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**POLYMER-AZOBENZENE COMPLEXES: FROM
SUPRAMOLECULAR CONCEPTS TO EFFICIENT
PHOTORESPONSIVE POLYMERS**

Doctoral Dissertation

Arri Priimägi



**Helsinki University of Technology
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Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Faculty of Information and Natural Sciences for public examination and debate in Auditorium F239a at Helsinki University of Technology (Espoo, Finland) on the 30th of October, 2009, at 12 noon.

**Helsinki University of Technology
Faculty of Information and Natural Sciences
Department of Applied Physics**

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Abstract Linear and nonlinear optical properties of azobenzene-containing polymers give rise to a range of exciting optical phenomena due to the unique response of the azobenzene chromophores to light fields. The light-induced motions of the azobenzene molecules can be used to inscribe large and stable in-plane anisotropy, nonlinear optical response, and surface-relief structures into the material system, showing great potential for various photonics applications. This thesis deals with a common drawback often encountered in amorphous azobenzene-containing polymers: when the chromophores are dissolved in the polymer matrix, they tend to form aggregates even at moderate doping levels, which is generally detrimental to the optical response of the system. Aggregation can be suppressed by covalently attaching the chromophores to the polymer backbone, which improves the optical performance but requires a laborious organic synthesis process for each polymer–chromophore combination. We have addressed this issue by using supramolecular concepts: instead of covalent functionalization we use <i>spontaneous</i> non-covalent interactions to attach the chromophores to the polymer backbone to form <i>polymer–azobenzene complexes</i> . In the thesis we systematically explore the connection between the aggregation of strongly dipolar chromophores and the photoresponse of the material system. In particular, we show that the aggregation can be suppressed by properly choosing the polymer matrix. Moreover, by using <i>phenol–pyridine hydrogen bonding</i> to attach the chromophores to the polymer backbone, the chromophore content can be increased up to the point where each polymer repeat unit is occupied, yielding photoresponsive polymers with (i) high and stable photoinduced anisotropy and (ii) efficient formation of photoinduced surface-relief gratings. Hydrogen bonding makes a difference, and due to the generality of the supramolecular concepts, we anticipate that the proposed method provides a pathway to enhancing a wide range of optical phenomena where chromophore aggregation or phase separation is a limiting factor for the system performance.			
Keywords: azobenzene, aggregation, hydrogen bonding, photoinduced anisotropy, surface-relief grating			
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Väitöskirjan nimi Valoherätteinen kahtaistaittavuus ja pintahilat vetysidotuissa polymeeri-atsobentseenikomplekseissa	
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Työn valvoja	Prof. Matti Kaivola
Työn ohjaajat	Prof. Olli Ikkala ja Prof. Martti Kauranen
Tiivistelmä Atsobentseeniä sisältävien polymeerien erikoislaatuinen vaste optisiin kenttiin johtaa lukuisiin mielenkiintoisiin optisiin ilmiöihin, joita voidaan käyttää useissa ftoniikkasovelluksissa. Atsobentseenin <i>fotoisomerisaatiota</i> hyödyntämällä materiaaliin voidaan synnyttää valoherätteistä kahtaistaittavuutta ja epälineaarista optista vastetta. Lisäksi siihen voidaan kirjoittaa erilaisia pintarakenteita optisin menetelmin. Työ käsittelee amorfisten atsobentseeniä sisältävien polymeerien keskeisintä ongelmaa: kun atsobentseenit liuotetaan polymeerimatriisiin, ne muodostavat aggregaatteja, mikä pienentää materiaalin optista vastetta ja heikentää sen suorituskykyä merkittävästi. Aggregaatiota voidaan vähentää liittämällä kromoforit polymeeriketjuihin kovalentein sidoksin. Tämä parantaa materiaalin optisia ominaisuuksia, mutta monimutkainen orgaaninen synteesiprosessi tekee menetelmästä hankalan ja kalliin. Tässä työssä aggregaatio-ongelmaan tartutaan supramolekyläärin konseptin: kovalenttien sidosten sijaan kromoforit liitetään polymeeriketjuihin <i>spontaanein</i> ei-kovalentein sidoksin. Työn puitteissa olemme tutkineet systemaattisesti dipolaaristen atsobentseenimolekyylien aggregaation vaikutusta materiaalin valoherätteisiin optisiin ominaisuuksiin. Työssä on osoitettu, että aggregaatiota voidaan vähentää merkittävästi valitsemalla sopiva polymeerimatriisi, mikä parantaa materiaalin optista vastetta monelta osin. Mikäli atsobentseenit liitetään polymeeriketjuihin <i>fenoli-pyridiini-vetysidoksella</i> , kromoforikonsentraatiota voidaan kasvattaa kunnes atsobentseeni on liittynyt jokaiseen polymeerin tois-toyksikköön. Näin saavutettavat valolla ohjattavat polymeerit johtavat korkeaan ja stabiiliin valoherätteeseen kahtaistaittavuuteen sekä tehokkaaseen pintarakenteiden muodostumiseen. Materiaalin optisia ominaisuuksia voidaan näin parantaa merkittävästi vetysidoksen avulla, ja konseptin yleisyydestä johtuen on uskottavaa, että menetelmällä on käyttöä lukuisissa ftoniikkasovelluksissa, joissa molekyylien aggregaatio tai faasierottuminen rajoittavat materiaalin suorituskykyä.	
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Preface

The research reported in this thesis has been carried out in the (former) Laboratory of Optics and Molecular Materials of the Helsinki University of Technology, and in the Optics Laboratory of the Tampere University of Technology. I am indebted to my supervisor, Prof. Matti Kaivola, for providing me the opportunity to work on this topic as well as for his guidance along the way. I am also most grateful to my instructors, Prof. Olli Ikkala and Prof. Martti Kauranen. Your contribution and support has been an invaluable asset, without which I would not have been able to finish this work.

I wish to express my sincerest gratitude to Dr. Stefano Cattaneo for helping me to get started, and to Dr. Francisco J. Rodriguez for paving my way for many fascinating optical phenomena in photoresponsive polymers. I also acknowledge all the other co-authors for an excellent collaboration, especially Jaana Vapaavuori for enthusiasm and an endless stream of questions. Special thanks goes to my friend and co-worker Klas Lindfors for instruction and encouragement, as well as for common adventures with optical tweezers. I would also like to thank all my present and former colleagues for providing a pleasant working environment and for teaching me many important aspects regarding cynicism, communist party, Tom Waits & Nick Cave, as well as for the diverse and unconventional ways of using olive oil. Especially Timo Hakkarainen, Ossi Kimmelma, Sami Kujala, Ari Laiho, Jussi Ojanen, Andriy Shevchenko, and Sami Valkama have contributed to my work and well-being, each in their unique way.

During the summer 2008 I had a pleasure to visit the research groups of Prof. Paul Rochon (Royal Military College) and Prof. Jean-Michel Nunzi (Queen's University) in Kingston, Canada. I deeply acknowledge their hospitality and guidance, as well as their time for stimulating scientific discussions. I would also like to thank Prof. Arto Nurmikko (Brown University, Providence, USA) for new openings and for hospitality during my visit in the fall 2007. The seeds from these visits have emerged as important parts of this thesis, and are hopefully to lead to fruitful collaboration in the future to come.

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Finally, I thank my parents and siblings for support and encouragement. And most of all, I would like to thank Sonja, Oliver and Venla for your love, without which this would all be meaningless.

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Arri Priimägi

List of publications

- I. A. Priimagi, S. Cattaneo, R. H. A. Ras, S. Valkama, O. Ikkala and M. Kauranen, *Polymer–dye complexes: a facile method for high doping level and aggregation control of dye molecules*, Chem. Mater. **17**, 5798 (2005).
- II. A. Priimagi, F. J. Rodriguez, M. Kauranen, and O. Ikkala, *Enhanced photoinduced birefringence in polymer–dye complexes: hydrogen bonding makes a difference*, Appl. Phys. Lett. **90**, 121103 (2007).
- III. A. Priimagi, J. Vapaavuori, F. J. Rodriguez, C. F. J. Faul, M. T. Heino, O. Ikkala, M. Kauranen, and M. Kaivola, *Hydrogen-bonded polymer–azobenzene complexes: enhanced photoinduced birefringence with high temporal stability through interplay of intermolecular interactions*, Chem. Mater. **20**, 6358 (2008).
- IV. A. Priimagi, K. Lindfors, M. Kaivola, and P. Rochon, *Efficient surface-relief gratings in hydrogen-bonded polymer–azobenzene complexes*, ACS Appl. Mater. Interfaces **1**, 1183 (2009).
- V. A. Priimagi, S. Cattaneo, and M. Kauranen, *Real-time monitoring of all-optical poling by two-beam second-harmonic generation*, Opt. Lett. **31**, 2178 (2006).

Author's contribution

The author has played a central role in all aspects of the research work summarized in this thesis. He has planned the experiments, prepared and characterized the samples, built the experimental setups, and performed the measurements for all the publications, with the exception of Publication **III**, where the author instructed in performing the experiments. He has had a key role in the interpretation of the experimental results, and he has written the manuscripts for all the publications included in this thesis.

Contents

Abstract	iii
Tiivistelmä	v
Preface	vii
List of Publications	viii
Author's contribution	ix
Contents	xi
1 Introduction	1
2 Azobenzene: photocontrol through photoisomerization	3
2.1 Spectral and photochemical properties	3
2.2 Aggregation	7
2.3 Photoswitching and photomechanics	9
3 Polymer–azobenzene complexes	12
3.1 Polymeric optical materials: a brief introduction	12
3.2 Supramolecular side-chain polymers	14
4 Photoinduced processes in azobenzene-containing polymers	17
4.1 Photoinduced anisotropy	17
4.2 Photoinduced surface-relief structures	21
4.3 Azobenzene in nonlinear optics: all-optical poling	25
5 Photoinduced processes in polymer–azobenzene complexes	30
5.1 Review of related studies	30
5.2 The role of aggregation on photo-orientation: a case study	32
5.3 Equimolar complexes via phenol–pyridine hydrogen bonding	36
6 Conclusions and outlook	41
References	43
Original Publications	53

– when more than thirty years are told,
as good as dead is one indeed –
J. W. von Goethe; Faust, Part II

1

Introduction

Organic polymeric materials are expected to play a key role in the next-generation photonics and multimedia technology. The main thrust comes from their structural versatility and low cost, combined with the strong and fast response of organic molecules to optical fields.^{1–4} Due to such reasons they are expected to meet the growing demand for processing and storage capacity of the future. A particularly attractive feature inherent to many organic chromophores is the fact that they exhibit *photochromism*, *i.e.*, they can be reversibly switched by light between two different conformational states that exhibit distinct spectroscopic and physical properties.⁵ Various types photochromic materials are currently considered as viable candidates for reversible information storage and optical switching applications.^{6,7}

Perhaps the most extensively studied photochromic compounds are the azobenzene derivatives. The interest towards azobenzene-containing materials lies in the fact that the efficient and reversible *photoisomerization* of the azobenzene derivatives can be used to induce various types of molecular motions into the material system, being the key to a number of unique optical and photomechanical effects.^{8,9} The light-induced motions of the azobenzene chromophores can result in large and stable in-plane anisotropy, nonlinear optical response, and strong refractive-index modulation. Moreover, perhaps the most attractive target in the current azobenzene research is the inscription of photoinduced surface-relief structures onto the material system.¹⁰ The richness of photoisomerization-induced optical and photomechanical effects has attracted tremendous research interest towards the fundamental properties as well as the practical applicability of azobenzene-containing polymers. But nevertheless, many issues regarding the light-induced motions in these materials remain unclear up to date, and novel materials concepts with optimized optical performance are continuously explored.

The present work arose from a common effort of the Laboratory of Optics and Molecular Materials of the Helsinki University of Technology and the Optics Laboratory of the Tampere University of Technology, to apply *supramolecular concepts* to developing self-assembled polymeric nonlinear optical materials. At present, supramolecular self-assembly is still only a future prospect, and we are only now getting more into the nonlinear optical properties of the class of materials we refer to as *polymer–dye (or chromophore) complexes*. Instead, we have concen-

trated on preventing the aggregation of the photoactive chromophores through spontaneous non-covalent interactions between the chromophores and the polymer backbone. The study is realized by using the photoinduced anisotropy and surface-relief formation in azobenzene-containing polymers *as a probe* to investigate (i) the connection between chromophore aggregation and the optical response of the material system, and (ii) the strength of the chromophore–polymer intermolecular interactions. However, the non-covalent functionalization strategies not only facilitate such fundamental studies but also provide a promising materials concept from the point of view of various optical applications where chromophore aggregation or phase separation set a limit to the system performance.

The compendium of this thesis is organized as follows: Chapter 2 gives an introduction to the spectroscopy and photochemistry of azobenzene derivatives in different environments, including a brief review on the use of azobenzene in photoswitching applications. Chapter 3 contains a simplified discussion of polymeric optical materials and introduces the basic design principles behind the non-covalent functionalization strategy used in this work. The general features of photoinduced anisotropy, surface-relief formation, and all-optical poling (Publication V) in azobenzene-containing polymers are the topic of Chapter 4. The core results of this work, which treat the light-induced processes in polymer–azobenzene complexes, are presented in Chapter 5, where we show that the aggregation of dipolar *Disperse Red 1* chromophores can be suppressed by properly choosing the polymer matrix (Publication I), and that the reduced aggregation tendency leads to an enhancement in the obtained photoinduced birefringence (Publication II). Moreover, we demonstrate that *phenol–pyridine hydrogen bonding* allows one to attach a chromophore to each polymer repeat unit without phase separation, yielding efficient photoresponsive polymers with (i) high and stable photoinduced anisotropy (Publication III) and (ii) efficient formation of photoinduced surface-relief gratings (Publication IV). Finally, the main conclusions and future prospects are summarized in Chapter 6.

– what we observe is not nature
itself, but nature exposed to our
mode of questioning –

Werner Heisenberg

2

Azobenzene: photocontrol through photoisomerization

Azobenzene[†] is an aromatic molecule where two phenyl rings are bridged by an azo ($-N=N-$) linkage. The extended conjugation gives rise to strong absorption in the ultraviolet and visible wavelengths. The spectral and photophysical properties of azobenzene are highly sensitive to its substitution pattern, but a common feature to all azobenzene derivatives is the efficient and reversible photoisomerization between a thermally stable *trans*-state and a metastable *cis*-state upon absorption of a photon. The isomerization reaction produces large structural changes in the azobenzene conformation and significantly affects its spectroscopic and physical properties, being the key to the unique optical and photomechanical effects in azobenzene-containing material systems.

Historically, research on azobenzene molecules has been closely connected to the development of dyes and pigments. As one of the most important requirements for a commercially viable dye is good light stability and lack of discoloration, at the time of its discovery¹¹ the photoisomerization reaction was considered as an undesirable feature. Hence, a great deal of research was put into inhibiting photoisomerization and into reducing the lifetime of the *cis*-isomer.¹² It took some 30 years before the potential of the azobenzene photoisomerization as a light switch or as a probe of the local environment was realized,¹³ and ever since, a wealth of novel photoisomerization-induced phenomena and applications have been discovered.

2.1 Spectral and photochemical properties

Azobenzenes are typically divided into three classes, distinguished by their spectroscopic characteristics (see Figure 2.1): azobenzene-type molecules, aminoazobenzene-type molecules, and pseudostilbene-type[‡] molecules.¹⁵ The classifica-

[†]Throughout this work, we use the term "azobenzene" in reference to both unsubstituted azobenzene and substituted azobenzene derivatives.

[‡]Although widely used, the term "pseudostilbene" is misleading. Stilbene refers to a class of molecules where the phenyl rings are connected with a $-C=C-$ linkage. They also exhibit *trans-cis* photoisomerization whereas the thermal *cis-trans* isomerization is negligible.¹⁴

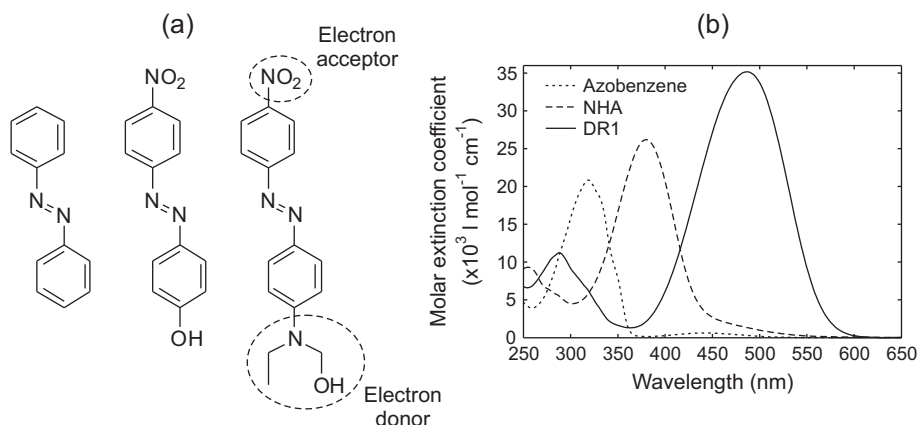


Figure 2.1. (a) Examples of azobenzene molecules of azobenzene-type [unsubstituted azobenzene, left], aminoazobenzene-type [4-nitro-4'-hydroxyazobenzene (NHA), center], and pseudostilbene-type [Disperse Red 1 (DR1), right]. (b) Absorption spectra of azobenzene, NHA, and DR1 in $2 \cdot 10^{-5}$ mol/l tetrahydrofuran solution.

tion is based on the relative energies of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.^{16,17} The azobenzene-type molecules have an intense $\pi \rightarrow \pi^*$ band in the UV region, and a weak $n \rightarrow \pi^*$ band at *ca.* 440 nm. For aminoazobenzenes, the $\pi \rightarrow \pi^*$ band is red-shifted to the proximity of the $n \rightarrow \pi^*$ band which is insensitive to substituent effects.¹² Pseudostilbenes are substituted with strong electron-donating and electron-withdrawing groups. For these so called *push-pull* molecules, the $\pi \rightarrow \pi^*$ is considered to be of the lowest energy, and the $n \rightarrow \pi^*$ is overshadowed by this intense transition. A representative of each class, together with their electronic absorption spectra, are given in Fig. 2.1. Note that the classification rests on the absorption spectrum rather than the chemical structure of the compound. Accordingly, molecules with weak push-pull character, such as 4-nitro-4'-hydroxyazobenzene (NHA), can be classified into the aminoazobenzene category.

The most prominent feature of the azobenzene compounds is their ability to photoisomerize. Light within the absorption band of the *trans*-form will elicit *trans-cis* isomerization while the reverse isomerization can be either light-induced or thermal (Fig. 2.2a). The rate of thermal reversion depends strongly on the substitution pattern of the azobenzene: typical lifetimes for azobenzenes, aminoazobenzenes, and pseudostilbenes are on the order of hours, minutes, and seconds, respectively.¹⁵ Photoisomerization results in significant changes in the absorption spectrum of the azobenzene compounds, as illustrated in Fig. 2.2b for an azobenzene-type molecule. The intensity of the $\pi \rightarrow \pi^*$ transition is significantly reduced and the band is slightly blue-shifted whereas the $n \rightarrow \pi^*$ transition is intensified upon *trans-cis* isomerization. For aminoazobenzenes and pseudostilbenes, the thermal isomerization reaction takes place much more rapidly than for azobenzenes and the spectra of the *cis*-forms can only be estimated through extrapolation techniques.¹⁸ However, the photochromic nature inherent to all azo compounds provides a pathway to conveniently monitor the isomer-

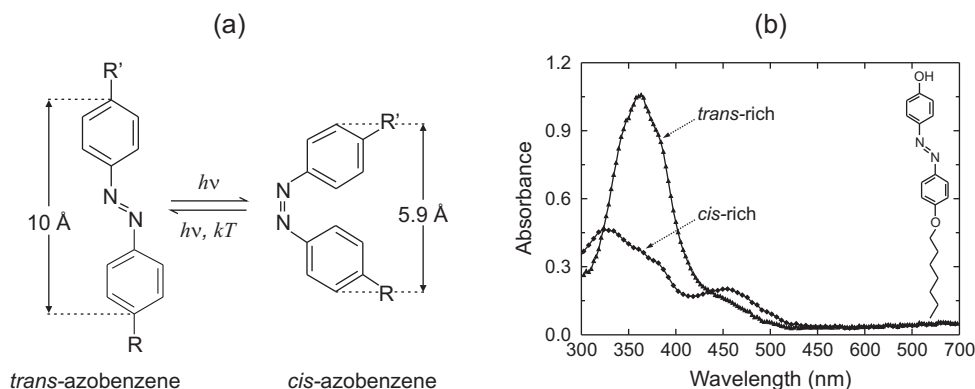


Figure 2.2. (a) *trans*–*cis* isomerization of azobenzene. (b) Absorption spectra of the *trans*-rich and *cis*-rich photostationary states of 4-(4'-heptyloxyphenyl)azophenol, shown in the inset. The spectra are measured from a polymeric thin film before and after irradiating with a circularly polarized 375 nm diode laser.

ization kinetics and steady-state composition through absorption spectroscopy.

The fraction of *trans*- and *cis*-isomers of an azobenzene-containing sample in a photostationary state depends on the quantum yields of the two isomerization processes as well as on the thermal relaxation rate, being highly sensitive to the local environment and the irradiation conditions. The photostationary state is strongly wavelength dependent: for the unsubstituted azobenzene the fraction of *cis*-isomers is 91% and 12% when irradiated with 365 nm and 405 nm, respectively.¹⁹ Once the irradiation is ceased, the metastable *cis*-form tends to thermally relax to the stable *trans*-form with a time constant determined by the chemical structure and local environment of the molecule. This can be considered undesirable for applications requiring stable photoswitchable two-state systems, and considerable work has been directed towards elongating the lifetime of the *cis*-isomer.^{20,21}

From the point of view of optics and photonics, of particular interest are the pseudostilbene-type molecules. Pseudostilbenes are characterized by a highly asymmetric electron distribution due to the substitution with strong electron donating and withdrawing groups. Such a substitution pattern gives rise to a strong nonlinear optical response, which can be transformed to a macroscopic level by poling the sample using either static electric fields or light fields.^{22,23} Moreover, pseudostilbenes have a short *cis*-lifetime and a significant overlap between the spectra of the *trans* and *cis*-forms.²⁴ Hence, the same wavelength drives both the *trans*–*cis* and *cis*–*trans* photoisomerization, which results in continuous cycling of the molecules between the two states and leads to acceleration and enhancement of many photoinduced effects.⁸

The photochemical properties of azobenzene compounds can most conveniently be studied in dilute solutions. However, the photoisomerization reaction also takes place in a macromolecular environment and in the solid state. The non-equilibrium nature of the polymeric environment in its glassy state increases the level of complexity of the material system, which affects both the composition of

the photostationary state and the rate of thermal isomerization. The content of the *cis*-isomers in the photostationary state is typically lower in the glassy state of the polymer than in solution because a fraction of the volume is too rigid to allow the photoisomerization to proceed.^{25,26} Moreover, in solutions or in polymers above their glass-transition temperature (T_g) the thermal *cis*–*trans* isomerization obeys first-order (monoexponential) relaxation kinetics. In the glassy state of the polymer, a fraction of the molecules isomerizes with a *higher* rate due to the nonuniform distribution of the free volume, and the relaxation process has to be considered as either a two-exponential process or a process consisting of a continuous distribution of decay rates.^{25–29} The sensitivity of the isomerization kinetics to the local environment enables one to use azobenzene as a site-specific probe to determine for instance the free volume distribution or cross-linking behavior of the polymers.^{13,30,31}

Azobenzene in acidic environment

The spectroscopic and photochemical properties of azobenzene derivatives can change drastically in an acidic environment. These changes are brought about by the basic nature of the azo group as well as by many of the substituent groups, which can act as proton acceptors. The interaction between the azobenzene and the protons in the acid molecules can take place via hydrogen bonding or proton transfer, depending on the interaction strength. These two types of interactions have distinctly different roles on the spectral and photochemical properties of azobenzene molecules. They can also be exploited to obtain thin films of *polymer–azobenzene complexes*, which are the central theme of this work and will be treated in more detail in Chapter 3.

When considering the role of hydrogen bonding on the photochemistry of azobenzene, it warrants to make a distinction between *intramolecular* and *intermolecular* hydrogen bonding. Intramolecular hydrogen bonding, which occurs for instance in *ortho*-substituted hydroxyazobenzenes, lowers the activation energy of the *cis*–*trans* isomerization, but more importantly, it drastically decreases the quantum yield of *trans*–*cis* isomerization and inhibits the photoisomerization process.^{18,32} The role of intermolecular hydrogen bonding on the photoisomerization depends on which part of the azobenzene molecule participates in the bonding. Hydrogen bonding at the electron donor (see Figure 2.1) is expected to raise the activation barrier for thermal isomerization and increase the lifetime of the *cis*-isomer, while hydrogen bonding at the electron acceptor would lead to opposite behavior.³³ On the other hand, hydrogen bonding at the azo linkage in an acidic solution environment has been shown to accelerate the thermal isomerization rate even by a factor of 70.³⁴

The role of *proton transfer* on the electronic excitation and photoisomerization of azobenzenes is still actively studied.^{35–37} If the interaction between the acid and the azo group leads to proton transfer from the acid to the azo linkage, the conformation and the electronic structure of the molecule change dramatically, which appears as a red-shift in the absorption spectrum.^{38,39} This is illustrated in

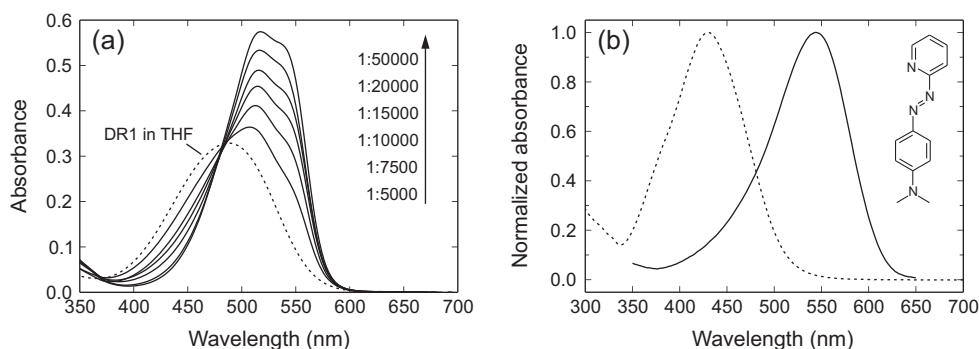


Figure 2.3. (a) UV-Vis absorption spectrum of DR1 in dilute THF solution with different amounts of methanesulfonic acid (MSA) added to protonate the DR1 molecules. The labels indicate the relative number of DR1:MSA molecules. (b) Normalized absorption spectra for unprotonated (dashed line) and protonated (solid line) PADA molecules in a dilute DMF solution. The chemical structure of PADA is shown in the inset, and the protonation is induced by adding MSA to the DMF solution.

Fig. 2.3 for two molecules relevant to this work: Disperse Red 1 (DR1; treated in Publications I & II) and 4-(2-Pyridylazo)-N,N-dimethylaniline (PADA; treated in Publication IV). In addition to the azo linkage, these molecules contain also other basic functional groups that can act as proton acceptors, but we have not studied the exact nature of the proton transfer reaction in these compounds. We have observed that protonation of azobenzene generally inhibits photoisomerization, but have not studied their photoresponsive behavior in detail. Based on a number of recent studies, it seems more favorable to use acidic azobenzene moieties to protonate the surrounding environment. The resulting ionic complexes have been shown to form extremely interesting and efficient photoresponsive materials.^{40–46}

2.2 Aggregation

Azobenzene moieties, like most other chromophores with an extended π -system, are sensitive to packing and aggregation effects due to chromophore–chromophore intermolecular interactions. The nature of these interactions and the packing arrangement of the chromophores depend on the structure and physical properties of the chromophores as well as on their local environment.^{47–49} In general, however, proximity of the chromophores to one another leads to extensive changes in their electronic transition energies.

The aggregation-induced spectral shifts can be qualitatively described by the molecular exciton model introduced by Kasha *et al.*⁵⁰ In this model, Coulombic interactions between closely-spaced chromophores (which are treated as point dipoles; also more elaborate models exist^{51,52}) give rise to excitonic splitting of the electronic transitions into states with different transition energies and oscillator strengths.⁵³ For the case of a dimer consisting of identical molecules with

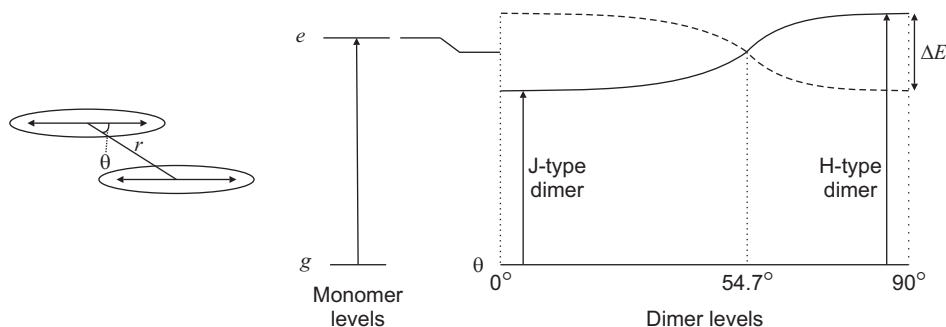


Figure 2.4. Schematic exciton band diagram for a molecular dimer with parallel transition dipoles inclined by an angle θ . The dashed line depicts the forbidden out-of-phase dipole arrangement.

parallel transition dipole moments μ_{ge} , the energy splitting is given by⁵⁰

$$\Delta E = \frac{2|\mu_{ge}|^2}{r^3}(1 - 3\cos^2\theta), \quad (2.1)$$

where r is the center-to-center distance between the molecules and θ is the inclination angle (see Fig. 2.4). The exciton splitting is seen to be directly related to the square of the transition dipole moment of the constituent molecules and is significant only for intense transitions, *e.g.*, for the $\pi \rightarrow \pi^*$ transition in case of azobenzenes. The inclination angle θ determines whether the excitonic coupling leads to higher (H-type dimers) or lower (J-type dimers) transition energies compared to isolated chromophores. A schematic exciton band diagram for the inclined dipoles with parallel transition dipoles is illustrated in Fig.2.4. Note that the transition from the J-type dimer to the H-type dimer takes place at an angle of 54.7° , at which the band splitting is zero irrespective of the chromophore separation.

The effect of chromophore aggregation on the electronic absorption spectrum of DR1 (see Fig. 2.1 for the chemical structure) is shown in Fig. 2.5. The aggregates are clearly of the H-type, giving rise to a *ca.* 60 nm blue shift in the absorption maximum (in polystyrene matrix) compared to isolated DR1 molecules. Such blue shifts are commonly observed in material systems containing planar conjugated molecules like azobenzene and arise from *antiparallel* stacking of the chromophores, which is thermodynamically more favored than parallel stacking for these strongly dipolar chromophores.^{54,55} Note, however, that the aggregates in azobenzene-containing polymers are likely to exist in a wide range of forms including various types of dimers and larger aggregates with different packing geometries. Hence, the spectral signature illustrated in Fig. 2.5 attests the onset of aggregation, but does not allow quantitative analysis on the supramolecular architecture. However, the relative amounts of the chromophores in aggregated and non-aggregated states can be estimated by peak fitting procedures.⁵⁶

Aside from distinct spectral signatures, the H-type and J-type aggregates have a fundamentally different impact on the optical response of the material sys-

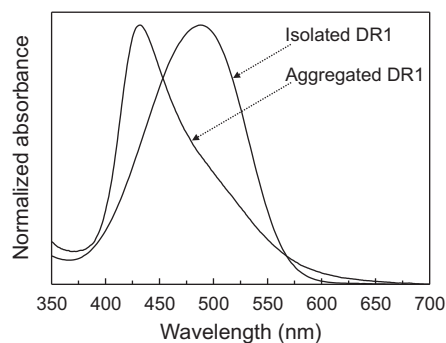


Figure 2.5. Normalized absorption spectra of isolated (measured from dilute THF solution) and aggregated (measured from DR1-doped polystyrene matrix) DR1 molecules.

tem. The formation of H-aggregates is generally detrimental, resulting in fluorescence quenching⁵⁰ and extinguishing of the nonlinear optical response of the material system.⁵³ J-aggregates, on the other hand, exhibit fluorescence, with a quantum yield that quite often surpasses that of the isolated molecules.⁵⁷ Often times driven by specific intermolecular interactions, head-to-tail association of the chromophores also yields highly interesting nonlinear optical materials.^{55,58,59} Unfortunately, the predominant association between planar molecules, particularly for the strongly dipolar push-pull molecules, is of H-type.^{54,60} A great deal of research effort has been directed to preventing these undesired intermolecular interactions,⁶¹⁻⁶⁴ and on the other hand to attaining quantitative understanding on their role on the optical response of the material system.⁶⁵⁻⁶⁸

Naturally, chromophore-chromophore interactions also influence the photoisomerization-induced effects in azobenzene-containing materials. Studies on Langmuir-Blodgett films have revealed that the strong aggregation tendency of the *trans*-azobenzenes restrains conformational changes and hampers *trans-cis* isomerization.^{69,70} On the other hand, interactions between the rod-like *trans*-azobenzenes may give rise to self-assembled liquid-crystalline (LC) phases where *collaborative motions* enhance for instance the photo-orientation of the azobenzene moieties with linearly polarized light (see Sec. 4.1).⁷¹⁻⁷³ Aggregates can also be broken by light irradiation, hence pre-irradiation as well as the intensity of irradiation can significantly modify the photoresponse.⁷⁴⁻⁷⁶ Altogether, the role of chromophore-chromophore interactions on the photoresponsive behavior of azobenzene-containing materials is an elaborate issue which depends on the constitution of the material system, sample preparation conditions, and experimental details in a complicated manner.

2.3 Photoswitching and photomechanics

Besides being useful as photochromic probes that are highly sensitive to the local environment and specific intermolecular interactions, azobenzene compounds can be exploited to design functional materials whose chemical and physical

properties as well as phase behavior can be controlled with light.⁷⁷ Photoisomerization provides reversible control over, *e.g.*, the viscosity and solubility of polymer-containing solutions,^{78,79} and over the conductivity in the solid state,^{80,81} to mention but a few of the potential uses.

A fascinating and widely studied research area employs azobenzene and other photochromic molecules to optically control the structure and functions of biomaterials, and to use them as model compounds to study complex light-triggered biochemical processes such as vision.^{82,83} In polypeptides, azobenzenes can induce, *e.g.*, reversible order–disorder transitions or α -helix– β -sheet transformations.^{84–86} Also, duplex formation of DNA has been controlled through *trans*–*cis*–*trans* isomerization.⁸⁷ Conversely, photocontrollable biomaterials exhibit interesting optical properties, showing potential for applications such as holographic storage and all-optical switching.^{88–93}

The optical and photomechanical properties of azobenzene-containing materials have attracted a great amount of research effort recently.^{5,8,9,94–96} The photoisomerization reaction enables one to photo-orient the chromophores with linearly polarized light, giving rise to birefringence, dichroism, and under certain conditions, to nonlinear optical response in the material system. Moreover, photoisomerization can lead to macroscopic motions of the material, even over distances of several microns, which enables the inscription of photoinduced surface-relief structures. These phenomena form the core of this thesis and will be discussed in more detail in Chapter 4, with the main emphasis on the light-induced processes in *amorphous* azobenzene-containing polymers.

The rigid and anisotropic structure of the *trans*-azobenzene also allows it to be incorporated into many LC systems, and various azobenzenes and azobenzene-containing polymers exhibit LC mesophases as such. The large structural changes associated with the isomerization process provide control over the LC phase: due to the nonmesogenic nature of the *cis*-azobenzene, isomerization can lead to reversible LC–isotropic phase transitions.^{94,97} Another level of control is provided by the *collaborative motions*^{8,95} taking place in LC systems. Together, photoisomerization and photoreorientation provide a facile way to control not only the LC phase but also the LC director.^{95,98} This photocontrol can be achieved by incorporating only a small amount of azobenzene molecules into the LC system: even 1 mol % of azobenzene dopant suffices to induce an alignment change or a phase transition to the whole system.^{9,94}

Another function of azobenzene is that the photoisomerization can be exploited to convert light energy into mechanical energy by inducing reversible shape and volume changes into the material system.^{9,94} Such photoinduced deformations are present also in amorphous polymers, where they occur in an isotropic manner with no preferential deformation direction and are relatively weak: the photoinduced contraction in amorphous polymers is at most on the order of a few percents.⁹⁹ In LC polymers, the mechanical power that can be produced is amplified by the inherent anisotropy of the material system, leading to reversible photoinduced contraction up to tens of percents.¹⁰⁰ Another striking example of the photomechanical effect is light-driven bending of polymer films

with response times in the millisecond range and with the bending direction being controlled by the polarization of the incident light.^{101,102} The light-induced mechanical forces are comparable in strength to the contraction force of human muscles, and may lead to potential applications, for instance, as artificial muscles or photodriven oscillators.^{103,104}

– the best scientists are poets, the
real engineer is an artist –

Sue Birchmore

3

Polymer–azobenzene complexes

The light-induced processes initiated by the photoisomerization of azobenzenes have been studied in various environments, including self-assembled monolayers,^{105,106} Langmuir–Blodgett films,^{69,107} vacuum-evaporated thin films,¹⁰⁸ hybrid organic–inorganic composites,¹⁰⁹ electrostatically self-assembled multilayers,¹¹⁰ and polymeric materials.^{8,111} Among these, polymers offer significant advantages in view of their high processability, good film-forming properties, and flexibility in the molecular design, making them the most studied class of azobenzene-containing materials. However, despite their promising features, polymers also have several restrictions regarding reproducibility, lifetime, and stability of the optical response, that limit their practical applicability. Due to these limitations, novel materials concepts are still actively investigated. The central theme of this work is to exploit supramolecular concepts¹¹² to form *polymer–azobenzene complexes* and to study their photoresponsive behavior. This chapter introduces the design principles behind this non-covalent functionalization strategy.

3.1 Polymeric optical materials: a brief introduction

The interest in polymeric optical materials[†] is a consequence of the intriguing optical properties of organic molecules, which can be optimized to meet the requirements of a specific application through organic synthesis. Often times the optical response arises from *single* chromophores while chromophore aggregation suppresses the response (see Section 2.2). Therefore the task of the polymer matrix is not only to ensure good film-forming, thermal, and mechanical properties but also to prevent excessive chromophore–chromophore interactions. The function of the chromophores can be based, *e.g.*, on their photochromism, photoluminescence, or nonlinear optical response. In fact, quantitative understanding of the structure–property relationships, orientational ordering, and relaxation phenomena in polymer–chromophore systems has largely been driven by the nonlinear optics community and was later applied to analyze the photoinduced orienta-

[†]In the course of this work, polymeric optical materials refer to material systems where the optical response is provided by guest molecules that are either doped into or bonded to the host polymer, excluding for instance conjugated polymers.

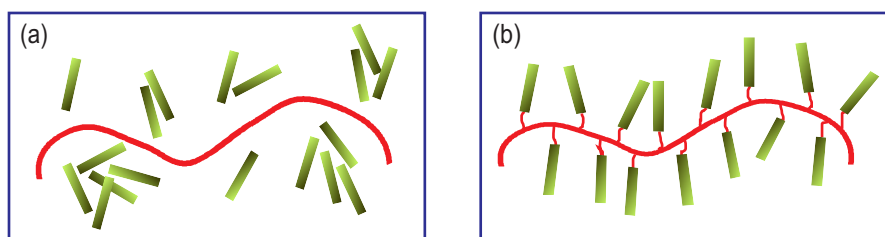


Figure 3.1. Schematic representation of (a) conventional guest–host system with essentially no interaction between the chromophores and the polymer chains, (b) covalently-functionalized side-chain polymer.

tional mobility of azobenzene-containing polymers.^{113–116} Each application requires an active chromophore with a different structure and properties, and when it comes to practical device applications, the sample composition and the nature of bonding to the polymer matrix have to be carefully designed and optimized.^{3,4} Also the preparation process is highly elaborate, consisting of various steps, each of which has to be well planned in order to yield high and reproducible optical performance. Hence, the following discussion is in many aspects oversimplified but suffices to bring out the motivation and context of the present work.

The incorporation of the photoactive chromophores into the polymer matrix can be done in different ways.²² The simplest approach is to dissolve the chromophores into the host polymer to form a guest–host system (Figure 3.1a). These systems are simple and cost-effective as they only require mixing of the constituents in order to produce the desired compound. So in principle, the chromophore concentration and the composition of a guest–host system can be easily controlled. In practice, however, there are numerous undesirable features that limit the practical usability of guest–host systems. The solubility of the dopant molecules is limited to moderate levels because of aggregation effects and macroscopic phase separation. Another severe issue is the high degree of orientational mobility of the chromophores within the polymer matrix due to the lack of chromophore–polymer interactions. Due to these issues, the temporal and thermal stability of conventional guest–host systems is unacceptably low for applications that require net alignment of the chromophores.

To overcome the problems of guest–host systems, the active molecules have been chemically attached to the polymer backbone (Figure 3.1b). Such covalently-functionalized polymers allow high concentration of the active chromophores to be homogeneously incorporated into the polymer without phase separation. Hence, their optical response is generally much higher and optical losses lower than in the guest–host systems.^{3,117} Another important advantage is that the orientational relaxation of the chromophores is hindered by the covalent attachment and the T_g is generally higher than in corresponding guest–host systems, resulting in superior temporal and thermal stabilities in applications that require net alignment of the chromophores.^{118–120} The cost of the improved optical performance is that tedious multistep synthesis is required for each combination of a

polymer and an active molecule, making the sample preparation relatively expensive and time-consuming.

3.2 Supramolecular side-chain polymers

Supramolecular side-chain polymers[†] consist of a polymeric backbone to which the side chains are attached through non-covalent bonds.¹²² This can be accomplished through a number of interactions, including single and multiple hydrogen bonds, ionic interactions, metal coordination, or a combination of these.^{123–125} As opposed to traditional synthesis strategies based on covalent bonds, non-covalent interactions form spontaneously. This provides obvious advantages compared to covalently-functionalized polymers: if the polymer and the side chains have complementary recognition motifs, the side-chain concentration can be tuned over a wide range, up to the point where each repeat unit of the polymer is occupied. Furthermore, the polymer can be functionalized with two or more side chains, each possessing a specific role in the material system.¹²⁶ Such modular tunability can be realized without sacrificing the ease of preparation of conventional guest–host systems. Hence, one could anticipate that non-covalently functionalized polymeric optical materials, *polymer–dye complexes* (Figure 3.2), combine the advantages of guest–host systems and covalently-functionalized polymers.

Non-covalent polymer functionalization strategies were first reported for the synthesis of side-chain liquid-crystalline (LC) polymers.^{127,128} Conventionally such polymers are prepared via covalent tethering of the mesogenic entities to the polymer backbone via flexible spacers. The spacers need to be long enough to separate the mesogens from the polymer backbone to allow them to assemble into a liquid-crystalline phase. In supramolecular side-chain LC polymers the design principle is the same, yet the functionalization is performed through spontaneous non-covalent interactions. The motivation behind these studies is that the concept adds simplicity to the preparation of side-chain LC polymers: one can employ standard (commercially available) polymers in combination with mesogenic side chains bearing complementary functional groups to yield the LC structures.^{129,130} In fact, supramolecular side-chain LC polymers can be generated by complexing non-mesogenic precursors even *without* the presence of a spacer between the polymer and the side-chains.^{44,131} But even more importantly, the dynamic and reversible nature of specific non-covalent interactions brings about functionalities beyond conventional synthesis strategies to the material system, allowing to design highly complex structures whose functionality and phase behavior can be controlled by external influences.^{123,132–134}

Liquid-crystalline-like self-assembly can also take place in polymer–surfactant complexes.^{135,136} In such complexes, self-assembly is driven by the interplay between the attractive (specific non-covalent bonding between the constituents)

[†]A distinction should be made to *supramolecular polymers*, which are defined as polymeric materials consisting of monomeric units that are brought together by non-covalent interactions.¹²¹

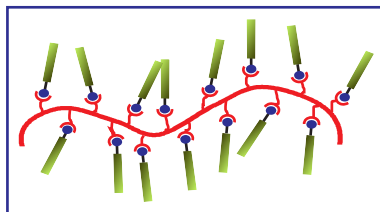


Figure 3.2. Schematic representation of a polymer–dye complex where spontaneous non-covalent interactions are used to attach the chromophores to the polymer chains and to suppress chromophore aggregation [Publication I].

and repulsive (the tendency of the nonpolar alkyl chains of the amphiphilic surfactants to phase separate from the polar polymer backbone) interactions present in the material system. Particularly well-studied are systems employing phenolic surfactants that are hydrogen-bonded to poly(4-vinylpyridine) (P4VP) backbone.^{137–142} Such complexes typically yield lamellar morphology whose period and phase behavior can be controlled by the degree of complexation and the nature of the surfactant.^{137,138,142} Extending the concept to P4VP-containing block-copolymers, one can design hierarchical structures that self-assemble in two length scales (Figure 3.3a):^{139–141} the micro-phase separation of the block copolymers gives rise to self-assembled nanostructures with a characteristic length scale in the 10–100 nm range¹⁴³ while the inner structure which is selectively bonded to the P4VP block contains a layered structure in the 3–5 nm range (Figure 3.3b).

An important feature of the relatively weak phenol–pyridine hydrogen bonding is that it can be reversibly broken by external triggers which allows one to tune the structure and functionality of the material system through order–disorder transitions.¹⁴⁵ The hydrogen-bonded side chains can also be extracted from the material system altogether by dissolving them with a suitable solvent. This can be exploited to prepare porous structures or polymeric nano-objects whose pore size and thickness can be adjusted by varying the block lengths.^{146,147} The obtained polymeric nano-objects can be further used as templates as they can be subsequently coated with metals or insulators to yield, for instance, ordered metallized nanowires or inorganic nano-objects.^{148,149}

Azobenzene brings an additional degree of control to the supramolecular nanostructures. As in biomaterials (Section 2.3), photochromic moieties allow one to photochemically stimulate reversible morphological transitions in both small-molecule and macromolecular assemblies.^{150,151} In block copolymers, photoinduced motions initiated by azobenzene units covalently attached to one of the blocks can be used to direct the self-assembly, allowing optical control over the domain orientation in three dimensions.^{152–154} Naturally, azobenzenes can also be complexed with polymeric backbones to yield photoresponsive supramolecular side-chain polymers.^{155–157} Considering the extent of studies on supramolecular side-chain polymers in the field of supramolecular materials science and the commercial potential of polymeric optical materials, surprisingly few reports exist on supramolecular polymeric *optical* materials. Only very recently, a

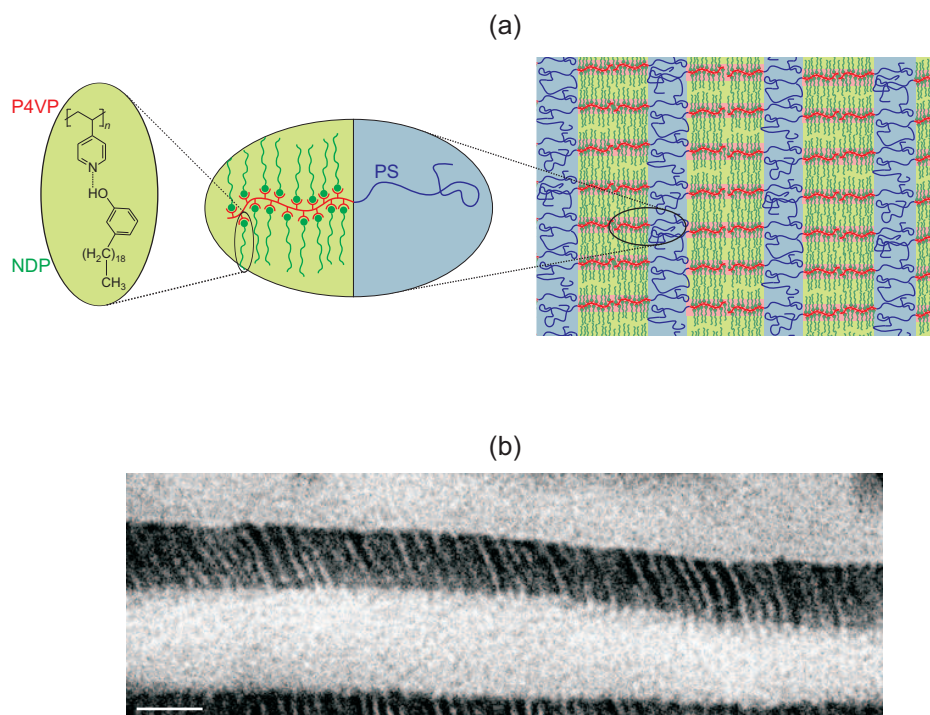


Figure 3.3. (a) Schematic representation of a hierarchical lamellar-*within*-lamellar nanostructure consisting of polystyrene–poly(4-vinylpyridine) (PS-*b*-P4VP) block copolymer where a nonadecylphenol (NDP) surfactant has been hydrogen bonded to each P4VP repeat unit.¹⁴⁴ (b) Transmission electron micrograph of the PS-*b*-P4VP(NDP)_{1.0}, showing clearly both the lamellar block copolymer morphology and the inner structure of the P4VP block.¹³⁹ The scale bar corresponds to *ca.* 20 nm.

number of research groups have started to investigate the photoresponsive behavior of non-covalent azobenzene-containing complexes, as reviewed in Section 5.1. The main thrust of carrying out the present work comes from the success of phenol–pyridine hydrogen bonding, being employed in Publications III & IV to obtain polymer–azobenzene complexes with an interesting and efficient photoresponsive behavior.

– I don't have any solution but I certainly admire the problem –

Ashleigh Brilliant

4

Photoinduced processes in azobenzene-containing polymers

The ability of some materials to become optically anisotropic upon irradiation with polarized light has been known since the beginning of the 1900s in photographic silver emulsions. In azobenzene-containing viscous liquids and polymers, such photoinduced anisotropy was observed in the 1960s, and was soon after associated with the photoisomerization reaction. In 1984, Todorov *et al.* suggested the use of azobenzene-containing polymers for polarization holography,^{158,159} but only the work of Wendorff *et al.* on reversible storage using liquid-crystalline polymers¹⁶⁰ triggered detailed and comprehensive studies on photo-orientation of azobenzenes in both liquid-crystalline and amorphous polymers. Soon after, the phenomena of light-assisted poling¹⁶¹ and all-optical poling¹⁶² were reported, and in 1994, the formation of photoinduced surface-relief structures was demonstrated.^{163–165} The richness of photoisomerization-induced optical and photomechanical phenomena has attracted tremendous research interest towards the fundamental properties as well as the practical applicability of azobenzene-containing polymers.

4.1 Photoinduced anisotropy

The photoinduced anisotropy in azobenzene-containing polymers is a consequence of polarization-sensitive excitation of the azobenzene moieties. *Trans*-azobenzene can be considered as a uniaxial molecule whose optical absorption cross section σ depends on the angle ϕ between the polarizability axis and the direction of light polarization as¹⁶⁶

$$\sigma(\phi) = (\sigma_a \cos^2 \phi + \sigma_i), \quad (4.1)$$

where σ_a and σ_i refer to the anisotropic and isotropic parts of $\sigma(\phi)$, respectively. When an isotropic azobenzene-containing sample is irradiated with linearly polarized light, the polarization-sensitive excitation leads to two processes: orientational hole burning (OHB) and angular redistribution (AR).¹⁶⁷ OHB results from the large anisotropic *cis*-population arising from the polarization-sensitive excitation, which "burns a hole" in the orientational distribution of the *trans*-isomer.

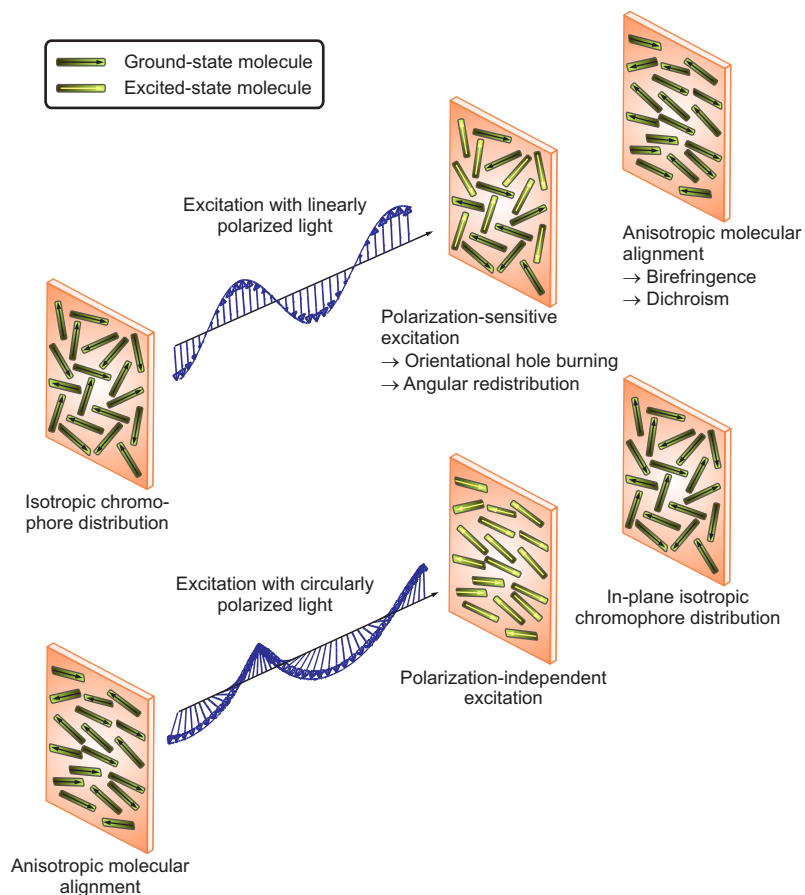


Figure 4.1. Top: Schematic illustration of the photoinduced in-plane alignment of azobenzenes upon excitation with polarized light. Bottom: The initial isotropic state can be restored by irradiating the sample with unpolarized or circularly polarized light.

AR arises from the fact that the *trans*–*cis*–*trans* photoisomerization cycle can give rise to reorientation of the azobenzene molecules.¹⁰⁵ As the selective pumping of an initially isotropic chromophore distribution activates the photoisomerization reaction only for molecules with the transition dipole component in the direction of polarization, the reorientation causes the molecules to accumulate in the direction perpendicular to the polarization direction after successive isomerization cycles (Figure 4.1). In general, both OHB and AR contribute to the overall anisotropy of the material system,^{168,169} but typically the anisotropy that remains after the irradiation is ceased arises from the angular redistribution of the chromophores.

Because of the inherent anisotropy of the *trans*-azobenzene and the significant spectral changes induced upon *trans*–*cis* isomerization, photoinduced dichroism measurements provide a useful tool for studying the orientational mobility of azobenzene in polymer matrices.¹⁷⁰ In addition, photoalignment of the rod-like chromophores gives rise to large and stable in-plane birefringence, even values exceeding 0.5 have been reported.^{171,172} The induced birefringence can be subse-

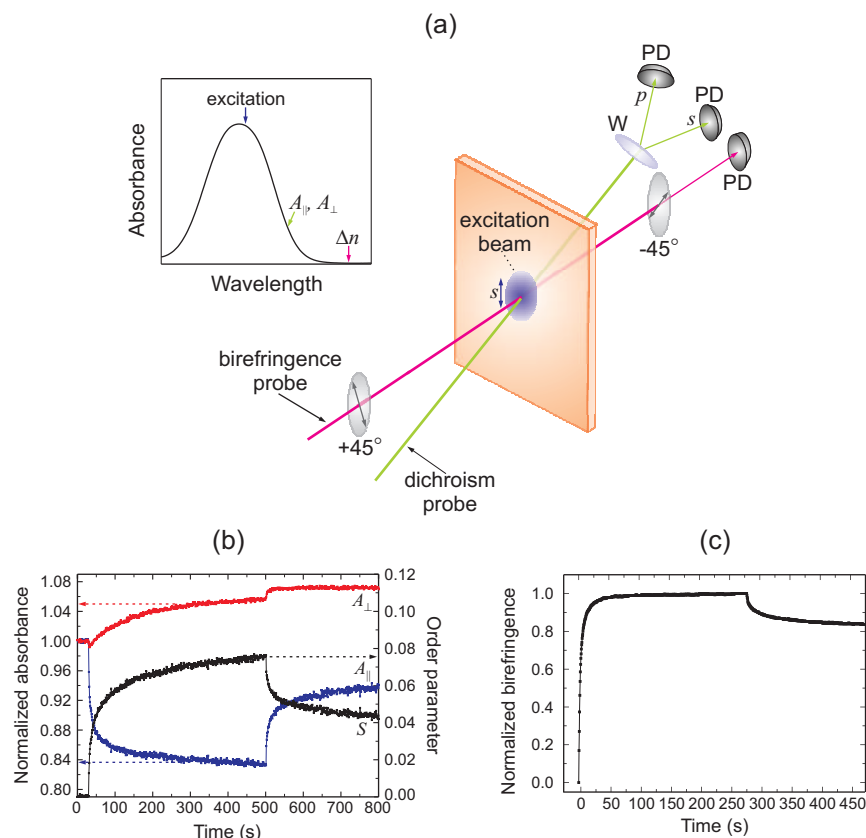


Figure 4.2. (a) Schematic representation of the experimental setup for photoinduced birefringence and dichroism measurements. Abbreviations: W, Wollaston prism; PD, photodiode; $\pm 45^\circ$; polarizers. (b) Dynamics of the photoinduced dichroism and the order parameter S , measured from a sample consisting of 10 mol % 4-(2-Pyridylazo)-*N,N*-dimethylaniline in a poly(4-vinyl phenol) matrix (Publication IV). The irradiation period is 30–500 s. (c) typical photoinduced birefringence measurement, obtained from a DR1-functionalized methacrylic side-chain polymer (pDR1M).¹⁷⁷ The irradiation period is 0–275 s.

quently erased (Figure 4.1) and rewritten even up to thousands of times¹⁷³ and it is the main motivation for considering azobenzene-containing polymers for optical-memory applications.^{174–176}

A typical experimental setup as well as experimental measurement results for the photoinduced dichroism and birefringence are shown in Figure 4.2. The excitation is typically performed with an *s*-polarized beam, the wavelength of which is chosen to match the absorption maximum of the chromophores.[†] The dichroism is measured with an unpolarized or circularly polarized beam, typically with a wavelength at the long-wavelength side of the absorption band of the chromophores. The transmitted light is divided into two orthogonally polarized beams with a Wollaston prism after crossing the sample. The data shown

[†]In some cases, irradiation at the absorption maximum does not give rise to anisotropy even if the isomerization process is highly efficient. This can be attributed to an isotropic chromophore distribution due to the high *cis*-population.^{144,178}

in Figure 4.2b depicts an important signature of the angular redistribution: the absorbances parallel (A_{\parallel}) and perpendicular (A_{\perp}) to the polarization direction of the irradiating light evolve in opposite directions, and the increase in A_{\perp} is associated with the accumulation of the molecules in that direction. In contrast, if OHB dominates the overall anisotropy, both A_{\parallel} and A_{\perp} decrease with respect to the isotropic absorbance due to the large *cis*-population.¹⁶⁹ A decrease in the overall absorbance can also be a consequence of the alignment of the chromophores in the light propagation direction, making them "invisible" to the normally incident monitoring beams. Such light-induced out-of-plane alignment can be particularly pronounced in LC polymers,^{72,179} and can be controlled with oblique irradiation geometries.¹⁸⁰

An often used quantity to study the photoalignment process, deduced from the photoinduced dichroism data, is the macroscopic order parameter

$$S = \frac{|A_{\parallel} - A_{\perp}|}{A_{\parallel} + 2A_{\perp}}. \quad (4.2)$$

The order parameter varies between 0 and 1, depicting an isotropic sample and a perfectly aligned sample, respectively. For amorphous polymers the order parameter is typically small, below 0.1 (see Figure 4.2b), while in LC polymers collaborative motions⁸ can lead to order parameters exceeding 0.5. Moreover, whereas in amorphous polymers the anisotropy decreases with increasing temperature and reaches zero at T_g , in LC polymers the order parameter can be markedly enhanced upon phase transition from the glassy to the LC state with increasing temperature.^{72,181} Note also that irradiation with polarized light can lead to significant changes in the shape of the absorption spectrum, for instance, by breaking the aggregates (see Section 2.2) in the direction parallel to the excitation beam polarization while leaving the aggregates in the perpendicular direction intact.¹⁸² In order to avoid misinterpretation of the data, it is important to measure also the polarized absorption spectra during the excitation.

Photoinduced birefringence is measured by placing the sample between crossed polarizers and monitoring the transmittance of the probe beam through the polarizer/sample/analyzer combination. In order to maximize the transmitted signal, the axes of the polarizer and analyzer are aligned to $\pm 45^\circ$ with respect to the polarization direction of the excitation beam. Assuming that the absorption of the probe beam is negligible, the birefringence Δn is related to the transmitted signal I as

$$I = I_0 \sin^2 \left(\frac{\pi |\Delta n| d}{\lambda} \right), \quad (4.3)$$

where I_0 is the signal for parallel polarizer/analyzer orientation (measured through an unirradiated spot on the sample to take into account reflection losses), d is the film thickness, and λ is the wavelength of the probe beam. Once the irradiation is ceased, the tendency of thermal randomization in the chromophore orientation results in a decrease in the birefringence (and order parameter), as shown in Figure 4.2c. The extent of the thermal randomization depends, *e.g.*, on

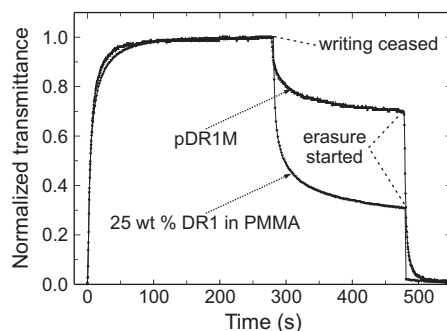


Figure 4.3. Writing–relaxation–erasure curves for the photoinduced birefringence in a DR1–PMMA guest–host system and in a DR1-functionalized side-chain polymer (pDR1M). The writing is performed using different irradiation wavelengths and intensities, hence the saturation times for the two samples are not comparable. The erasure is performed by randomizing the in-plane chromophore alignment with circularly polarized light.

the size of the chromophores and on the T_g of the polymer,^{119,183} but most of all, it depends on the type of polymer system: in guest–host systems the high mobility of the chromophores leads to rapid angular diffusion and low temporal stability of the induced anisotropy, whereas in covalently-functionalized polymers a significant fraction of the induced anisotropy is preserved in the long term. This is illustrated in Figure 4.3 for DR1-doped and DR1-functionalized poly(methyl methacrylate) (PMMA). Also shown in the Figure is the optical erasure by randomizing the anisotropic chromophore orientation in the plane of the film with circularly polarized light. The high temporal stability together with the possibility of using higher chromophore concentrations than in guest–host systems (see Section 3.1) has confined a majority of the photoinduced anisotropy studies to covalently-functionalized polymers.

4.2 Photoinduced surface-relief structures

Perhaps the most astonishing physical process in amorphous azobenzene-containing polymers is the formation of photoinduced surface-relief structures: the photoisomerization of the nanometer-sized chromophores can lead to large-scale mass migration of the polymer chains over distances of several microns.^{164,165} When exposed to an interference pattern of light with spatial variation of the intensity and/or polarization, the free surface of the film deforms in response to the incident light field and reproduces the intensity and/or polarization variation as a surface-relief structure. The process allows inscribing highly elaborate surface structures with a surface-modulation depth of hundreds of nanometers, opening a new approach for fabricating diffractive optical elements and photonic components.¹⁰ The inscribed gratings can be subsequently erased either thermally or in some cases even by light.¹⁸⁴

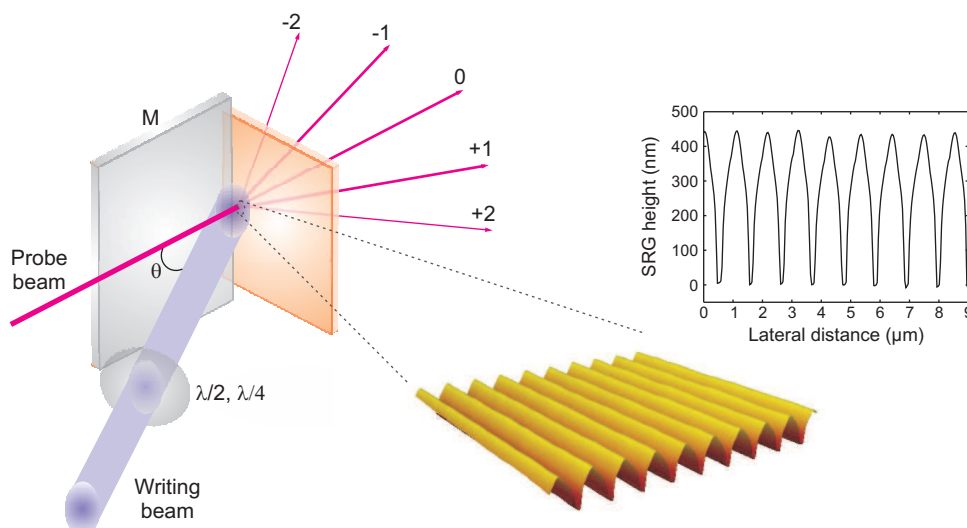


Figure 4.4. Experimental setup for the inscription of surface-relief gratings. $\lambda/2$ and $\lambda/4$ denote wave plates that are used to control the polarization of the irradiation beam, and M refers to a mirror that reflects half of the incident beam onto the sample to form the interference pattern. The setup can be used to inscribe surface-relief gratings with modulation depths of several hundred nanometers as illustrated by the atomic-force micrograph and the surface profile shown on the right (Publication IV).

The surface patterning occurs in a wide range of azobenzene-containing material systems, even at irradiation intensities of only $5 \text{ mW}/\text{cm}^2$.¹⁸⁵ It is a highly complex process, the efficiency of which depends on the nature of the material system as well as on the details of the experimental arrangement.^{185–187} In azobenzene-containing polymers, efficient photoinduced mass migration requires strong bonding between the chromophores and the polymer chains, hence only very weak surface-relief gratings (SRGs) can be inscribed in conventional guest–host type polymers.^{188,189} Despite extensive experimental and theoretical research since its discovery in 1995,^{164,165} the driving force behind this peculiar photomechanical process is not yet comprehensively understood.

The experimental setup for the inscription of SRGs, used throughout this work, is shown in Figure 4.4. The interference pattern is created by bringing half of the beam directly on the sample and reflecting the other half from a mirror set at right angle with the sample. For such a writing geometry, the fringe spacing Λ is determined by the angle between the beam propagation axis and the sample normal θ as

$$\Lambda = \lambda / (2 \sin \theta), \quad (4.4)$$

where λ is the wavelength of the irradiating laser beam. The inscription of the grating can be monitored in real time by measuring the first-order (and also the second-order if the grating spacing is sufficiently large) diffraction of a low-power probe beam, the wavelength of which is chosen such that it is not absorbed by the chromophores. Analytical methods, based on Jones matrix for-

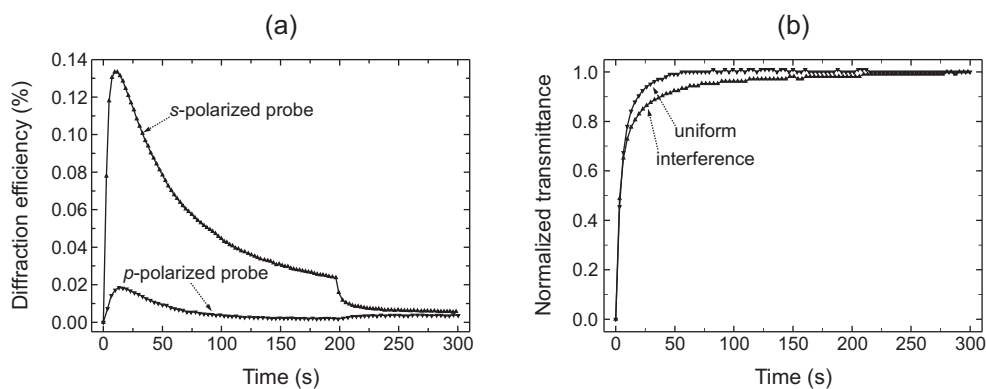


Figure 4.5. (a) First-order diffraction of a 650 nm probe beam from a pDR1M sample irradiated by an *s*-polarized interference pattern (488 nm, 20 mW/cm²). The pDR1M film was coated with a thin (100 nm) poly(vinyl alcohol) layer in order to inhibit SRG formation. (b) Normalized transmittance of the 650 nm probe beam through the same sample placed between crossed polarizers under uniform gaussian excitation and under excitation with an *s*-polarized interference pattern. The irradiation intensity was 80 mW/cm². In both cases, the saturated birefringence is *ca.* 0.1, indicating that the final degree of orientation is the same. The fact that the time to reach saturation is longer under excitation with the interference pattern supports the conclusion that saturation is reached at different times for different positions under the non-uniform light intensity distribution. Similar results were also obtained when using a *p*-polarized interference pattern.

malism, have been developed to separate the first-order diffracted signal into contributions arising from the surface-relief and from the refractive-index modulation in the bulk of the film.^{190,191} Such a separation is enabled by the distinct dynamics and polarization dependence of the bulk birefringence and the surface-relief grating formation.^{191–193} Their relative contributions depend on the material system: in LC polymers diffraction arises mainly from the bulk birefringence grating whereas in amorphous polymers the bulk contribution is overwhelmed by diffraction from the SRG. In fact, based on our recent experiments, the bulk contribution can in amorphous polymers be neglected altogether when using *p*- or *s*-polarized writing beams.¹⁹⁴ This is rationalized by the fact that the intensity minima of the sinusoidal interference pattern are always non-zero, and for constant polarization throughout the pattern, the photo-orientation occurs at different time scales under the interference maxima and minima until reaching saturation throughout the irradiated area. Such a behavior leads to an initial increase followed by a gradual decrease of the first- (and second-) order diffraction efficiency, as illustrated in Figure 4.5 and supported by a phenomenological model.¹⁹⁴ At the same time, the birefringence increases continuously and causes the bulk birefringence grating to disappear on the same time scale as required for the birefringence to saturate also in the areas of low intensity.

The efficiency of SRG formation depends strongly on the polarization of the writing beam. This is illustrated in Figure 4.6 for a DR1-containing side-chain polymer (pDR1M): a *p*-polarized writing beam gives rise to a diffraction efficiency of almost 40 %, but when the sample is exposed to an *s*-polarized writing

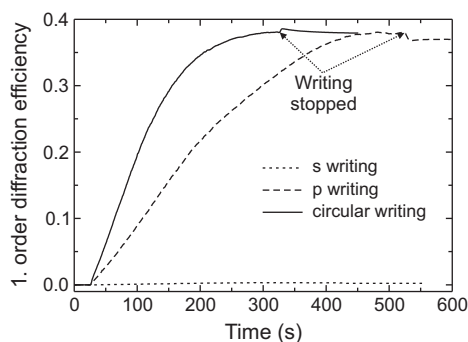


Figure 4.6. Diffraction efficiency (monitored with a 650 nm diode laser) of thin films of pDR1M exposed to writing beam (488 nm, 100 mW/cm²) with different polarizations.

beam, the diffraction efficiency remains well below 1 %. Hence the presence of an intensity gradient alone does not lead to SRG formation but the field must also have a polarization component in the direction of the grating vector, which rules out significant contribution from thermal effects or photodegradation on the SRG formation. For pDR1M, the rate of the grating inscription is seen to be most efficient when the writing beam is circularly polarized, *i.e.*, when the interference pattern gives rise to periodic modulation of the polarization and only weak modulation in the intensity.^{185,195} However, this is not always the case and for some azobenzene-containing polymers *p*-polarized writing beam gives rise to the largest surface modulation (for instance for the complexes studied in Publication IV). Furthermore, in some LC polymers a prerequisite for mass migration is pre-exposure with UV light, after which the process is driven by intensity variations, irrespective of the polarization state of irradiation.^{196,197}

Various models have been proposed to explain the underlying mechanism behind SRG formation,^{185,198–201} none of which accounts for all the experimental observations. The photoinduced SRG formation in azobenzene-containing polymers is likely to be driven by several microscopic mechanisms whose relative importance depends on the details of the material system. For example, there are fundamental differences in the SRG formation in amorphous and LC polymers: in amorphous polymers the maxima of the surface pattern typically coincide with the dark regions of the intensity distribution whereas in many LC polymers the molecules migrate into the irradiated regions.^{202,203} In both cases, efficient *trans-cis-trans* isomerization of the azobenzene moieties is an essential prerequisite for the mass migration to occur. Recently, it was elegantly shown using near-field imaging²⁰⁴ that in amorphous azobenzene-containing sol-gel films the SRG is *in phase* with the intensity maxima for *s*-polarized interference pattern, due to the photoexpansion of the material resulting from azobenzene photoisomerization.^{77,99} This happens also for a *p*-polarized interference pattern at the beginning stage of the inscription process, but subsequently another grating builds up with a spatial phase opposite to that of the interference pattern. Conversely, for a polarization modulation with only weak intensity modulation, the photoexpansion is spatially homogeneous and does not give rise to SRG, but the overall efficiency

of the photoinduced mass migration is increased.²⁰⁴ These measurements imply that *no* mass migration takes place for *s*-polarized inscription even though a SRG is formed, and unambiguously demonstrate that at least two distinct processes contribute to the SRG formation.

4.3 Azobenzene in nonlinear optics: all-optical poling

Aside from efficient photoisomerization, many azobenzene derivatives exhibit strong nonlinear optical (NLO) response. Nonlinear optical phenomena occur as a consequence of the modification of the optical properties of a material system by the presence of light.²⁰⁵ The term "nonlinear" refers to the fact that at sufficiently high field strengths, the relationship between the electric-field-induced molecular dipole moment \mathbf{p} and the applied field \mathbf{E} can no longer be taken as being linear but has to be expressed more accurately as a series expansion

$$\mathbf{p} = \alpha \cdot \mathbf{E} + \beta : \mathbf{E}^2 + \gamma : \mathbf{E}^3 + \dots, \quad (4.5)$$

where α is the linear molecular polarizability, and β and γ are the first- and second-order hyperpolarizabilities that give rise to second- and third-order NLO response of the molecule, respectively. Second-order NLO materials are particularly promising for a number of photonics applications as they can be used for *frequency conversion* and they exhibit *linear electro-optic effect* in which the refractive index of the material can be controlled through the application of an external electric field. An important symmetry requirement for the second-order NLO effects to occur is that the molecules must lack a center of inversion for β to be nonvanishing. Furthermore, in order for the material system to exhibit *macroscopic* second-order response, the non-centrosymmetric molecules must be arranged in such a manner that also the bulk material is non-centrosymmetric.²⁰⁶ This requirement is not fulfilled by the photo-orientation process described in Section 4.1, which leads to net alignment of the chromophores, but is insensitive to the sense of orientation.

Polymeric materials show promise for both second- and third-order NLO applications. The main thrust comes from the exceptionally high and fast NLO response of organic molecules, combined with the high processability of the polymeric materials.³ Molecules for second-order NLO applications are typically based on aromatic π -electron systems where charge asymmetry is introduced by substitution with strong electron-donating and electron-accepting groups.²⁰⁷ Hence pseudostilbenes, such as DR1 (Figure 2.1), can be considered as prototype-NLO chromophores. Most polymeric materials are inherently isotropic, posing no macroscopic second-order NLO response unless the symmetry is broken by external influences. The noncentrosymmetric chromophore alignment is typically obtained by making use of the permanent dipole moment of the NLO molecules due to the asymmetric electronic distribution. Provided that the mobility of the chromophores in the host polymer is high enough, they can be aligned

with a static electric field through coupling between the permanent dipole moment and the external field.²² The increased mobility is achieved by increasing the temperature close to T_g , and the polar chromophore orientation is frozen by cooling the sample to room temperature while the field is being still applied to the sample. The technique is referred to as thermally-assisted poling.

Using azobenzene derivatives as the NLO units provides some unique possibilities.⁹⁶ The molecular hyperpolarizability can be reversibly switched through the photoisomerization reaction.^{5,24} Moreover, photoisomerization and photo-orientation of azobenzene moieties have launched two novel poling techniques: photoassisted poling¹⁶¹ and all-optical poling¹⁶². In photoassisted poling, a combination of a static electric field and an optical field is used to break the centrosymmetry of the medium. The sample is resonantly irradiated with circularly polarized light, which gives rise to *trans-cis-trans* cycling of the chromophores and tends to orient them along the direction of light propagation. The torque induced by a simultaneously applied dc field causes the dipoles to preferentially orient in the direction of the dc field, giving rise to net polar alignment of the chromophores and a macroscopic NLO response. The main advantages of the technique are that poling can be performed at room temperature, and that it allows inscribing patterns of oriented molecules without complex electrode structures. However, the induced nonlinearity is smaller than that obtained in thermally-assisted poling,¹⁰⁵ and the method is limited by the penetration depth of the resonant excitation.

All-optical poling exploits purely optical fields to break the centrosymmetry of the material. Unlike the thermally-assisted and photoassisted poling techniques where the symmetry is broken via out-of-plane orientation of the molecules, all-optical poling is based on in-plane photo-orientation of the azobenzene chromophores. Instead of the conventional resonant excitation, the technique exploits a coherent superposition of two beams, one at frequency ω (writing beam) and the other at 2ω (seeding beam).²³ Separately, the writing and seeding beams give rise to nonpolar photo-orientation of the chromophores perpendicular to their polarization directions, driven by two-photon and one-photon absorption, respectively. However, the *interference between the one- and two-photon processes* leads to polar excitation of the chromophores.²⁰⁸ In other words, the excitation probability is different for the dipoles pointing in the "upward" and "downward" directions, as illustrated in Figure 4.7a.

If the polarization directions of the writing and seeding beams are parallel, a majority of the chromophores will be axially oriented perpendicular to the polarization direction and will not contribute to the second-order response. Instead, the nonlinearity is determined by the molecules that remain in the parallel orientation, as schematized in Figure 4.7b.²⁰⁹ However, the poling process is by no means restricted to parallel linear polarizations of the writing and seeding beams. In fact, the molecular polar alignment and hence the symmetry properties of the induced nonlinearity can be controlled by tuning the polarization properties of the writing and seeding beams,²¹⁰⁻²¹² which is a unique feature of the all-optical method compared to other poling techniques.

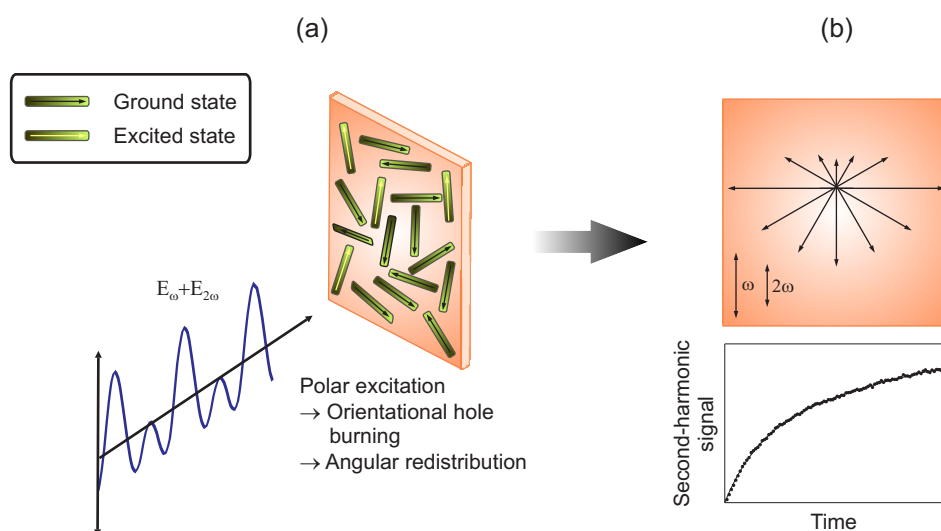


Figure 4.7. Schematic illustration of the all-optical poling process. (a) The sample is irradiated with a coherent dual-frequency field $E_\omega + E_{2\omega}$, which gives rise to polarization-sensitive *polar* photoexcitation of the chromophores. (b) If the polarization directions of the writing and seeding beams are parallel, the amount of molecules oriented "upward" and "downward" will be different, and the noncentrosymmetric chromophore distribution gives rise to second-harmonic response of the material system.

All-optical poling possesses also other important advantages compared to thermally-assisted and photoassisted poling. As there are no static electric fields involved, the conductivity of the material is not an issue and for instance ionic complexes can be poled. Moreover, the technique is not restricted to chromophores with a permanent dipole moment and is thus extremely useful for the nonlinear optical studies of, *e.g.*, molecules with octupolar symmetry.^{213,214} Together, these issues extend the applicability of poling to molecules that are inaccessible by the conventional poling techniques. Another important feature of all-optical poling, especially as device applications are concerned, is that the technique can be applied to samples that absorb neither the fundamental nor the second-harmonic wavelength:^{215,216} in such cases the penetration depth of the optical fields is not an issue, and samples with thicknesses exceeding 100 μm have been successfully poled.²¹⁷ All-optical poling of azobenzene-containing polymers is rather well understood.²³ However, the technique can also be applied to, *e.g.*, inorganic glasses or polymers containing non-photoisomerizable chromophores where no well-established photophysical reactions can be invoked to explain the origin of the nonlinearity, rendering the basic underlying mechanism of the process still unclarified.^{215,218,219}

All-optical poling is of importance also for the characterization of molecular motions in polymeric environment, for which not only the absolute value of the induced nonlinearity but also the growth kinetics should be reliably determined. This poses a problem for typical experimental procedures for all-optical poling, which consist of separate seeding and readout phases (Figure 4.8a): ev-

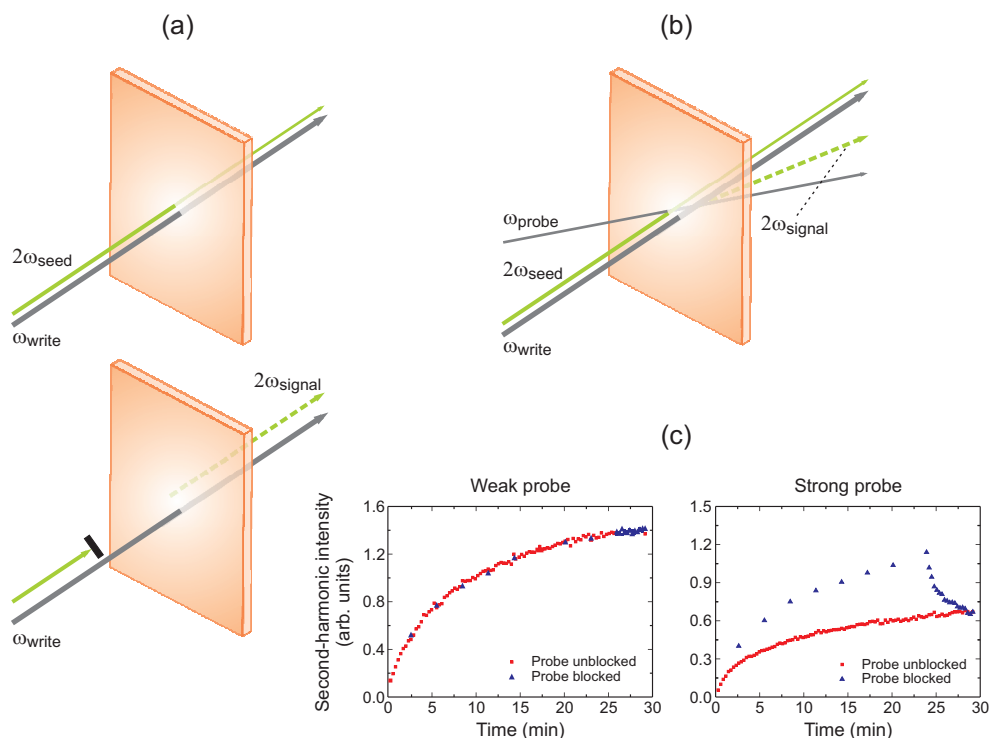


Figure 4.8. (a) Typical experimental procedure for all-optical poling consists of separate seeding (top) and readout (bottom) phases. (b) Schematic representation of the real-time monitoring based on two-beam second-harmonic generation between the fundamental writing beam and a non-collinear probe beam at the fundamental frequency [Publication V]. (c) Comparison of the poling dynamics for a weak and a strong probe when the probe beam is applied on the sample during the whole measurement (red squares) and when it is applied for a short time at 3 min intervals (blue triangles). The curves are measured from different points on the sample and are normalized to eliminate point-to-point variations in the signal level caused by sample inhomogeneities. The sample is a guest-host system of 10 wt % DR1 doped in poly(methyl methacrylate).

ery time the signal is monitored, the seeding beam is blocked and the poling process ceased. The frequent interruption of the writing process has been shown to distort the poling dynamics which complicates the understanding of the molecular motions involved.²²⁰ This has led to efforts towards non-perturbative real-time monitoring of the process kinetics.^{220,221} This issue was addressed also in this work by proposing a particularly simple method for real-time monitoring of all-optical poling [Publication V]. The technique is based on *two-beam second-harmonic generation*²²² between the fundamental writing beam and a non-collinear probe beam at the fundamental frequency (Figure 4.8b). Such a second-harmonic signal is spatially separated from the seeding beam and can therefore be easily detected without ceasing the buildup procedure. The requirement for non-perturbative monitoring is fulfilled when the probe beam is sufficiently weak, as shown in Figure 4.8c. For a weak probe ($I_{\text{write}}/I_{\text{probe}} \approx 750$), the poling dynamics is observed to be identical when the probe beam is incident on the sam-

ple during the whole measurement and when it is applied on the sample at 3 min intervals to obtain measurement points. In addition, when the probe beam is left on after 25 min of poling, the evolution of the signal is unaffected. For a strong probe ($I_{\text{write}}/I_{\text{probe}} \approx 5$), the evolution of the signal differs significantly in the two cases: when the probe beam is left on after 25 min of poling, the signal decreases biexponentially, which indicates that competing processes occur due to the presence of the strong probe beam. However, for a low probe beam intensity the real-time monitoring is non-destructive, and because the signal is partly driven by the strong writing beam, the overall signal level remains relatively high.

– an expert is one who knows more
and more about less and less un-
til he knows absolutely everything
about nothing –

Nicholas Murray Butler

5

Photoinduced processes in polymer–azobenzene complexes

This chapter presents the core results of this thesis. First, we demonstrate that the aggregation tendency of dipolar push–pull chromophores can be suppressed by optimizing the chromophore environment, and that the reduced aggregation directly leads to an enhanced photoresponse [Publications I & II]. Second, we show that phenol–pyridine hydrogen-bonding allows attaching a chromophore to essentially each polymer repeat unit and that the resulting polymer–azobenzene complexes give rise to high and stable photoinduced birefringence and efficient formation of surface-relief gratings [Publications III & IV].

5.1 Review of related studies

Until very recently, only few studies have specifically examined the role of chromophore–polymer intermolecular interactions on the optical performance of polymeric materials. The first indications of the significance of non-covalent interactions were given by the observations that the temporal stability of the polar chromophore alignment in doped polymers is improved if the chromophores and the polymer repeat units contain hydroxyl and carbonyl functional groups, capable of forming weak hydrogen bonds.^{114,223} Soon after it was shown that acid–base interactions between sulfonic-acid-containing polymers and nonlinear chromophores containing a pyridyl acceptor could be exploited to obtain much higher (up to 45 wt %) chromophore concentrations without aggregation or phase separation than what is possible in conventional guest–host systems.^{224,225} The studies concentrated on the miscibility of the constituents. No results on the optical response of these ionic complexes were published.

The above demonstrations were combined by Banach *et al.*, who studied the electro-optic response of DR1 in PMMA and P2VP.⁶¹ They showed that P2VP allows a higher DR1 doping level to be used and that it improves the temporal stability of the chromophore alignment compared to PMMA. The enhancement of the optical properties was unambiguously assigned to the hydrogen-bond formation between the DR1 molecules and the P2VP matrix. Very recently, Gopalan *et al.* carried out an interesting study on the nonlinear optical response and poling

dynamics of block copolymer architectures where the active chromophores were selectively encapsulated to one of the blocks through hydrogen bonding. The response of their system turned out to depend delicately on the domain structure and annealing conditions.²²⁶

All the previous studies deal with the role of chromophore–polymer intermolecular interactions in the *nonlinear optical response* of polymeric materials. The photo-orientation and photoinduced SRG formation in polymer–azobenzene complexes have attained considerable research interest only in the past few years.^{40–46,227,228} A significant contribution to the study of photosensitive small-molecule complexes as well as supramolecular polymeric materials has been provided by Stumpe *et al.*^{40–43} They have shown that ionic polyelectrolyte–azobenzene complexes can yield highly efficient mass migration of the polymer chains and have successfully inscribed gratings with modulation depths up to 1.8 μm . At the same time, Gao *et al.* studied the SRG formation in hydrogen-bonded polymer–azobenzene complexes and demonstrated that even hydrogen bonding can be strong enough to induce light-initiated mass transport of the polymer chains.²²⁷ They employed carboxyl groups to attach the chromophores to the host polymer but ran into solubility problems when using chromophores with strong electron donors. Soon after, Zettsu *et al.* studied the photo-triggered surface-relief formation^{196,197} in supramolecular side-chain liquid-crystalline polymers and demonstrated that the azobenzene moieties can be selectively removed after the grating inscription without changing the periodicity of the structure.²²⁸ They also highlighted the significance of hydrogen bonding for the SRG formation by showing that no mass migration takes place if the hydrogen bonding is inhibited.

The photoresponsive behavior of an ionic polymer–azobenzene complex consisting of a P4VP matrix and Methyl Orange chromophores has been independently studied by two research groups.^{44–46} Zhang *et al.* showed that the complex exhibits high values of photoinduced birefringence (up to 0.3) with impressive temporal and thermal stability.⁴⁴ The other studies performed on the same complex yielded comparable temporal stability of the induced birefringence, but the obtained saturation value was significantly lower than the value reported by Zhang *et al.*, below 0.1. This discrepancy brings about an important issue associated with the photoresponse of azobenzene-containing polymers: the details of the sample preparation process such as the solvent used, the film-casting method, and the annealing conditions can greatly influence the aggregation properties and phase behavior of the material system and thereby affect its photoresponse. Considering that the response is also influenced by various experimental parameters such as the irradiation wavelength and intensity, a meaningful and reliable comparison between the studies performed by different research groups is challenging.

The focus of the present work lies in preventing aggregation of dipolar chromophores in amorphous polymeric materials through spontaneous non-covalent interactions between the chromophores and the polymer backbone, and in exploring the connection between chromophore aggregation and the photoresponse of the material system (Section 5.2). Moreover, we study the applicability of

phenol–pyridine hydrogen bonding to attach the chromophores to the polymer backbone, and study the photoinduced anisotropy and SRG formation in the resulting polymer–azobenzene complexes over a wide concentration range (Section 5.3). The motivation for these studies is twofold. On one hand, we use the photoresponse *as a probe* to clarify the role of chromophore–chromophore interactions on the optical response of polymeric materials. On the other hand, polymer–azobenzene complexes are interesting from the point of view of potential applications. The most obvious advantage is the ease of sample fabrication and optimization of the composition of the material system, allowing for instance complexation of chromophores with different functionalities to the same polymer backbone. But non-covalent interactions may also provide novel functionalities to the material system through their dynamic nature: the bonds can be reversibly broken by external triggers or the chromophores can be extracted from the material system altogether. These potential advantages render polymer–azobenzene complexes a promising class of materials for various photonics applications.

5.2 The role of aggregation on photo-orientation: a case study

As discussed in Section 2.2, excessive chromophore aggregation can be detrimental for the optical response of the chromophores. Aggregation tendency is particularly strong for dipolar chromophores, limiting their doping level in conventional guest–host systems to moderate values. Figure 5.1a presents the absorption spectra for different concentrations of DR1 doped in a nonpolar polystyrene (PS) matrix where the aggregation-induced blue shift in the absorption maximum occurs when the doping level exceeds 10 wt %. The aggregation tendency of dipolar chromophores is highly dependent on the chromophore environment [Publications I & II]: for a polar host polymer the onset of aggregation is shifted to higher concentrations. This is demonstrated in Figure 5.1b for DR1 in poly(4-vinylphenol) (PVPh) matrix, in which majority of the DR1 molecules remain isolated at least up to 30 wt % concentration.

The destructive role of excessive DR1 aggregation in the photo-orientation process is demonstrated in Fig. 5.1c. The photoinduced birefringence of the DR1–PS system saturates already when 10 wt % DR1 concentration is exceeded, and even decreases when the concentration is increased from 20 wt % to 30 wt %. By comparing the obtained birefringences to the absorption spectra shown in Figure 5.1a, the detrimental role of DR1 aggregation on the photo-orientation is evident: at 20 wt % a fraction of the chromophores is aggregated, and the birefringence is induced by those DR1 molecules that are still isolated. If the DR1 concentration is further increased to 30 wt %, a majority of the chromophores takes part in the aggregate formation and only few chromophores contribute to the overall anisotropy. The destructive impact of aggregation on the photoinduced anisotropy can be further attested by comparing photoinduced dichroism of the 30 wt % DR1–PS sample at the long-wavelength side (isolated DR1 molecules)

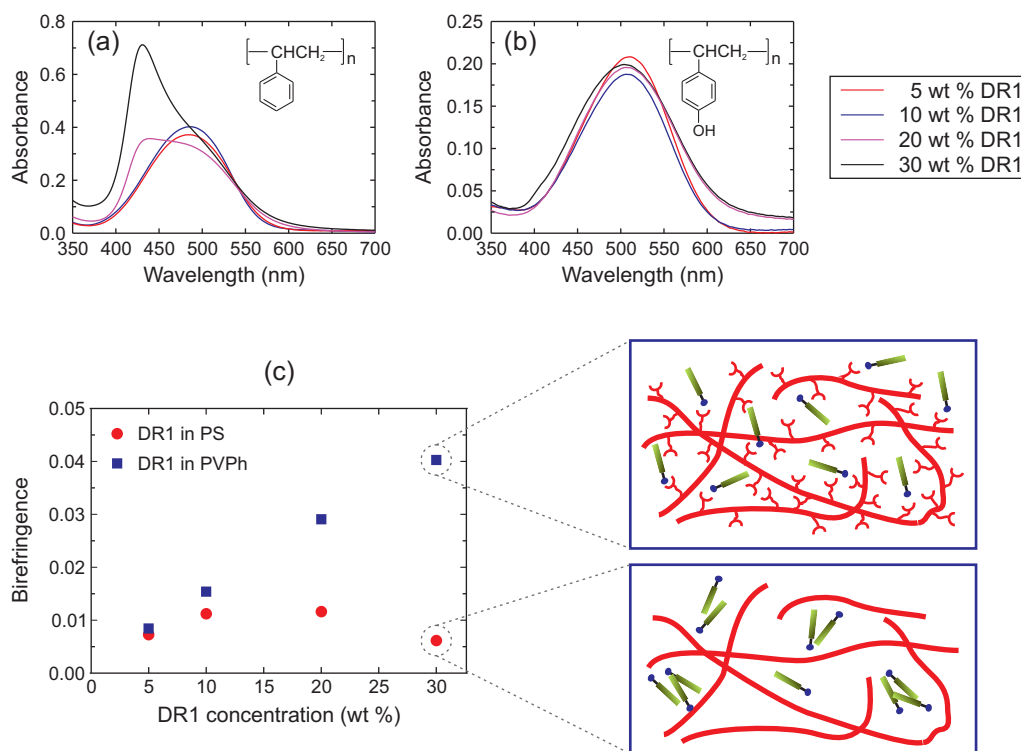


Figure 5.1. Absorption spectra of thin films of (a) DR1 in PS and (b) DR1 in PVPPh at various DR1 concentrations. The chemical structures of PS and PVPPh are shown in the insets. (c) Photoinduced birefringence as a function of concentration for DR1 in PS and PVPPh. The reported values are the steady-state birefringence (measured at 820 nm) while the writing beam (532 nm, 150 mW/cm²) is applied on the sample. On the right: Schematic illustration of the significance of the polar environment on the aggregation tendency of DR1: in PVPPh the molecules remain isolated at least up to 30 wt % concentration whereas in PS the molecules aggregate already at even lower concentrations.

and the short-wavelength side (aggregated DR1 molecules) of the absorption spectrum. As shown in Figure 5.2a, irradiation at 457 nm (chosen to lie in between the absorption maxima of isolated and aggregated DR1) brings about clear dichroism at 530 nm while the dichroism at 420 nm is barely measurable. In both cases, however, both A_{\parallel} and A_{\perp} are seen to decrease, which indicates that the major part of the overall anisotropy arises from the polarization-sensitive excitation (orientational hole burning) rather than reorientation of the chromophores. Conversely, in the DR1–PVPPh system where aggregation is suppressed, birefringence increases monotonically with the chromophore concentration at least up to 30 wt %. Moreover, the photoinduced dichroism of the sample of 30 wt % DR1 in PVPPh (Figure 5.2b) illustrates that unlike in PS, A_{\perp} increases upon photoirradiation, indicating that the DR1 molecules are indeed photo-oriented although the steady-state order parameter is small (<0.04).

Another issue that can be addressed by properly choosing the host polymer is the temporal stability of the induced birefringence. PS is a nonpolar matrix with no functional groups capable of interacting with DR1. But as DR1 con-

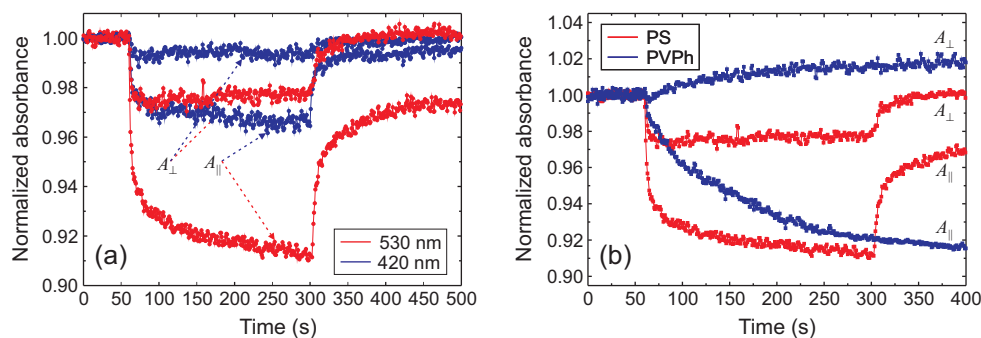


Figure 5.2. (a) Photoinduced dichroism of 30 wt % DR1 in PS at 530 nm (isolated DR1 molecules; red curves) and 420 nm (aggregated DR1 molecules; blue curves). (b) Photoinduced dichroism of 30 wt % DR1 in PS (red curves) and PVPh (blue curves), measured at 530 nm. The excitation wavelength was 457 nm ($10 \text{ mW}/\text{cm}^2$).

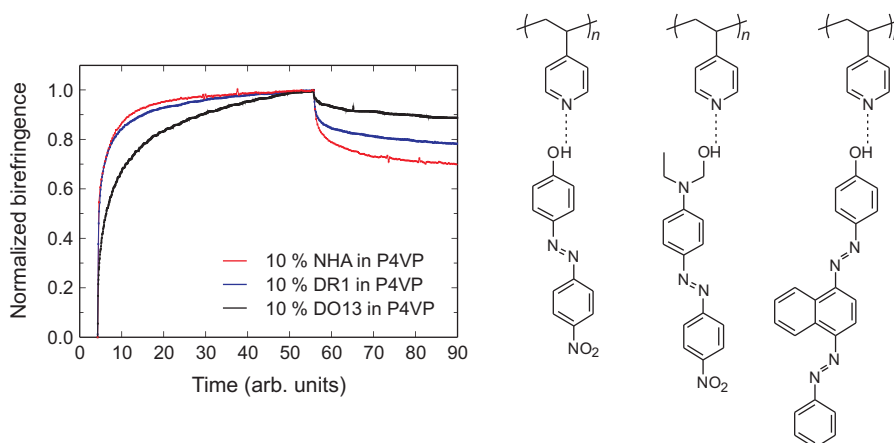


Figure 5.3. Normalized writing–relaxation of the photoinduced birefringence for 10 wt % of NHA, DR1, and DO13 in P4VP. The writing is performed for samples with different thicknesses using different irradiation wavelengths and intensities, hence the time scales for the different samples are incomparable. The chemical structures for the three complexes are shown on the right (from left to right: NHA, DR1, DO13).

tains various basic groups and a hydroxyl group that can take part in hydrogen-bond formation, host polymers with hydrogen-bond donating (PVPh) or accepting (P4VP) capabilities not only improve the solubility of the polar DR1 chromophores into the polymer matrix but also decrease the mobility of the chromophores,⁶¹ resulting in a larger fraction of the birefringence to be preserved once the irradiation is ceased [Publication II]. The remnant birefringence of DR1 in both PVPh and P4VP is approximately 80 % of the saturation value, being roughly equal to the values reported for DR1-containing covalently-functionalized side-chain polymers.²²⁹ However, although the chromophore–polymer interactions increase the temporal stability of the net alignment of the chromophores, a more critical factor than the interaction strength seems to be the size of the chromophore. Figure 5.3 presents the writing/relaxation curves for pho-

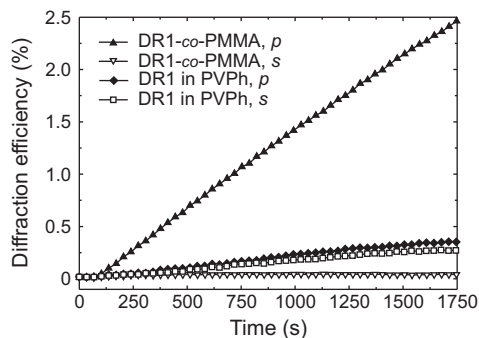


Figure 5.4. First-order diffraction efficiency for 15 mol % DR1-*co*-PMMA and 30 wt % DR1 in PVPh using both *s*- and *p*-polarized writing beams. The writing intensity was 100 mW/cm² and the probe beam was a bandpass-filtered (670 nm, FWHM 10 nm) white-light source.

photoinduced birefringence for samples of 10 wt % of NHA, DR1, and Disperse Orange 13 (DO13) in P4VP matrix. Both NHA and DO13 contain a phenol group which forms a stronger hydrogen bond with P4VP than the aliphatic hydroxyl group of DR1. Nevertheless, the remnant birefringence follows the size of the chromophores, being approximately 70%, 80 %, and 90 %, for NHA, DR1, and DO13, respectively. For all three, the remnant birefringence is systematically higher in P4VP than in PS.²³⁰

Based on the above results, PVPh and P4VP are clearly superior matrices for the polar DR1 chromophores (as well as for the other chromophores studied in this work) compared to the nonpolar PS matrix. This behavior can be attributed to the weak non-covalent interactions between the guest molecules and the polymer matrix. P4VP and PVPh enable using higher DR1 content than PS (or PMMA²³¹). However, they do not allow an equimolar degree of complexation to be reached: for instance in the PVPh matrix, DR1 aggregation starts to occur when 40 wt % (25 mol %) concentration is exceeded [Publication I]. Hence, we conclude that chromophore–polymer interactions are not strong or specific enough to keep the dipolar chromophores isolated at high concentrations. The strength of the interaction can be indirectly probed by studying the photoinduced SRG formation in the sample of 30 wt % DR1 in PVPh and comparing the diffraction efficiency to that in a covalently-functionalized side-chain polymer (DR1-*co*-PMMA) bearing the same DR1 concentration. Recall that SRG formation is highly dependent on the polarization of the writing beams (see Figure 4.6), and that in order for the mass migration to take place, the bonding between the chromophores and the polymer chains must be sufficiently strong (Section 4.2). As shown in Figure 5.4, the diffraction efficiency for the DR1-*co*-PMMA is negligible for an *s*-polarized writing beam whereas a significantly larger diffraction efficiency is obtained when using *p*-polarized writing beam, as expected (see Figure 4.6).¹⁹⁵ For the 30 wt % DR1 in PVPh, the diffraction efficiency is low (<0.5 %) for both *p*-polarized and *s*-polarized irradiation, indicating that the interactions between DR1 and PVPh are not strong or spe-

cific enough to induce macroscopic motion of the polymer chains. Note also that although low for both polarizations, the diffraction efficiency for DR1 in PVPh is still considerably higher than for DR1-*co*-PMMA with an *s*-polarized writing beam. This is presumably caused by photodegradation of the DR1 chromophores under the intensity maxima, which is more pronounced in guest–host systems than in covalently-functionalized polymers.^{232–234} Overall, the performance of DR1 in PVPh/P4VP is promising, but leaves room for further improvement: the chromophore concentration cannot be increased to the same level as in the covalently-functionalized polymers, and no photoinduced mass migration takes place. As shown in Publications III & IV and discussed in the next section, these limitations can be addressed by employing phenol–pyridine hydrogen bonding to attach the chromophores to the polymer chains.

5.3 Equimolar complexes via phenol–pyridine hydrogen bonding

As treated in Section 3.2, phenol–pyridine hydrogen bonding has been well established in the field of supramolecular materials science to yield functional self-assembled polymeric nanostructures,^{137–142} which motivated us to study the photoresponse of phenol–pyridine hydrogen-bonded polymer–azobenzene complexes. We used the two model compounds presented in Figure 5.5: P4VP(NHA)_{*x*} and PVPh(PADA)_{*x*}, where *x* denotes the number of chromophores per each polymer repeat unit. For both systems, an equimolar degree of complexation *x*=1.0 [corresponding to 70 wt % and 65 wt % chromophore concentration for P4VP(NHA)_{*x*} and PVPh(PADA)_{*x*}, respectively] was reached with no sign of macroscopic phase separation. The phenol–pyridine hydrogen bonding was verified with infrared spectroscopy by following the symmetric ring stretching mode of the pyridine group at 993 cm^{−1} for P4VP and 987 cm^{−1} for PADA (Figure 5.5). Upon complexation, a new band is seen to arise at higher wavenumbers (1009 cm^{−1} for P4VP and 998 cm^{−1} for PADA), which can be attributed to hydrogen bonding between the constituents.^{137,235} In P4VP(NHA)_{1.0} the original band is almost completely suppressed, suggesting that an NHA molecule can be attached to essentially each P4VP repeat unit. In PVPh(PADA)_{1.0}, the shoulder remaining at 987 cm^{−1} indicates that a fraction of the pyridine groups is not hydrogen-bonded. Probably also other bonds exist: both the azo group and the dimethylamino group may also serve as a hydrogen-bond acceptor. As the chromophore concentration can in both complexes be increased up to the equimolar degree of complexation, the phenol–pyridine hydrogen bonding provides a facile route to study the photoinduced anisotropy and SRG formation as a function of the degree of complexation.

The concentration dependence of the photoinduced anisotropy in covalently-functionalized polymers containing only one type of chromophore has been studied by several research groups.^{73,74,229,236} In amorphous polymers, the photoinduced birefringence increases linearly with the chromophore content provided

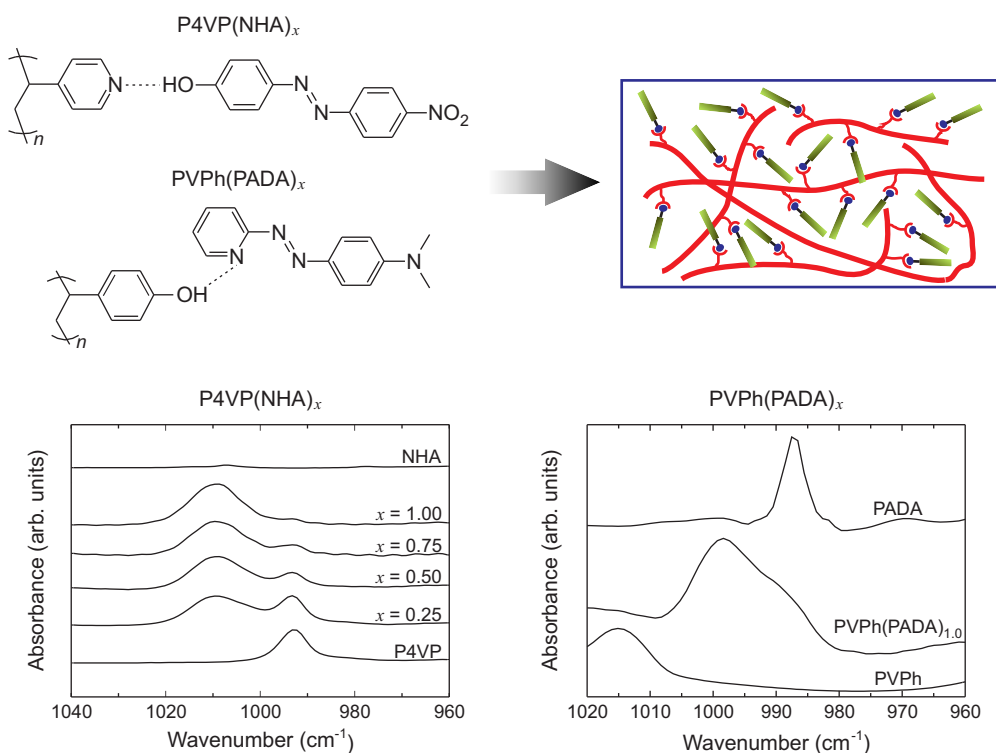


Figure 5.5. Top: The chemical structures of the P4VP(NHA)_{1.0} and PVPh(PADA)_{1.0} complexes and a schematic illustration of the phenol–pyridine hydrogen bonding allowing a chromophore to be attached to essentially each polymer repeat unit. The complex formation was verified with infrared absorption spectra (bottom), measured at wave number regions of 1040–690 cm⁻¹ and 1020–960 cm⁻¹ for P4VP(NHA)_x and PVPh(PADA)_{1.0}, respectively.

that no significant dipolar interactions between the chromophores take place.²³⁶ Dipolar interactions may cause deviations from linearity but do not destruct the photo-orientation as dramatically as reported in DR1-containing guest–host polymers (Publication II).²²⁹ An increased chromophore content can also give rise to phase changes in the material, inducing a transformation from an isotropic state to an LC phase⁷³ or turning the LC order from nematic to smectic,⁷⁴ which can significantly affect the photoresponsive behavior of the chromophores. If the chromophore contains two types of side groups, the cooperative motions of the side groups can significantly enhance the photoinduced birefringence,^{174,237,238} and the photo-orientation of the azobenzene groups can be used to orient also non-photoisomerizable chromophores through collaborative motions.^{239,240}

The role of chromophore concentration on the photoinduced SRG formation has to our knowledge been studied in three covalently-functionalized polymers.^{187,241,242} In methacrylic amorphous side-chain polymers, the depth of surface modulation has been observed to be constant above a threshold concentration of approximately 40–50 wt %.¹⁸⁷ On the other hand, in methacrylic LC polymers as well as in polymers functionalized with two types of chromophores there

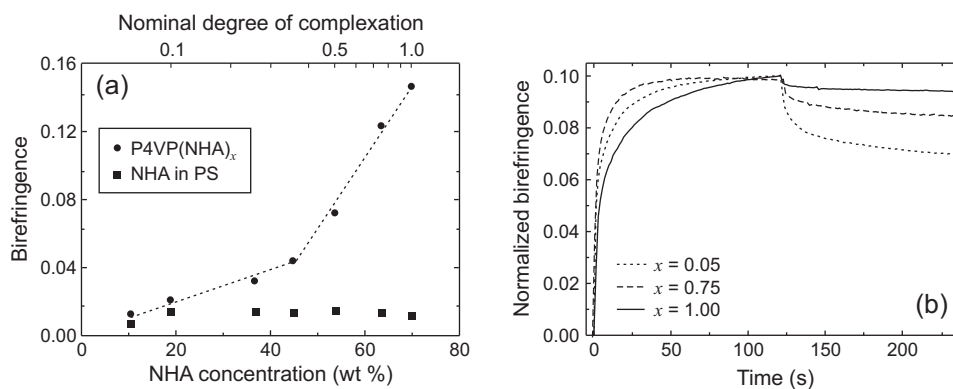


Figure 5.6. (a) Photoinduced birefringence as a function of chromophore content for P4VP(NHA)_x and for NHA–PS guest–host system. The dashed line is drawn to guide the eye. The reported values are the saturation values obtained by linearly polarized excitation at 375 nm (40 mW/cm²), probed with a low-power 633 nm He–Ne laser. (b) Normalized writing–relaxation curves for selected P4VP(NHA)_x complexes (irradiation period 0–120 s).

exists an optimum degree of functionalization, on the order of 75 mol %, above which the efficiency of SRG formation decreases.^{241,242} Börger *et al.* attributed this to the decrease of the *trans*–*cis*–*trans* isomerization rate at high concentrations, caused by chromophore–chromophore intermolecular interactions.²⁴²

The results on the photoinduced birefringence of the P4VP(NHA)_x complexes are shown in Figure 5.6. Being an aminoazobenzene-type chromophore (see Figure 2.1) with weak push–pull character, NHA does not exhibit as pronounced spectral changes upon chromophore aggregation as DR1. However, even if the intermolecular association is weak, it is still detrimental for the obtained birefringence in the nonpolar reference matrix, again chosen to be as PS: the birefringence is seen to saturate to approximately 0.01 already at moderate NHA concentrations due to chromophore aggregation (see Figure 5.6a). As expected based on the results of Publication II, the obtained birefringence in the P4VP(NHA)_x complexes increases with the degree of complexation, and behaves qualitatively in a similar manner as in the DR1–PVPh/P4VP systems. However, when the degree of complexation exceeds $x=0.35$, a concentration range which is unreachable for the DR1-containing systems, the birefringence continues to increase with a significantly steeper slope, obtaining a value of 0.15 at $x=1.0$ (Figure 5.6a). At the same concentration, the temporal stability of the induced birefringence is dramatically improved (Figure 5.6b): for the equimolar complex, the remnant birefringence is 95 % of the saturation value while it is 60–65 % for the complexes with a low ($x \leq 0.35$) degree of complexation. To the best of our knowledge, such improved temporal stability with increasing chromophore content has not been previously observed.

The origin of the enhanced optical performance of P4VP(NHA)_x at high degrees of complexation is presently unclear, but there are two important details that should be emphasized. First, based on the absorption spectra [Publica-

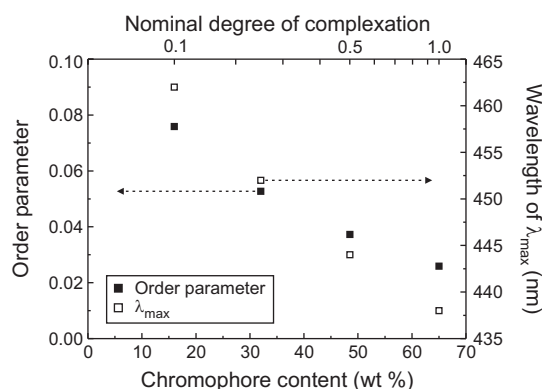


Figure 5.7. The macroscopic order parameter (filled squares) and the wavelength of absorption maximum (empty squares) as a function of PADA concentration. The reported order parameter is the steady-state value obtained upon illumination at the wavelength 457 nm (10 mW/cm^2), and it was probed with a bandpass-filtered (530 nm, FWHM 10 nm) white-light source.

tion III], chromophore–chromophore interactions *give rise to* the enhanced optical performance. Second, even for the equimolar degree of complexation the phenol–pyridine hydrogen bonding is essentially complete (Figure 5.5), which prohibits macroscopic phase separation and *excessive* chromophore aggregation (recall the detrimental role of aggregation in the noninteracting NHA–PS systems). The most plausible explanation for the present behavior would be that the material undergoes a phase transition from amorphous to liquid-crystalline state at the high degree of complexation.^{73,74} We note however that further studies on the optical properties of the complexes as well as on the supramolecular association of the constituents are required before conclusive statements can be made.

The photoinduced anisotropy in the PVPh(PADA)_x (complexes with $x = 0.1$, $x = 0.25$, $x = 0.50$, and $x = 1.0$ were investigated) is very different from that in the P4VP(NHA)_x complexes. The induced birefringence saturates to approximately 0.04, being approximately equal for the $x = 0.25$, $x = 0.50$, and $x = 1.0$ complexes. And conversely to P4VP(NHA)_x , the remnant birefringence *decreases* with increasing chromophore concentration, being approximately 65 % and 55 % of the saturation value for the $x = 0.1$ and $x = 1.0$ complexes, respectively. The macroscopic order parameter decreases monotonically with the chromophore content, which we attribute to chromophore–chromophore intermolecular interactions (see Figure 5.7) alike in covalently-functionalized polymers.²⁴²

Despite the deficient photo-orientation, the surface-relief formation in the PVPh(PADA)_x is very efficient. As shown in Figure 5.8a, the modulation depth of the gratings increases monotonically with chromophore content, even though at the same both the order parameter and the thermal *cis–trans* isomerization rate decrease with increasing chromophore concentration (Publication IV). More-

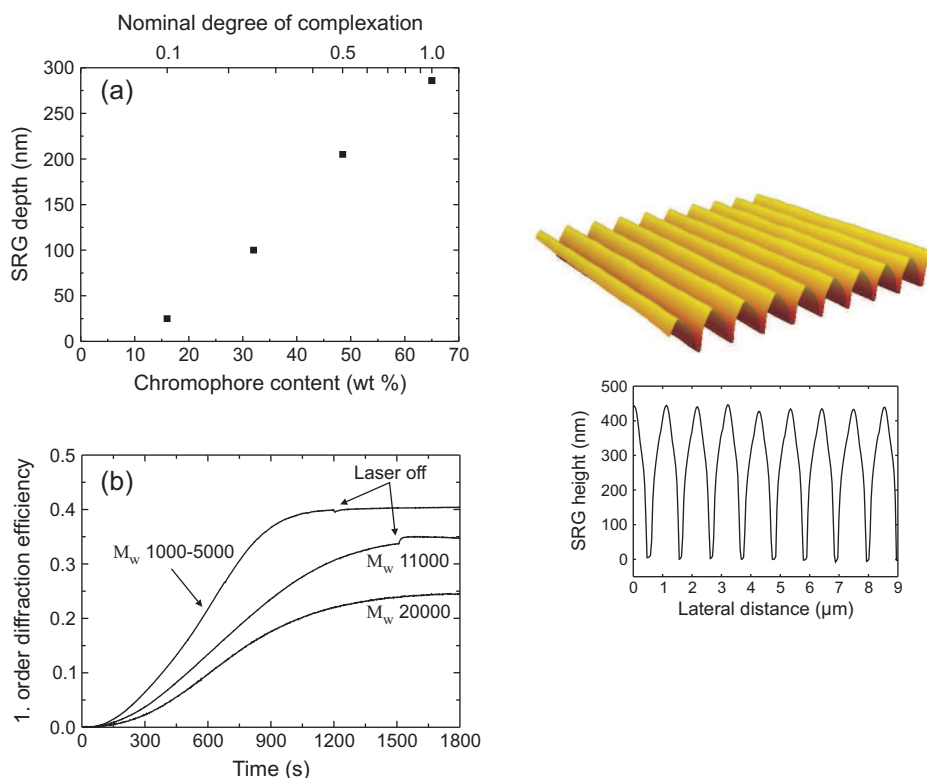


Figure 5.8. (a) Surface modulation depth of the PVPh(PADA)_x complexes as a function of chromophore content. The M_w of PVPh is 20 000 g/mol. (b) Growth of the first-order diffraction efficiency of $\text{PVPh(PADA)}_{1.0}$ for different molecular weights of PVPh. The gratings were inscribed with a 457 nm (200 mW/cm²) laser and the diffraction efficiency was monitored with a low-power 633 nm He–Ne laser. On the right: Atomic force micrograph (top) and surface profile (bottom) of a grating recorded on $\text{PVPh(PADA)}_{1.0}$. The M_w of the host polymer is 1000–5000 g/mol.

over, the inscription process depends strongly on the molecular weight (M_w) of the host polymer (Figure 5.8b): the surface modulation depths for 20 000 g/mol PVPh and for a polydisperse PVPh of 1000–5000 g/mol are 265 nm and 440 nm, respectively. As pointed out in Publication IV, the decreasing M_w does not result in lower thermal stability of the SRGs: the onset of thermal erasure stays at around 100 °C irrespective of the M_w .

Altogether, the above results on phenol–pyridine hydrogen-bonded complexes emphasize the fact that concepts of supramolecular materials science can have a profound impact on the design of polymer-based optical materials. Polymer–azobenzene complexes have proven to give rise to efficient and temporally stable photo-orientation and photoinduced mass migration. At the same time, the results of Sections 5.2 & 5.3 highlight the complexity of these material systems: the photoresponse of each complex is unique and depends elaborately on the properties of the constituents as well as on the intermolecular interactions present in the material system.

– every sentence that I utter must
be understood not as an affirmation,
but as a question –

Niels Bohr

6

Conclusions and outlook

The results presented in this thesis demonstrate that supramolecular concepts can be used to significantly improve the performance of polymeric optical materials. We have shown that spontaneous non-covalent interactions can suppress the aggregation tendency of dipolar chromophores, which enables one to enhance the photoinduced anisotropy in the material system and to improve the temporal stability of the net alignment of the chromophores (Publications I & II). Particularly promising results were obtained by complexing the chromophores to the polymer backbone via *phenol–pyridine hydrogen bonding*, which enables attaching a chromophore to essentially each polymer repeat unit without macroscopic phase separation taking place. In the course of this work, such complexes were shown to give rise to efficient photoresponse, yielding high and temporally stable photoinduced birefringence (Publication III) as well as efficient formation of photoinduced surface-relief gratings (Publication IV). The modular tunability provided by the spontaneous non-covalent bonding allowed us to study the photoinduced anisotropy and SRG formation over a wide concentration range.

Throughout the work, we focused on *polymer–azobenzene complexes* and studied the processes that arise from the efficient and reversible photoisomerization of the azobenzene moieties. However, the applicability of the supramolecular concepts extends beyond the azobenzene-containing polymers and can potentially be used to enhance a wide range of optical phenomena in materials where chromophore aggregation or phase separation sets a limit to the system performance. A particularly interesting future direction would be to study whether non-covalent interactions can be used to prevent fluorescence quenching of laser dyes, which could enable increasing the gain coefficient of the medium, thereby providing new materials concepts for, *e.g.*, polymeric solid-state dye lasers. Also nonlinear optics provides many interesting pathways to follow: we have already taken the first steps to show that the *macroscopic* nonlinear optical response obtained by all-optical poling can be enhanced through optimization of the chromophore environment, in a similar manner as reported in Publication II. Similar studies on electric-field poling and electro-optic modulation are in progress. In addition, non-covalent interactions also provide means to tailor the nonlinear response at the *molecular* level, for instance, through selective protonation of the electron donor/acceptor groups.

During this work, significant development driven by various research groups

around the world, has taken place regarding the light-induced processes in supramolecular azobenzene-containing materials. In particular, polymer–azobenzene complexes have proven to be able to compete successfully with covalently-functionalized polymers in terms of the magnitude and stability of the photoinduced anisotropy as well as in the efficiency of the photoinduced surface-relief formation. The significance of the present work lies in exploring the connection between chromophore aggregation and the optical response of the material system by making use of the modular tunability provided by the spontaneous non-covalent interactions. We believe that such studies will not only contribute to the basic understanding of the role of intermolecular interactions on the optical response of polymeric materials, but they may also facilitate investigations into the basic underlying mechanisms behind the photoinduced processes in azobenzene-containing polymers, especially into those behind the surface-relief formation.

Altogether, this work has aroused a number of questions, many of which remain unanswered. Therefore, the work as such should be considered as a beginning, not the end. What are the key advantages and ultimate limitations of the polymer–chromophore complexes in optical applications? Does the concept work with highly dipolar chromophores, optimized, *e.g.*, to produce extremely high optical nonlinearity at the molecular level? How do different non-covalent interactions, such as phenol–pyridine hydrogen bonding, carbonyl–pyridine hydrogen bonding, and the proton transfer interaction, perform with respect to each other? Can we attain further functionalities by extending the concept towards *block copolymer*–chromophore complexes? Those are some of the questions that are to be addressed in the near future.

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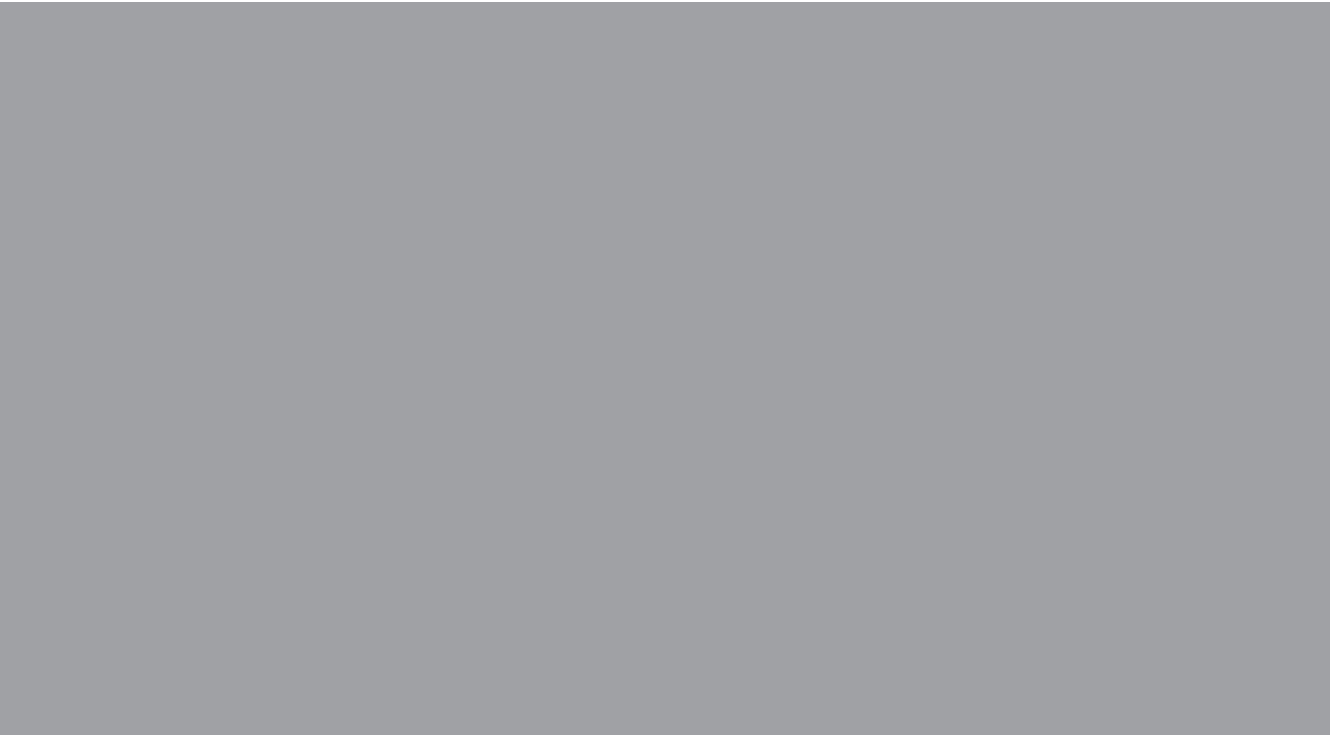
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