Hydrogen-Bonded Polymer−Azobenzene Complexes: Enhanced Photoinduced Birefringence with High Temporal Stability through Interplay of Intermolecular Interactions

Arri Priimagi,*[,†] Jaana Vapaavuori,[†] Francisco J. Rodriguez,[‡] Charl F. J. Faul,[§]
Markku T. Heino,[||] Olli Ikkala,*[,†] Martti Kauranen,[‡] and Matti Kaivola[†]

Department of Engineering Physics and Center for New Materials, Helsinki University of Technology, P.O. Box 3500, FI-02015 TKK, Espoo, Finland, Institute of Physics, Tampere University of Technology, P.O. Box 692, FI-33101 Tampere, Finland, School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom, and Nokia Research Center, Nanosciences, Itämerenkatu 11−13, FI-00180 Helsinki, Finland

Received March 31, 2008. Revised Manuscript Received June 30, 2008

We study the photoresponsive behavior of thin films of supramolecular 4-nitro-4′-hydroxyazobenzene−poly(4-vinylpyridine) complexes. Hydrogen bonding between the phenol and pyridine moieties allows attaching a chromophore to essentially each repeat unit of the polymer, thereby suppressing macroscopic phase separation and crystallization. Moreover, the noncooperative nature of hydrogen bonding leads to random complexation of the chromophores to the polymer backbone, which enables a systematic study of the effect of chromophore concentration on the photo-orientation of the complexes. Two regimes are observed: Photoinduced birefringence increases linearly with the chromophore concentration until nominally every third polymer repeat unit is occupied. Beyond that concentration, a new regime is observed with a drastically steeper slope of increase. The latter regime is connected to the interplay between the formation of a hydrogen-bonded supramolecular complex and intermolecular interactions between the mesogenic chromophores. Such a behavior significantly enhances the birefringence at high concentrations and also leads to high remnant birefringence. Hence, the supramolecular approach yields a superior optical performance compared to guest−host polymers and even surpasses the properties of many covalently functionalized polymers, while still allowing modular tunability of the materials properties.

1. Introduction

Photoresponsive polymers containing azobenzene chromophores are actively investigated for various applications, including optical information storage,[1,2] holographic recording,[3] and frequency doubling.[4] Their optical properties stem from reversible photoisomerization of the azobenzene moiety,[5] providing a mechanism for chromophore photo-orientation[6] and for the inscription of volume and surface-relief gratings.[7−9] The photo-orientation is achieved by excitation of the azobenzene chromophores with linearly polarized light, which leads to successive isomerization and reorientation of the chromophores with a sufficiently large transition dipole moment along the direction of the exciting field. The molecules tend to line up perpendicular to the polarization direction of the excitation beam, thus becoming inert to the incident irradiation. The anisotropic orientation of the chromophores leads to in-plane birefringence, which can be nondestructively read with a nonresonant probe beam and erased by randomizing the molecular orientation with, for example, circularly polarized light. Once the excitation light has been turned off, the birefringence decreases because of thermal diffusion and cis−trans isomerization of the chromophores. Both the fraction of remnant birefringence and the efficiency of photo-orientation are highly dependent on the structure of the chromophores as well as on their local environment.[7] In particular, the role of chromophore−chromophore intermolecular interactions in the photoinduced processes is not well understood despite various studies employing different polymer systems.[10−12]

Most of the recent efforts on photoinduced anisotropy of azo-containing polymers have been concentrated on exploring new material concepts to obtain efficient and stable photo-orientation. The state-of-the-art materials typically use covalent bonding to attach the chromophores to the polymer

---

* Corresponding authors. Fax +358 9 451 3155. E-mail: arri.priimagi@tkk.fi (A.P), olli.ikkala@tkk.fi (O.I.).
[†] Helsinki University of Technology.
[‡] Tampere University of Technology.
[§] University of Bristol.
[||] Nokia Research Center.

(1) Natansohn, A.; Rochon, P. *Adv. Mater.* **1999**, *11*, 1387.
(2) Kawata, S.; Kawata, Y. *Chem. Rev.* **2000**, *100*, 1777.
(3) Zilker, S. J.; Bieringer, T.; Haarer, D.; Stein, R. S.; van Egmond, J. W.; Kostromine, S. G. *Adv. Mater.* **1998**, *10*, 855.
(4) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817.
(5) Rau, H. In *Photoreactive Organic Thin Films*; Sekkat, Z., Knoll, W. Eds.; Academic Press: San Diego, CA, 2002; Chapter 1.
(6) Dumont, M.; El Osman, A. *Chem. Phys.* **1999**, *245*, 437.
(7) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139.
(8) Todorov, T.; Nikolova, L.; Tomova, N. *Appl. Opt.* **1984**, *23*, 4309.
(9) Viswanathan, N. K.; Kim, D. Y.; Bian, S.; Williams, J.; Liu, W.; Li, L.; Samuelson, L.; Kumar, J.; Tripathy, S. K. *J. Mater. Chem.* **1999**, *9*, 1941.
(10) Brown, D.; Natansohn, A.; Rochon, P. *Macromolecules* **1995**, *28*, 6116.
(11) Labarthet, F. L.; Freiberg, S.; Pellerin, C.; Pézolet, M.; Natansohn, A.; Rochon, P. *Macromolecules* **2000**, *33*, 6815.
(12) Fischer, T.; Läsker, L.; Rutloh, M.; Czapla, S.; Stumpe, J. *Mol. Cryst. Liq. Cryst.* **1997**, *299*, 293.

10.1021/cm800908m CCC: $40.75

backbone.[13−15] Such covalently functionalized polymers can contain a high chromophore concentration without aggregation, providing a large response to optical fields. Moreover, the induced anisotropy in such systems can be highly stable. However, the laborious synthesis and lack of simple modular tunability reduce their practical feasibility. A facile and easy-to-process alternative is provided by guest−host polymers where the chromophores are simply mixed into the polymer matrix. However, their performance is limited by chromophore aggregation and phase separation, resulting in increased optical scattering losses, lowered optical response, and poor temporal stability.[16,17]

To combine the advantages of covalently functionalized polymers and guest−host polymers, concepts developed in supramolecular chemistry become useful, allowing complexation (or association) of the chromophores to the polymer backbone using matching intermolecular physical interactions.[18−21] This was first pointed out through the demonstration that noncovalent attachment of chromophores to the polymer backbone increases the second-order nonlinear optical response of the material compared to conventional guest−host polymer systems.[22] Recently, it was shown that ionic polymer−chromophore complexes exhibit liquid-crystalline order and yield very high photoinduced birefringence with impressive temporal and thermal stability.[23] Furthermore, hydrogen-bonded and ionically bonded complexes have recently also been used to efficiently inscribe surface-relief gratings,[23−26] and hydrogen-bonded side-chain polymers have been shown to be applicable for liquid-crystal alignment.[27]

We have previously demonstrated that even weak noncovalent interactions between the polymer matrix and the chromophores reduce the tendency of the chromophores to aggregate and that such interactions can thereby be exploited to enhance the chromophore photo-orientation.[28] Here, we employ the relatively strong phenol−pyridine hydrogen bonding and systematically investigate the effect of chromophore concentration on the photoinduced birefringence. The modular tunability is provided by the noncooperative nature of hydrogen bonding, leading to random complexation of the chromophores to the polymer backbone, as opposed to ionic complexes where cooperative binding, which takes place in a zipper-like fashion, typically leads to a 1:1 stoichiometry between the constituents.[20] We show that hydrogen bonding between 4-nitro-4′-hydroxyazobenzene and poly(4-vinylpyridine) enables attaching a chromophore to each repeating unit of the polymer without macro-phase-separation. Moreover, the photoinduced birefringence of the investigated complexes is significantly enhanced and stabilized at high chromophore concentrations. We attribute this enhancement to the onset of mutual interactions between the mesogenic chromophores, which opens up the possibility to engineer the optical properties of these supramolecular materials in a wide range.

2. Materials and Experimental Methods

4-nitro-4′-hydroxyazobenzene (NHA) was synthesized according to the following method:[29] 4-nitroaniline (5 g, 0.036mol) was dissolved in a mixture of concentrated HCl (13 cm^3) and distilled water (13 cm^3), by gently heating and stirring. After complete dissolution, the solution was cooled in an ice bath to a temperature of ca. 3 °C. A solution of $NaNO_2$ (3.7 g, 0.054mol) in distilled water (8 cm^3) was added in a dropwise fashion to cold nitroaniline-containing solution. The diazonium salt solution formed in this way was then placed in a freezer to keep its temperature below 5 °C. Separately, phenol (3.3 g, 0.035mol) was dissolved in a NaOH solution (4%, 25 cm^3) and placed in an ice bath. The diazonium salt solution was added dropwise to the phenol solution. The reaction mixture was then left to stir for 2 h at 3−5 °C. It was then acidified with a few drops of concentrated HCl and allowed to reach room temperature slowly with stirring. A brown precipitate was filtered off and washed thoroughly with water. Repeated recrystallization was carried out from hot ethanol. Yield: 7.79 g (88%). ^{1}H NMR (200 MHz, DMSO): $\delta = 6.97-7.01$ (d, $J = 8.58$ Hz, 2H), 7.87−7.91 (d, $J = 8.91$, 2H), 7.98−8.01 (d, $J = 9.24$, 2H), 8.38−8.42 (d, $J = 8.91$, 2H), 10.63 (s, 2H). MS (EI+): m/z 76 (C_6H_4), 93 (OC_6H_5), 121 ($ON_2C_6H_5$), 243 ($O_2N_3C_{12}H_9$ molecular ion).

The supramolecular complexes studied in this work consist of NHA chromophores that are hydrogen bonded to a poly(4-vinylpyridine) (P4VP; $T_g \sim 148$ °C, $M_W = 50\,000$ g/mol, Polysciences Inc.) matrix. The chemical structure of the P4VP(NHA)$_x$ complexes is presented in Figure 1. As reference guest−host systems we used NHA in polystyrene (PS; $M_W = 50\,000$ g/mol, Polysciences Inc.) and 4-nitroazobenzene (NAB; Sigma-Aldrich) in P4VP (see Figure 1). In the former case, hydrogen bonding is lacking due to the inert styrene moieties of the host polymer and, in the latter case, due to the missing phenolic hydrogen-bond donor of the chromophore. The host polymers P4VP, PS, and NAB were used without further purification. P4VP and NHA were dissolved separately in dimethylformamide (DMF) and mixed to obtain the desired nominal degree of complexation. The reference systems were prepared similarly from tetrahydrofuran (PS/NHA) or DMF (P4VP/NAB). The resulting solutions were filtered through a 0.2 μm syringe filter and spin-coated on clean quartz substrates. No annealing was performed to the samples prior to the optical measurements. The absorbance of the films with

---

(13) Lachut, B. L.; Maier, S. A.; Atwater, H. A.; de Dood, M. J. A.; Polman, A.; Hagen, R.; Kostromine, S. *Adv. Mater.* **2004**, *16*, 1746.
(14) Fukuda, T.; Kim, J. Y.; Barada, D.; Yase, K. *J. Photochem. Photobiol., A* **2006**, *182*, 262.
(15) Okano, K.; Shishido, A.; Ikeda, T. *Adv. Mater.* **2006**, *18*, 523.
(16) Barto, R. R.; Frank, C. W.; Bedworth, P. V.; Taylor, R. E.; Anderson, W. W.; Ermer, S.; Yen, A. K.-Y.; Luo, J. D.; Ma, H.; Tang, H.-Z.; Lee, M.; Ren, A. S. *Macromolecules* **2006**, *39*, 7566.
(17) Lagugne-Labarthet, F.; Buffeteau, T.; Sourisseau, C. *J. Phys. Chem. B* **1998**, *102*, 2654.
(18) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; Wiley-VCH: Weinheim, Germany, 1995.
(19) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491.
(20) Faul, C. F. J.; Antonietti, M. *Adv. Mater.* **2003**, *15*, 673.
(21) Ikkala, O.; ten Brinke, G. *Chem. Commun.* **2004**, *19*, 2131.
(22) Banach, M. J., Jr.; Caracci, S.; Vaia, R. A. *Chem. Mater.* **1999**, *11*, 2554.
(23) Zhang, Q.; Bazuin, C. G.; Barrett, C. J. *Chem. Mater.* **2008**, *20*, 29.
(24) Gao, J.; He, Y.; Liu, F.; Zhang, X.; Wang, Z.; Wang, X. *Chem. Mater.* **2007**, *19*, 3877.
(25) Kulikovska, O.; Goldenberg, L. M.; Stumpe, J. *Chem. Mater.* **2007**, *19*, 3343.
(26) Zettsu, N.; Ogasawara, T.; Mizoshita, N.; Nagano, S.; Seki, T. *Adv. Mater.* **2008**, *20*, 516.
(27) Uchida, E.; Kawatsuki, N. *Macromolecules* **2006**, *39*, 9357.
(28) Priimagi, A.; Kaivola, M.; Rodriguez, F. J.; Kauranen, M. *Appl. Phys. Lett.* **2007**, *90*, 121103.
(29) Panambur, G.; Robert, C.; Zhang, Y.; Bazuin, C. G.; Ritcey, A. M. *Langmuir* **2003**, *19*, 8859.

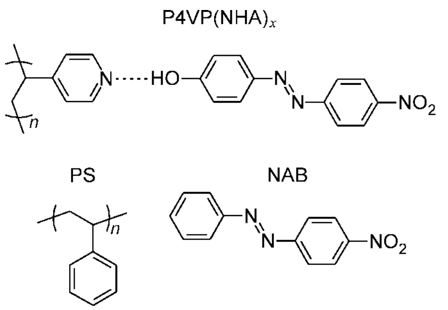

Figure 1. The chemical structure of nominally stoichiometric (x = 1.0) hydrogen-bonded complex between poly(4-vinylpyridine) and 4-nitro-4′-hydroxyazobenzene P4VP(NHA)$_x$ as well as the reference materials polystyrene (PS) and nitroazobenzene (NAB).

different chromophore concentrations was fixed to 0.28 at λ = 375 nm by changing the film thickness. The thicknesses were controlled by adjusting the spinning speed as well as the solute concentration prior to spin coating, and they varied between 40 and 300 nm. The UV−vis spectra of the thin films were measured with Perkin-Elmer Lambda 950 spectrophotometer and the sample thicknesses were determined with a DEKTAK 6 M stylus profiler. The infrared spectra were measured with a Nicolet 380 FTIR spectrometer by averaging 64 scans at a resolution of 2 cm^{-1}. The samples were drop-cast on KBr pellets. Polarized-light micrographs were taken using a Leica DM4500P optical microscope. The glass-transition temperatures (T_g) of selected complexes were determined with differential-scanning calorimetry (DSC; Mettler Toledo Star DSC 821, temperature range of 25−190 °C, heating and cooling rate 10 °C/min), and they were found to be approximately 78, 80, 93, and 105 °C for the complexes x = 0.05, 0.25, 0.50, and 1.00, respectively, where x is the nominal number of chromophores per each repeat unit of the polymer. Apart from the T_g, no indications of phase transitions were observed in the DSC curves in any of the complexes.

The birefringence was induced by exciting the chromophores with a linearly polarized beam of light from a 375 nm laser diode. The intensity of the excitation light was 40 mW/cm^2. The induced birefringence was measured with a normally incident low-power (200 μW) He−Ne laser (633 nm). The transmitted intensity of the probe beam through a polarizer/sample/analyzer combination was monitored with a photodiode. The orientation of the polarizer/analyzer was set to ±45° with respect to the polarization of the excitation beam, and the birefringence $|\Delta n|$ was calculated from the transmission data,

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

where I_0 is the photodiode signal for a parallel polarizer/analyzer orientation (in the absence of the sample), d is the film thickness, and λ the wavelength of the probe beam.

3. Results and Discussion

The complexation between P4VP and NHA was verified with infrared spectroscopy. Pure P4VP has a symmetric ring stretching mode at 993 cm^{-1} (Figure 2a). When complexed with NHA, a new band arises at 1009 cm^{-1}, which can be attributed to hydrogen bonding between the pyridine and phenol moieties of the polymer and the chromophores, respectively.[30,31] Note that the relative intensity of the 1009 cm^{-1} band increases systematically with respect to the 993 cm^{-1} band as the chromophore content is increased. For the equimolar complex P4VP(NHA)$_{1.0}$, the original band is almost completely suppressed, suggesting that an NHA molecule can be attached to essentially each repeating unit of P4VP. Complementary information on the complex formation can be obtained by following the spectral region for the hydroxyl stretching vibrations (Figure 2b). Pure NHA exhibits a broad absorption band centered at 3430 cm^{-1}, which can be assigned to overlapping stretching vibrations of free and self-associated hydroxyl groups.[31] Upon complexation, this band is replaced by a broad band around 3100 cm^{-1}, partly overlapping with the stretching vibrations of the pure P4VP. This verifies that the hydrogen bond is formed between the phenol and pyridyl functional groups.[32]

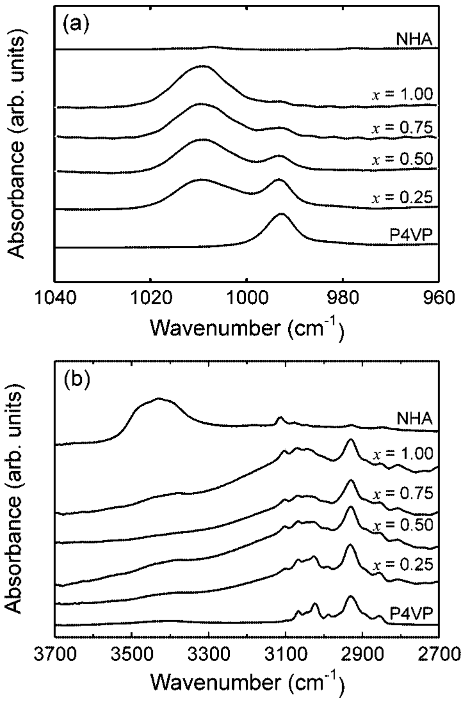

Figure 2. Infrared absorption spectra of P4VP(NHA)$_x$ at wavenumber regions (a) 1040−960 cm^{-1} and (b) 3700−2700 cm^{-1}. The nominal degrees of complexation x = 1.00, 0.75, 0.50, and 0.25 correspond to chromophore weight fractions of 70%, 63%, 54%, and 37%, respectively.

The UV−vis absorption spectra of a few selected complexes and the absorption maxima as a function of chromophore concentration are presented in parts (a) and (b) of Figure 3, respectively. As the chromophore concentration is increased, the absorption maximum gradually shifts to shorter wavelengths. We attribute this shift to two effects. First, the increased chromophore content changes the polarity of the local environment, which gives rise to a solvatochromic shift of the absorption peak.[33] This is probably the dominant effect at low chromophore concentrations. At high nominal degrees of complexation of x = 0.75 (chromophore weight fraction 63 wt %) and x = 1.00 (70 wt %), the blue shift is more pronounced and is accompanied with a slight broadening and deformation of the absorption band. This can be attributed to

---

(30) Ruokolainen, J.; ten Brinke, G.; Ikkala, O.; Torkkeli, M.; Serimaa, R. *Macromolecules* **1996**, *29*, 3409.

(31) Lee, L. T.; Woo, E. M.; Hou, S. S.; Förster, S. *Polymer* **2006**, *47*, 8350.

(32) Sallenave, X.; Bazuin, C. G. *Macromolecules* **2007**, *40*, 5326.

(33) Reichhardt, C. *Chem. Rev.* **1994**, *94*, 2319.

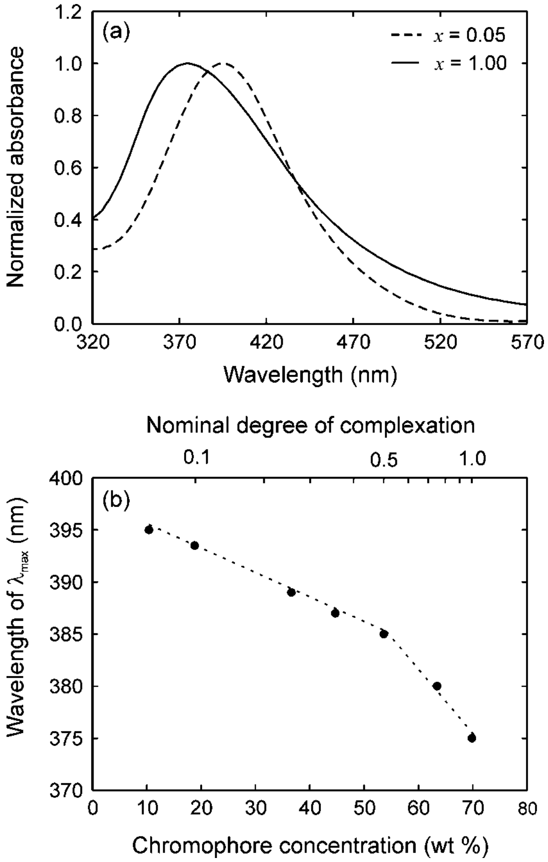

Figure 3. (a) Examples of the normalized UV−vis spectra of P4VP(NHA)$_x$ for $x = 0.05$ and 1.00. (b) The UV−vis absorption maxima as a function of NHA concentration. The dashed line is drawn to guide the eye.

chromophore−chromophore intermolecular interactions.[34,35] Note that the total shift in λ_{max} is small, only 20 nm. Such a small shift complicates the discrimination of the two effects but also indicates that the coupling between the chromophores is relatively weak. As a comparison, for Disperse Red 1 (DR1), which is a widely used molecule in photoinduced birefringence studies, the aggregation-induced blue shift can be up to 100 nm due to stronger dipolar interactions between the chromophores.[36] The smooth gradual shift of the absorption maximum as a function of chromophore concentration is also an indirect indication of the noncooperative nature of hydrogen bonding—cooperative binding would already give rise to chromophore−chromophore intermolecular interactions at significantly lower concentrations.

The saturated birefringence values of the P4VP(NHA)$_x$ complexes and the reference systems are presented in Figure 4. The reference systems behave as observed previously for DR1-containing guest−host polymers:[28] the obtained maximum birefringence is low (around 0.01) and levels off already at moderate concentrations. The leveling takes place once the chromophores start to aggregate (verified by UV−vis spectroscopy, data not shown), which highlights the destructive impact of chromophore aggregation on the photoorientation process in conventional guest−host polymers.

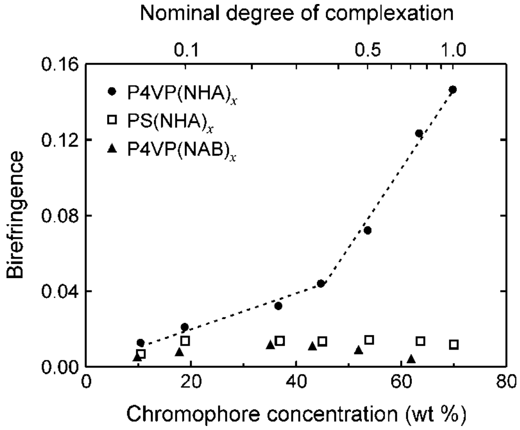

Figure 4. Photoinduced birefringence as a function of chromophore concentration for P4VP(NHA)$_x$, PS(NHA)$_x$, and P4VP(NAB)$_x$. The dashed line is drawn to guide the eye. The reported values are the saturation values when the writing beam is applied on the sample.

Moreover, at concentrations exceeding 40 wt %, the film quality is significantly reduced, presumably because of phase separation of the constituents. The behavior of the P4VP(NHA)$_x$ complexes differs dramatically from the non-hydrogen-bonded reference systems. The birefringence increases approximately linearly with chromophore concentration and reaches a value of 0.044 at 45 wt % concentration, i.e., when nominally one-third of the polymer repeating units are occupied. Interestingly, when this concentration is exceeded, birefringence continues to increase with a significantly steeper slope, reaching a value of 0.147 at 70 wt % concentration (nominally stoichiometric complex with $x = 1.0$). To exclude the possible role of surface effects in a series of samples with varying thickness, we also prepared another series with optical density of 0.55 and observed similar enhancement in birefringence, as shown in Figure 4. Moreover, the birefringence could be erased in each complex by illuminating the film with circularly polarized light.

Normalized writing−relaxation curves for selected P4VP(NHA)$_x$ complexes and the fractions of remnant birefringence as a function of NHA concentration are presented in parts (a) and (b) of Figure 5, respectively. The temporal stability of the induced birefringence increases systematically for concentrations of 54 wt % and higher, while it is approximately constant for lower concentrations. Notice also the excellent agreement and consistency between Figures 4 and 5: The enhancement of the absolute birefringence and the increase in the temporal stability are seen to take place at the same threshold concentration, i.e., for $x > 0.35$. For the stoichiometric complex P4VP(NHA)$_{1.0}$ (70 wt % chromophore concentration), the remnant birefringence is 95% of the saturation value. To ensure that the sample thickness plays no role on the birefringence relaxation, we also repeated the measurements for P4VP(NHA)$_{1.0}$ complexes with optical densities of 0.55 and 0.85 at the writing wavelength and observed no differences in the remnant birefringence. The improved stability at high concentrations cannot probably be accounted for by the relatively small change in the T_g, which increases from approximately 78 °C ($x = 0.05$) to 105 °C ($x = 1.0$). The temporal stability of P4VP(NHA)$_{1.0}$ is superior to guest−host polymers: for PS(NHA)$_x$ and P4VP(NAB)$_x$ as well as for the previously studied DR1-

---

(34) Czikklely, V.; Forsterling, H. D.; Kuhn, H. *Chem. Phys. Lett.* **1970**, *6*, 207.
(35) Kelley, A. M. *J. Chem. Phys.* **2003**, *119*, 3320.
(36) Priimagi, A.; Cattaneo, S.; Ras, R. H. A.; Valkama, S.; Ikkala, O.; Kauranen, M. *Chem. Mater.* **2006**, *17*, 5798.

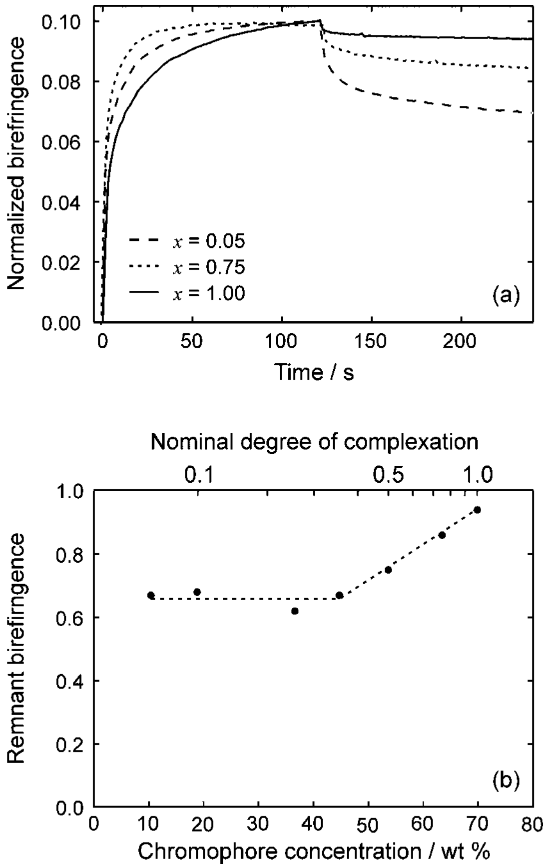

Figure 5. (a) Normalized writing−relaxation curves for selected P4VP(NHA)$_x$ complexes (irradiation period 0−120 s). (b) Fraction of remnant birefringence of P4VP(NHA)$_x$ as a function of chromophore concentration (measured at 240 s). The dashed line is drawn to guide the eye.

containing guest−host systems, the remnant birefringence is 60−65% of the saturation value.[28] This further manifests the potential of supramolecular polymer−azobenzene complexes compared to the more conventional polymer systems. We also note that the writing-relaxation curves are stable and reproducible: the measurements were repeated for samples that were stored in ambient conditions for at least 3 weeks, and essentially no changes in the photo-orientation dynamics, absolute birefringence, or relaxation behavior could be observed.

The essence of the optical studies above is summarized as follows: at a low chromophore concentration, the maximum birefringence (Figure 4) increases linearly with chromophore concentration, whereas the residual birefringence remains at a relatively low (ca. 67%) and constant value (Figure 5b). For the degree of complexation of $x > 0.35$, the birefringence starts to increase with significantly steeper slope, and the temporal stability of the response is dramatically improved. At the same time, a pronounced blue shift is noticed in the spectral signature of the chromophores (Figure 3b), emphasizing the importance of chromophore−chromophore intermolecular interactions on the enhancement of the birefringence and on the improved temporal stability. Most importantly, the hydrogen bonds are still intact (Figure 2), thus prohibiting the macroscopic phase separation and excessive chromophore−chromophore interactions. This indicates the interplay of these two types of interactions to allow enhanced optical properties in the present spin-cast thin films. More generally, it is known that the chromophore content can greatly influence the photo-orientation process through phase changes in the material: an increased chromophore concentration can lead to a transformation from an isotropic state to liquid-crystalline phase[37] and can also turn the liquid-crystalline order from nematic to smectic.[38] Furthermore, supramolecular polymer−azobenzene complexes can exhibit liquid-crystalline order with only a very short spacer[39] or even without any spacer at all.[23,40,41] However, we point out that the present P4VP(NHA)$_x$ complexes with their feasible optical properties are in the glassy state and that the spin-coated thin films used for optical measurements showed no textures that could be assigned with well-defined liquid-crystalline phases in the polarized-light micrographs.[42] Moreover, no indications of phase transitions in addition to the glass transition were observed in the DSC curves for the P4VP(NHA)$_x$ complexes. Having established this new concept, more detailed in situ studies on the structural and thermal properties of the complexes are needed to clarify the molecular mechanism behind the effect. However, the optical properties observed are highly reproducible and provide significant support to the potential benefits of supramolecular concepts in the design of optical materials.

4. Conclusions

We have systematically studied the effect of chromophore concentration on the photo-orientation of hydrogen-bonded 4-nitro-4′-hydroxyazobenzene−poly(4-vinylpyridine) complexes and showed that the photoinduced birefringence is significantly enhanced and stabilized at high degrees of complexation. For the equimolar complex, corresponding to 70 wt % chromophore concentration, the saturated birefringence is 0.15 and the remnant birefringence 95% of the saturation value. We suggest that the enhancement and stabilization of the photoinduced birefringence in P4VP(NHA)$_x$ with $x > 0.35$ is triggered by the interplay between hydrogen bonding and chromophore−chromophore intermolecular interactions. The phenol−pyridine hydrogen bonding is essential to prevent uncontrolled aggregation and macro-phase-separation of the constituents: In guest−host polymers, with no specific interactions between the polymer and the chromophores, intermolecular interactions between

---

(37) Rodríguez, F. J.; Sánchez, C.; Villacampa, B.; Alcalá, R.; Cases, R.; Millaruelo, M.; Oriol, L. *Polymer* **2004**, *45*, 2341.

(38) Wu, Y.; Zhang, Q.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Nagase, Y. *Macromolecules* **1999**, *32*, 3951.

(39) Malik, S.; Dhal, P. K.; Mashelkar, R. A. *Macromolecules* **1995**, *28*, 2159.

(40) Xiao, S.; Lu, X.; Lu, Q. *Macromolecules* **2007**, *40*, 7944.

(41) Wu, X.; Zhang, G.; Zhang, H. *Macromol. Chem. Phys.* **1998**, *199*, 2101.

(42) PLM images were also taken from thick drop-cast samples. For $x \leq 0.50$, no textures could be observed, indicating isotropic distribution of the chromophores. On the contrary, complexes with $x = 0.75$ and 1.00 exhibited birefringence. This could indicate the existence of a liquid-crystalline mesophase at high concentrations, but due to the differences in the sample thickness and preparation process, the correspondence between the PLM images and the birefringence measurements cannot be guaranteed. A separate in-depth study, preferably with in situ X-ray diffraction measurements, is required before conclusive and unambiguous statements about the effect of the materials structure on its optical properties can be made.

the chromophores suppress the photo-orientation. Hydrogen-bonded supramolecular complexes thus allow reaching and even surpassing the performance of covalently functionalized polymers while simultaneously maintaining the ease of processing of guest−host polymers. We strongly believe that the results of the present paper can open up new avenues for the design of polymer-based optical materials and can also provide novel concepts for modern supramolecular materials science.

Acknowledgment. This work was supported by Nokia Research Center, Finnish Funding Agency for Technology and Innovation, the Academy of Finland (108538 and 113245), and the Nanophotonics Research and Development Program funded by the Ministry of Education of Finland. We also thank Richard J. Oakley for synthesis of NHA, and Klas Lindfors for discussion and comments. Susanna Junnila and Minna Annala are acknowledged for their assistance with differential scanning calorimetry measurements. A.P. acknowledges the financial support of the National Graduate School in Materials Physics and of the Finnish Cultural Foundation. C.F.J.F. thanks the University of Bristol for support and the Helsinki University of Technology for a visiting professorship.

CM800908M