beam was a combination of the fundamental beam (1064 nm) of a Q-switched diode-pumped Nd:YAG laser (8 ns, 100 Hz), and its second-harmonic at 532 nm. The pulse energies were $20\,\mu J$ for the fundamental *writing* beam and $0{,}4\,\mu J$ for the second-harmonic *seeding* beam. The same ratio of the writing and seeding beams could be used for all samples due to their equal absorbance at 532 nm.[8] The phase difference between the beams was found to have minimal effect on the photoinduced noncentrosymmetry due to the coherence properties of the multimode laser used, hence no phase optimization was required.

The photoinduced birefringence was measured with a probe beam at small angle to the poling beam line. The probe was produced with a 5 mW diode laser at 780 nm. The sample was placed between crossed polarizers with ±45° orientation with respect to the polarization of the poling beams. The transmitted intensity was measured with a photodiode and the birefringence $|\Delta n|$ was obtained from[19]

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

where I_0 is the photodiode signal with the two polarizers in parallel orientation, d is the film thickness, and λ the wavelength of the probe beam.

The photoinduced noncentrosymmetry was probed by measuring the second-harmonic produced by the sample. The seeding beam was periodically blocked by placing a long-pass filter before the sample. During the brief interrup-
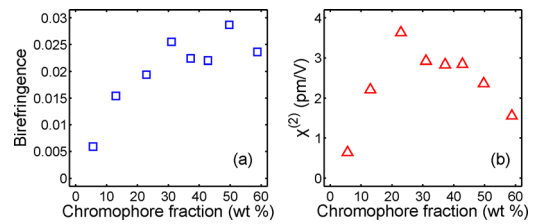

FIG. 3. (Color online) Saturation values of (a) photoinduced birefringence and (b) second-order susceptibility as a function of chromophore concentration during all-optical poling.

tion of poling, the SHG from the sample, I_{SHG}^S, was measured using a photomultiplier tube. A reference signal, I_{SHG}^Q, was measured from the maximum of the Maker fringes of a quartz crystal. The effective second-order susceptibility $\chi_{eff}^{(2)}$ of the sample is then

$$\chi_{eff}^{(2)} = \chi_{xxx,Q}^{(2)} \left(\frac{n_{\omega,S}}{n_{\omega,Q} d \Delta k_Q}\right)\sqrt{\frac{I_{SHG}^S \, n_{2\omega,S}}{I_{SHG}^Q \, n_{2\omega,Q}} 10^{OD}},\qquad(2)$$

where $\chi_{xxx,Q}^{(2)} = 0.6\,\text{pm/V}$ (Ref. 20) is the relevant susceptibility component of quartz, $n_{\omega,S}$ and $n_{\omega,Q}$ are the refractive indices of the sample and quartz at the fundamental frequency and $n_{2\omega,S}$ and $n_{2\omega,Q}$ at the second-harmonic frequency, $\Delta k_Q = 0.15 \times 10^6\,\text{m}^{-1}$ (Ref. 8) is the wave vector mismatch in quartz, and OD is the optical density of the sample at the second-harmonic wavelength.

The absorption spectra for selected samples are shown in Fig. 2(b) and the wavelengths of maximum absorption in Fig. 2(c). Increasing chromophore concentration leads to broadening and almost linear blue shift of the DR1 absorption maximum at ca. 500 nm. We attribute this gradual blue shift mainly to the fact that the increasing chromophore concentration changes the polarity of the local environment of the chromophores, which gives rise to solvatochromic shift in the absorption maximum.[21] Large-scale chromophore aggregates, on the other hand, would lead to much more pronounced changes in the absorption spectra,[17,22] but here their formation is prevented by the noncovalent coupling between the chromophores and the polymer matrix.

The saturation values for the photoinduced birefringence and second-order susceptibility are shown in Fig. 3. The birefringence increases systematically with chromophore concentration, before leveling off at the highest concentrations (Fig. 3(a)). The maximum value of 0.029 was obtained at 51 wt. % azobenzene concentration. Similar concentration dependence, with a more pronounced drop after 51 wt. %, was found also when the birefringence was induced with a 514 nm beam in separate measurements (data not shown). The concentration dependence of the second-order susceptibility, on the other hand, was very different compared to the birefringence (Fig. 3(b)), with a maximum value of 3.6 pm/V already at 23 wt. % chromophore concentration. Assuming homogeneous chromophore distribution, this corresponds to chromophore number density of $5.3 \times 10^{20}\,\text{1/cm}^3$ and 1.2 nm average distance between the chromophores. Our results are in reasonable agreement with reports for other Disperse Red type molecules.[10]

The notable difference in the concentration dependence of photoinduced birefringence and noncentrosymmetry can

be understood by considering the interactions between the chromophores at high concentrations. For high-dipole-moment chromophores, such as DR1, antiparallel molecular packing is favored over parallel one,[23] and such centrosymmetric packing is detrimental for the second-order response.[24,25] The macroscopic second-order response is thus determined by the competition between the poling field, which drives the molecules into noncentrosymmetric arrangement and the chromophore-chromophore interactions, which drive the molecules into centrosymmetric arrangement.[9] The latter is more prominent at high concentrations, hence decreasing the second-order susceptibility. At the same time, hydrogen bonding between the chromophores and the polymer matrix prevents the formation of large chromophore aggregates. The dipolar interactions that play against noncentrosymmetric chromophore alignment do not prevent their axial ordering, provided that the aggregates remain sufficiently small. We also note that the dynamics and the temporal stability of the photoinduced processes can depend on intermolecular interactions.[15,18] In the present case, however, both the dynamics and stability for different samples were essentially the same.

The results are in good agreement with Refs. 11 and 12 for electrically poled samples as well as with our previous work on photoinduced birefringence, demonstrating (1) that the concentration dependence of the second-order susceptibility is similar in all-optically poled and electrically poled polymer films and (2) that the concentration dependence of photoinduced birefringence is independent of whether it is induced directly with continuous-wave irradiation or during all-optical poling as here.

In conclusion, we have studied the effect of chromophore concentration on photoinduced birefringence and second-order nonlinear response in hydrogen-bonded DR1–P4VP complexes. The two effects exhibit very different concentration dependences even when induced simultaneously during all-optical poling. The second-order response is diminished at high concentrations due to chromophore-chromophore intermolecular interactions, whereas the photoinduced birefringence is more robust against such effects.

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