1

AZOBENZENE POLYMERS FOR PHOTONIC APPLICATIONS

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1.1. INTRODUCTION TO AZOBENZENE

Azobenzene, with two phenyl rings separated by an azo (–N=N–) bond, serves as the parent molecule for a broad class of aromatic azo compounds. These chromophores are versatile molecules, and have received much attention in research areas both fundamental and applied. The strong electronic absorption maximum can be tailored by ring substitution to fall anywhere from the ultraviolet (UV) to visible red regions, allowing chemical fine-tuning of color. This, combined with the fact that these azo groups are relatively robust and chemically stable, has prompted extensive study of azobenzene-based structures as dyes and colorants. The rigid mesogenic shape of the molecule is well suited to spontaneous organization into liquid crystalline (LC) phases, and hence polymers doped or functionalized with azobenzene-based chromophores (azo polymers) are common as LC media. With appropriate electron-donor–acceptor ring substitution, the π electron delocalization of the extended aromatic structure can yield high optical nonlinearity, and zo chromophores have seen extensive study for nonlinear optical applications as well. One of the most interesting properties of these chromophores however, and the main subject of this review, is the readily induced and reversible isomerization about the azo bond between the trans and cis geometric isomers and the geometric changes that result when azo chromophores are incorporated into polymers and other materials. This light-induced interconversion allows systems incorporating azobenzenes to be used as photoswitches, effecting rapid and reversible control over a variety of chemical, mechanical, electronic, and optical properties.

Smart Light-Responsive Materials. Edited by Yue Zhao and Tomiki Ikeda

Perhaps of a range as wide as the interesting phenomena displayed by azo aromatic compounds is the variety of molecular systems into which these chromophores can be incorporated. In addition to LC media and amorphous glasses, azobenzenes can be incorporated into self-assembled monolayers and superlattices, sol–gel silica glasses, and various biomaterials. The photochromic or photoswitchable nature of azobenzenes can also be used to control the properties of novel small molecules, using an attached aromatic azo group. A review will be presented here of the photochemical and photophysical nature of chromophores in host polymers, the geometric and orientational consequences of this isomerization, and some of the interesting ways in which these phenomena have been expolited recently to exert control over solution and biochemical properties using light. This photoisomerization can be exploited as a photoswitch to orient the chromophore (which induces birefringence), or even to perform all-optical surface topography patterning. These photomotions enable many interesting applications, ranging from optical components and lithography to sensors and smart materials.

1.1.1. Azobenzene Chromophores

In this text, as in most on the subject, we use “azobenzene” and “azo” in a general way: to refer to the class of compounds that exhibit the core azobenzene structure, with different ring substitution patterns (even though, strictly, these compounds should be referred to as “diazenes”). There are many properties common to nearly all azobenzene molecules. The most obvious is the strong electronic absorption of the conjugated π system. The absorption spectrum can be tailored, via the ring substitution pattern, to lie anywhere from the UV to the visible red region. It is not surprising that azobenzenes were originally used as dyes and colorants, and up to 70% of the world’s commercial dyes are still azobenzene-based (Zollinger, 1987, 1961). The geometrically rigid structure and large aspect ratio of azobenzene molecules make them ideal mesogens: azobenzene small molecules and polymers functionalized with azobenzene can exhibit LC phases (Möhlmann and van der Vorst, 1989; Kwolek et al., 1985). The most startling and intriguing characteristic of the azobenzenes is their highly efficient and fully reversible photoisomerization. Azobenzenes have two stable isomeric states, a thermally stable trans configuration and a metastable cis form. Remarkably, the azo chromophore can interconvert between these isomers upon absorption of a photon. For most azobenzenes, the molecule can be optically isomerized from trans to cis with light anywhere within the broad absorption band, and the molecule will subsequently thermally relax back to the trans state on a timescale dictated by the substitution pattern. This clean photochemistry is central to azobenzene’s potential use as a tool for nanopatterning.

Azobenzenes can be separated into three spectroscopic classes, well described by Rau (1990): azobenzene-type molecules, aminoazobenzene-type molecules, and pseudo-stilbenes (refer to Fig. 1.1 for examples). The particulars of their absorption spectra (shown in Fig. 1.2) give rise to their prominent colors: yellow, orange, and red, respectively. Many azos exhibit absorption characteristics similar to the unsubstituted azobenzene archetype. These molecules exhibit

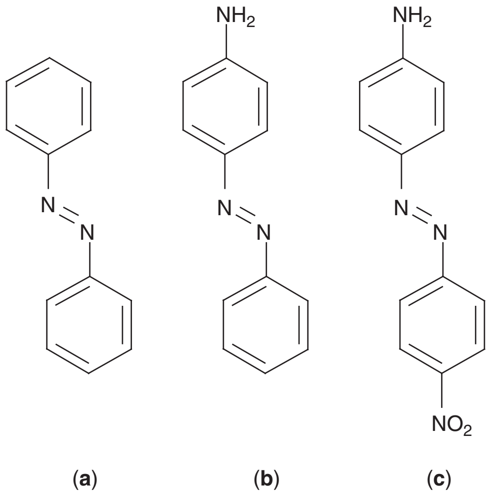

Figure 1.1. Examples of azomolecules classified as (**a**) azobenzenes, (**b**) aminoazobenzenes, and (**c**) pseudo-stilbenes.

a low intensity n → π* band in the visible region and a much stronger π → π* band in the UV. Although the n → π* is symmetry-forbidden for *trans*-azobenzene (C_{2h}), vibrational coupling and some extent of nonplanarity nevertheless make it observable (Rau, 1968).

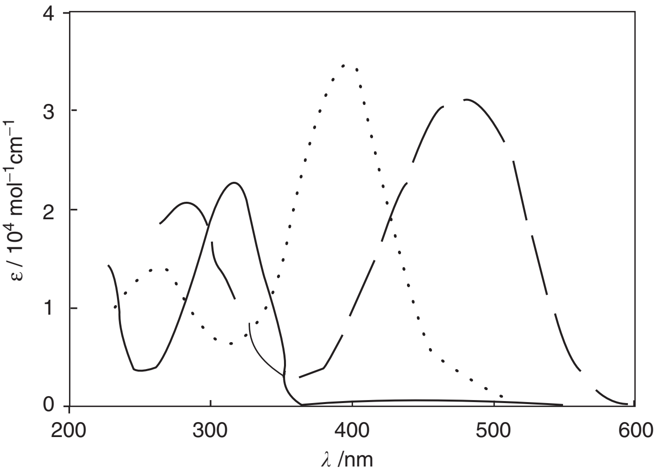

Figure 1.2. Schematic of typical absorbance spectra for *trans*-azobenzenes. The azobenzene-type molecules (*solid line*) have a strong absorption in the UV, and a low intensity band in the visible (barely visible in the graph). The aminoazobenzenes (*dotted line*) and pseudo-stilbenes (*dashed line*) typically have strong overlapped absorptions in the visible region.

Adding substituents to the azobenzene rings may lead to minor or major changes in spectroscopic character. Of particular interest is ortho- or para-substitution with an electron-donating group (usually an amino, –NH_2), which results in a new class of compounds. In these aminoazobenzenes, the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands are much closer. In fact, the $n \rightarrow \pi^*$ may be completely buried beneath the intense $\pi \rightarrow \pi^*$. Although azobenzenes are fairly insensitive to solvent polarity, aminoazobenzene absorption bands shift to higher energy in nonpolar solvents and shift to lower energy in polar solvents. Substituting azobenzene at the 4 and 4′ positions with an electron-donor and an electron-acceptor (such as an amino and a nitro, –NO_2, group) leads to a strongly asymmetric electron distribution (often referred to as a ‘‘push–pull’’ substitution pattern). This shifts the $\pi \rightarrow \pi^*$ absorption to lower energy, toward the red and past the $n \rightarrow \pi^*$. This reversed ordering of the absorption bands defines the third spectroscopic class, the pseudo-stilbenes (in analogy to stilbene, phenyl–C=C–phenyl). The pseudo-stilbenes are very sensitive to local environment, which can be useful in some applications.

Especially in condensed phases, the azos are also sensitive to packing and aggregation. The π–π stacking gives rise to shifts of the absorption spectrum. If the azo dipoles have a parallel (head-to-head) alignment, they are called J-aggregates, and give rise to a redshift of the spectrum (bathochromic) as compared with the isolated chromophore. If the dipoles are antiparallel (head-to-tail), they are called H-aggregates and lead to a blueshift (hypsochromic). Fluorescence is seen in some aminoazobenzenes and many pseudo-stilbenes but not in azobenzenes, whereas phosphorescence is absent in all the three classes. By altering the electron density, the substitution pattern necessarily affects the dipole moment, and in fact all the higher order multipole moments. This becomes significant in many nonlinear optical (NLO) studies. For instance, the chromophore's dipole moment can be used to orient with an applied electric field (poling), and the higher order moments of course define the molecule's nonlinear response (Delaire and Nakatani, 2000). In particular, the strongly asymmetric distribution of the delocalized electrons that results from push–pull substitution results in an excellent NLO chromophore.

1.1.2. Azobenzene Photochemistry

Key to some of the most intriguing results and interesting applications of azobenzenes is the facile and reversible photoisomerization about the azo bond, converting between the trans (E) and cis (Z) geometric isomers (Fig. 1.3). This photoisomerization is completely reversible and free from side reactions, prompting Rau to characterize it as ‘‘one of the cleanest photoreactions known.’’(Rau, 1990) The trans isomer is more stable by $\sim 50\,\mathrm{kJ\,mol^{-1}}$ (Mita et al., 1989; Schulze et al., 1977), and the energy barrier to the photoexcited state (barrier to isomerization) is on the order of $200\,\mathrm{kJ\,mol^{-1}}$ (Monti et al., 1982). Thus, in the dark, most azobenzene molecules will be found in the trans form. On absorption of a photon (with a wavelength in the trans absorption band), the azobenzene will convert, with high efficiency, into the cis isomer. A second wavelength of light (corresponding to the cis absorption band) can cause the back-conversion.

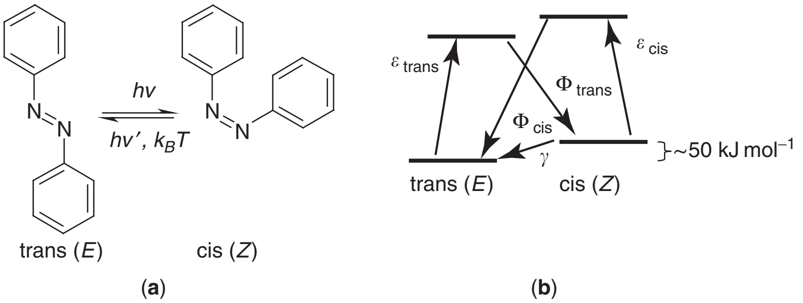

Figure 1.3. **(a)** Azobenzene can convert between trans and cis states photochemically and relaxes to the more stable trans state thermally. **(b)** Simplified state model for azobenzenes. The trans and cis extinction coefficients are denoted by $\varepsilon_{\text{trans}}$ and ε_{cis}. The Φ refer to quantum yields of photoisomerization, and γ is the thermal relaxation rate constant.

These sphotoisomerizations usually have picosecond timescales (Lednev et al., 1996; Kobayashi et al., 1979). Alternately, azos will thermally reconvert from the cis into trans state, with a timescale ranging from milliseconds to hours, depending on the substitution pattern and local environment. More specifically, the lifetimes for azobenzenes, aminoazobenzenes, and pseudo-stilbenes are usually on the order of hours, minutes, and seconds, respectively. The energy barrier for thermal isomerization is on the order of $90\,\text{kJ}\,\text{mol}^{-1}$ (Brown and Granneman, 1975; Haberfield et al., 1975). Considerable work has gone into elongating the cis lifetime, with the goal of creating truly bistable photoswitchable systems. Bulky ring substituents can be used to hinder the thermal back reaction. For instance, a polyurethane main-chain azo exhibited a lifetime of 4 days (thermal rate constant of $k = 2.8 \times 10^{-6}\,\text{s}^{-1}$, at 3°C) (Lamarre and Sung, 1983), and an azobenzene parasubstituted with bulky pendants had a lifetime of 60 days ($k < 2 \times 10^{-7}\,\text{s}^{-1}$, at room temperature) (Shirota et al., 1998). The conformational strain of macrocylic azo compounds can also be used to lock the cis state, where lifetimes of 20 days ($k = 5.9 \times 10^{-7}\,\text{s}^{-1}$) (Norikane et al., 2003), 1 year (half-life 400 days, $k = 2 \times 10^{-8}\,\text{s}^{-1}$) (Rottger and Rau, 1996; Rau and Roettger, 1994), or even 6 years ($k = 4.9 \times 10^{-9}\,\text{s}^{-1}$) (Nagamani et al., 2005) were observed. Similarly, using the hydrogen bonding of a peptide segment to generate a cyclic structure, a cis lifetime of ~40 days ($k = 2.9 \times 10^{-7}\,\text{s}^{-1}$) was demonstrated (Vollmer et al., 1999). Of course, one can also generate a system that starts in the cis state and where isomerization (in either direction) is completely hindered. For instance, attachment to a surface (Kerzhner et al., 1983), direct synthesis of ringlike azo molecules (Funke and Gruetzmacher, 1987), and crystallization of the cis form (Hartley, 1938, 1937) can be used to maintain one state, but such systems are obviously not bistable photoswitches.

A bulk azo sample or solution under illumination will achieve a photostationary state, with a steady-state trans–cis composition based on the competing effects of photoisomerization into the cis state, thermal relaxation back to the trans state, and possibly cis reconversion upon light absorption. The steady-state composition is unique to each system, as it depends on the quantum yields for the two processes (Φ_{trans} and Φ_{cis}) and the thermal relaxation rate constant. The composition also depends on irradiation intensity, wavelength, temperature, and the matrix (gas phase, solution, liquid crystal, sol–gel, monolayer, polymer matrix, etc.). Azos are photochromic (their color changes on illumination), since the effective absorption spectrum (a combination of the trans and cis spectra) changes with light intensity. Thus absorption spectroscopy can be conveniently used to measure the cis fraction in the steady state (Rau et al., 1990; Fischer, 1967), and the subsequent thermal relaxation to an all-trans state (Beltrame et al., 1993; Hair et al., 1990; Eisenbach, 1980a; Gabor and Fischer, 1971). Nuclear magnetic resonance (NMR) spectroscopy can also be used (Magennis et al., 2005). Under moderate irradiation, the composition of the photostationary state is predominantly cis for azobenzenes, mixed for aminoazobenzenes, and predominantly trans for pseudo-stilbenes. In the dark, the cis fraction is below most detection limits, and the sample can be considered to be in an all-trans state. Isomerization is induced by irradiating with a wavelength within the azo's absorption spectrum, preferably close to $\lambda_{\max}$. Modern experiments typically use laser excitation with polarization control, delivering on the order of 1–100 mW cm^{-2} of power to the sample. Various lasers cover the spectral range of interest, from the UV (Ar^{+} line at 350 nm) through blue (Ar^{+} at 488 nm), green (Ar^{+} at 514 nm, YAG at 532 nm, HeNe at 545 nm), and into the red (HeNe at 633 nm, GaAs at 675 nm).

The ring substitution pattern affects both the trans and the cis absorption spectra, and for certain patterns, the absorption spectra of the two isomers overlap significantly (notably for the pseudo-stilbenes). In these cases, a single wavelength of light effectuates both the forward and reverse reaction, leading to a mixed stationary state and continual interconversion of the molecules. For some interesting azobenzene photomotions, this rapid and efficient cycling of chromophores is advantageous, whereas in cases where the azo chromophore is used as a switch, it is clearly undesirable.

The mechanism of isomerization has undergone considerable debate. Isomerization takes place either through a rotation about the N–N bond, with rupture of the π bond, or through inversion, with a semilinear and hybrizidized transition state, where the π bond remains intact (refer to Fig. 1.4). The thermal back-relaxation is agreed to be via rotation, whereas for the photochemical isomerization, both mechanisms appear viable (Xie et al., 1993). Historically, the rotation mechanism (as necessarily occurs in stilbene) was favored for photoisomerization, with some early hints that inversion may be contributing (Gegiou et al., 1968). More recent experiments, based on matrix or molecular constraints to the azobenzene isomerization, strongly support inversion (Altomare et al., 1997; Liu et al., 1992; Naito et al., 1991; Rau and Lueddecke, 1982). Studies using picosecond Raman and femtosecond fluorescence show a double bond (N=N) in the excited state, confirming the inversion mechanism (Fujino et al., 2001; Fujino

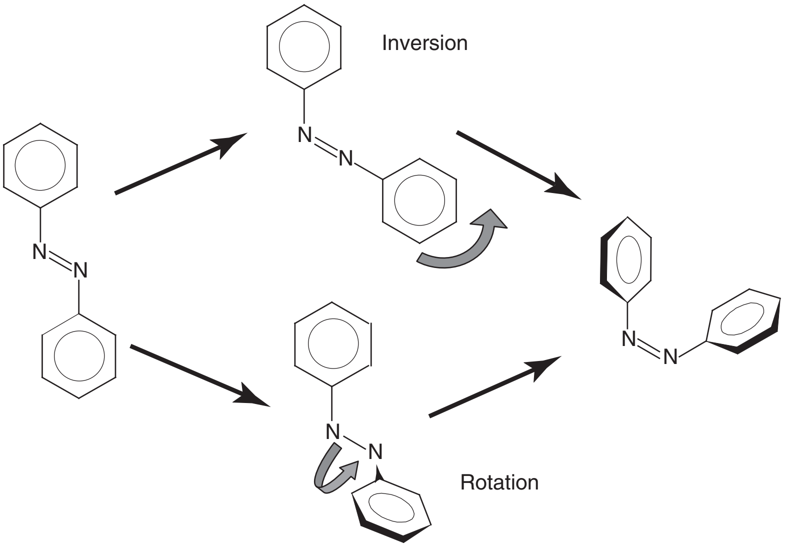

Figure 1.4. The mechanism of azobenzene isomerization proceeds either via rotation or inversion. The cis state has the phenyl rings tilted at 90° with respect to the CNNC plane.

and Tahara, 2000). In contrast, Ho et al. (2001) found evidence that the pathway is compound-specific: a nitro-substituted azobenzene photoisomerized via the rotation pathway. Furthermore, ab initio and density functional theory calculations indicate that both pathways are energetically accessible, although inversion is preferred (Angeli et al., 1996; Jursic, 1996). Thus, both mechanisms may be competing, with a different one dominating depending on the particular chromophore and environment. The emerging consensus nevertheless appears to be that inversion is the dominant pathway for most azobenzenes (Ikeda and Tsutsumi, 1995). The availability of the inversion mechanism explains how azos are able to isomerize easily even in rigid matrices, such as glassy polymers, since the inversion mechanism has a much smaller free volume requirement than rotation.

The thermal back-relaxation is generally first order, although a glassy polymer matrix can lead to anomalously fast decay components (Barrett et al., 1995, 1994; Paik and Morawetz, 1972; Priest and Sifain, 1971), attributed to a distribution of chromophores in highly strained configurations. Higher matrix crystallinity increases the rate of decay (Sarkar et al., 2001). The decay rate can act as a probe of local environment and molecular conformation (Tanaka et al., 2004; Norman and Barrett, 2002). The back-relaxation of azobenzene is acid catalyzed (Rau et al., 1981), although strongly acidic conditions will lead to side reactions (Hartley, 1938). For the parent azobenzene molecule, quantum yields (which can be indirectly measured spectroscopically (Shen and Rau, 1991; Priest and Sifain, 1971; Malkin and Fischer, 1962) are on the order of 0.6 for the trans→cis photoconversion, and 0.25 for the back photoreaction. Solvent has a small effect, increasing the trans → cis and decreasing the cis → trans yield as polarity increases (Bortolus and Monti, 1979). Aminoazobenzenes and pseudo-stilbenes isomerize very quickly and can have quantum yields as high as 0.7–0.8.

1.1.3. Classes of Azobenzene Systems

Azobenzenes are robust and versatile moieties, and have been extensively investigated as small molecules, pendants on other molecular structures, or incorporated (doped or covalently bound) into a wide variety of amorphous, crystalline, or LC polymeric systems. Noteworthy examples include self-assembled monolayers and superlattices (Yitzchaik and Marks, 1996), sol–gel silica glasses (Levy and Esquivias, 1995), and biomaterials (Gallot et al., 1996; Willner and Rubin, 1996; Sisido et al., 1991a). A number of small molecules incorporating azobenzene have been synthesized, including crown ethers (Shinkai et al., 1983), cyclodextrins (Jung et al., 1996; Yamamura et al., 1996), proteins such as bacteriorhodopsin (Singh et al., 1996), and three-dimensional (3-D) polycyclics such as cubane (Chen et al., 1997b) and adamantane (Chen et al., 1995). Typically, azo chromophores are embedded in a solid matrix for studies and devices. As a result, matrix effects are inescapable: the behavior of the chromophore is altered due to the matrix, and in turn, the chromophore alters the matrix (Ichimura, 2000). Although either could be viewed as a nuisance, both are in fact useful: the chromophore can be used as a probe of the matrix (free volume, polarizability, mobility, etc.), and when the matrix couples to chromophore motion, molecular motions can be translated to larger length scales. Thus, the incorporation strategy is critical to exploiting azobenzene's unique behavior.

1.1.3.1. Amorphous Polymer Thin Films. Doping azobenzenes into polymer matrices is a convenient inclusion technique (Birabassov et al., 1998; Labarthet et al., 1998). These "guest–host" systems can be cast or spin-coated from solution mixtures of polymer and azo small molecules, where the azo content in the thin film is easily adjusted via concentration. Although doping leaves the azo chromophores free to undergo photoinduced motion unhindered, it has been found that many interesting photomechanical effects do not couple to the matrix in these systems. Furthermore, the azo mobility often leads to instabilities, such as phase separation or microcrystallization. Thus, one of the most attractive methodologies for incorporating azobenzene into functional materials is by covalent attachment to polymers. The resulting materials benefit from the inherent stability, rigidity, and processability of polymers, in addition to the unusual photoresponsive behavior of the azo moieties. Both side-chain and main-chain azobenzene polymers have been prepared (Viswanathan et al., 1999) (Fig. 1.5). Reported synthetic strategies involve either polymerizing azobenzene-functionalized monomers (Ho et al., 1996; Natansohn et al., 1992) or postfunctionalizing

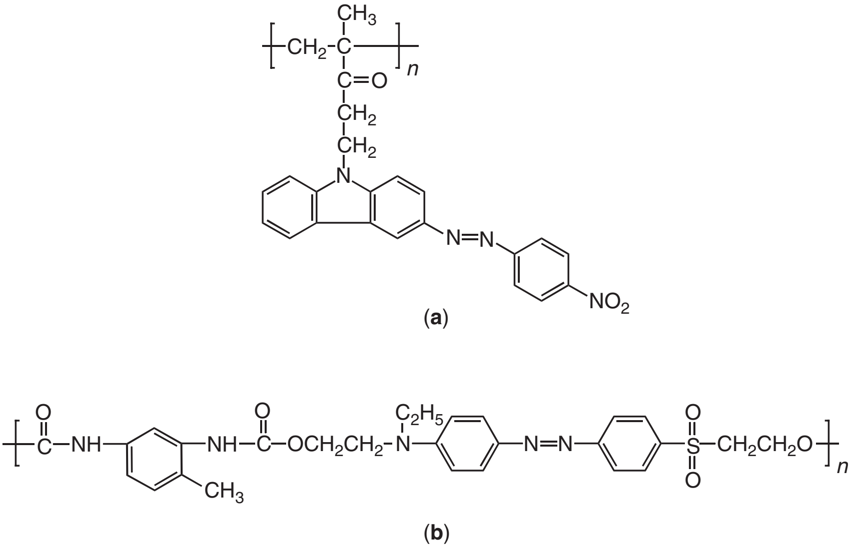

Figure 1.5. Examples of azo polymer structures, showing that both (**a**) side-chain and (**b**) main-chain architectures are possible.

a polymer that has an appropriate pendant group (usually a phenyl) (Wang et al., 1997a,b,c). The first method is preferred for its simplicity and control of sequence distribution. The second takes advantage of commonly available starting materials, but may require more reaction steps. Many different backbones have been used as scaffolds for azo moieties, including imides (Agolini and Gay, 1970), esters (Anderle et al., 1989), urethanes (Furukawa et al., 1967), ethers (Bignozzi et al., 1999), organometallic ferrocene polymers (Liu et al., 1997), dendrimers (Junge and McGrath, 1997; Mekelburger et al., 1993), and even conjugated polydiacetylenes (Sukwattanasinitt et al., 1998), polyacetylenes (Teraguchi and Masuda, 2000), and main-chain azobenzenes (Izumi et al., 2000a,b). The most common azo polymers are acrylates (Morino et al., 1998), methacrylates (Altomare et al., 2001), and isocyanates (Tsutsumi et al., 1996). Thin films are usually prepared by spin-coating (Han and Ichimura, 2001; Blinov et al., 1998; Weh et al., 1998; Ichimura et al., 1996), although there are also many examples of using solvent evaporation, the Langmuir–Blodgett technique (Silva et al., 2002; Razna et al., 1999; Jianhua et al., 1998; Seki et al., 1993), and self-assembled monolayers (Evans et al., 1998). Spin-cast films are typically annealed above the polymer glass transition temperature (T_g) to remove residual solvent and erase any hydrodynamically induced anisotropy. Recently molecular glasses have been investigated as alternatives to amorphous polymer systems (Mallia and Tamaoki, 2003). These monodisperse systems appear to maintain the desirable photomotions and photoswitching properties, while allowing precise control of molecular architecture and thus material properties (Naito and Miura, 1993).

1.1.3.2. Liquid Crystals. Azobenzenes are anisotropic, rigid molecules and as such are ideal candidates to act as mesogens: molecules that form LC mesophases. Many examples of small-molecule azobenzene liquid crystals have been studied. Some azo polymers also form LC phases (refer to Fig. 1.6 for a typical structure). For side-chain azobenzenes, a certain amount of mobility is required for LC phases to be present; as a rule, if the tether between the chromophore and the backbone is less than 6 alkyl units long, the polymer will exhibit an amorphous and isotropic solid-state phase, whereas if the spacer is longer, LC phases typically form. The photoisomerization of azobenzene leads to modification of the phase and alignment (director) in LC systems (Shibaev et al., 2003; Ichimura, 2000). The director of a liquid crystal phase can be modified by orienting chromophores doped into the phase (Sun et al., 1992; Anderle et al., 1991) by using an azobenzene-modified "command surface" (Chen and Brady, 1993; Ichimura et al., 1993; Gibbons et al., 1991), using azo copolymers (Wiesner et al., 1991), and, of course, in pure azobenzene LC phases (Hvilsted et al., 1995; Stumpe et al., 1991). One can force the LC phase to adopt an in-plane order (director parallel to surface), homeotropic alignment (director perpendicular to surface), tilted or even biaxial orientation (Yaroschuk et al., 2001). These changes are fast and reversible. Although the *trans*-azobenzenes are excellent mesogens, the cis-azos typically are not. If even a small number of azomolecules are

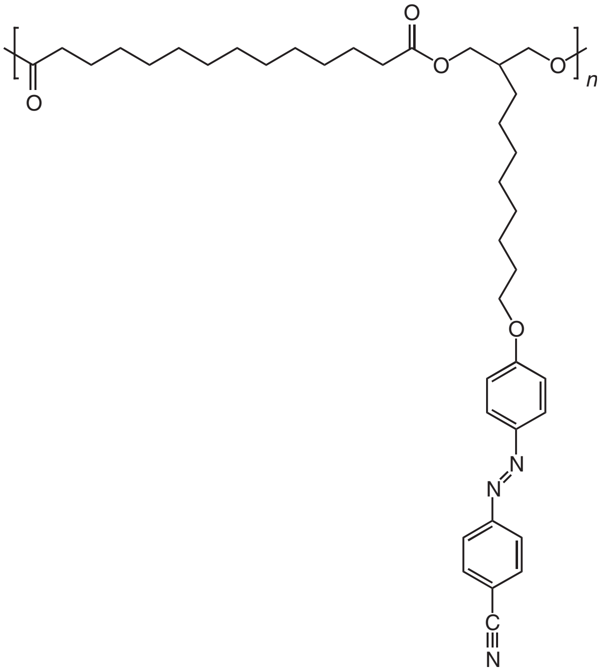

Figure 1.6. A typical liquid-crystalline side-chain azobenzene polymer.

distributed in an LC phase, trans→cis isomerization can destabilize the phase by lowering the nematic-to-isotropic phase transition temperature (Eich and Wendorff, 1990). This enables fast isothermal photocontrol of phase transitions (Kato et al., 1996; Hayashi et al., 1995; Ikeda and Tsutsumi, 1995; Ikeda et al., 1990). Since these modulations are photoinitiated, it is straightforward to create patterns (Shannon et al., 1994). These LC photoswitching effects are obviously attractive in many applications, such as for display devices, optical memories (Gibbons et al., 1991), electro-optics (Luk and Abbott, 2003), and modulating the polarization of ferroelectric liquid crystals (Fischer et al., 1997; Ikeda et al., 1993).

1.1.3.3. Dendrimers. Dendrimers have been investigated as unique structures to exploit and harness azobenzene's photochemistry (Momotake and Arai, 2004a,b; Villavicencio and McGrath, 2002). Dendritic and branched molecular architectures can have better solubility properties and can be used to control undesired aggregation, resulting in higher quality films for optical applications (Campbell et al., 2006; Ma et al., 2002). Dendrimers with strongly absorbing pendants can act as antenna, harvesting light and making it available, via intramolecular energy transfer, to the dendrimer core. In dendrimers with azo cores, this allows for the activation of isomerization using a wavelength outside of the azo-absorption band (since the dendrimer arms absorb and transfer energy to the core) (Aida et al., 1998; Jiang and Aida, 1997). Furthermore, the configurational change that results from the core isomerization will translate into a larger scale geometric change. For instance, in a dendrimer with three azobenzene arms (Fig. 1.7), the various isomerization combinations (EEE, EEZ, EZZ, and ZZZ) could all be separated by thin-layer chromatography because of their different physical properties (Junge and McGrath, 1999). The conformational change associated with isomerization modifies (typically reduces) the hydrodynamic volume, with the specific extent of conformational change depending strongly on where the azo units are incorporated (Li and McGrath, 2000).

1.1.3.4. Polyelectrolyte Multilayers. A new facile and versatile film preparation technique, layer-by-layer electrostatic self-assembly, has become the subject of intensive research since its introduction by Decher (Decher, 1997; Decher and Schmitt, 1992; Decher and Hong, 1991; Decher et al., 1991). In this technique, a charged or hydrophilic substrate is immersed in a solution of charged polymers (polyelectrolytes), which adsorb irreversibly onto the substrate. After rinsing, the substrate is then immersed in a solution containing a polyelectrolyte of opposite charge, which adsorbs electrostatically to the charged polymer monolayer. Because each layer of adsorbed polymer reverses the surface charge, one can build up an arbitrary number of alternating polycation–polyanion layers. These polyelectrolyte multilayers (PEMs) are easy to prepare, use benign (all-aqueous) chemistry, and are inherently tunable (Decher et al., 1998; Hammond, 1999; Knoll, 1996). Specifically, by adjusting the ionic strength (Steitz et al., 2000; Linford et al., 1998; Lösche et al., 1998; Sukhorukov et al., 1996) or pH (Burke and Barrett, 2003a; Chung and Rubner, 2002; Wang et al., 2002; Shiratori and

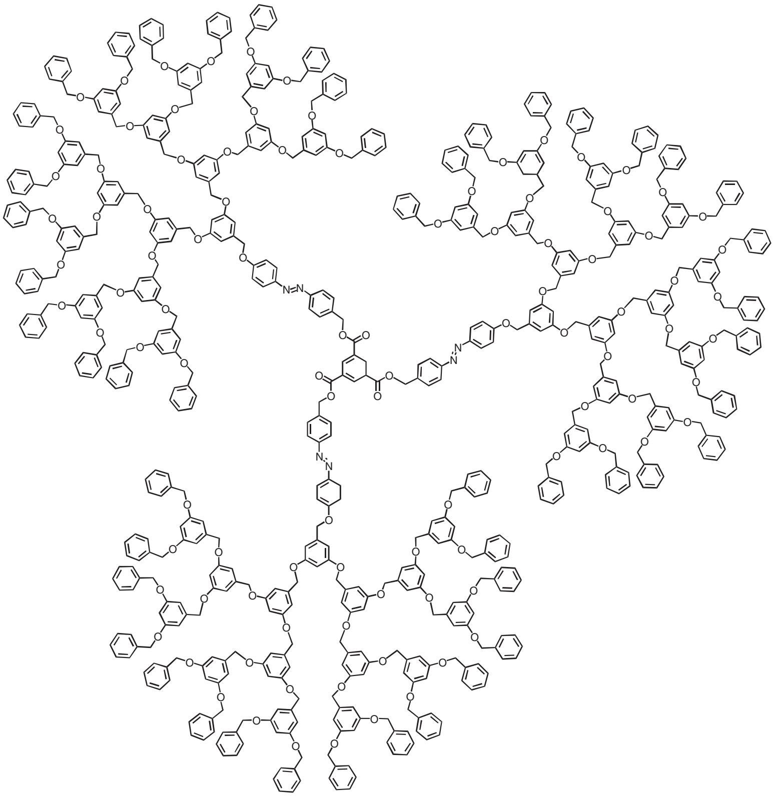

Figure 1.7. An azobenzene dendrimer containing three azo moieties. Each chromophore has two isomerization states (trans and cis), leading to four distinct photoisomers for the dendrimer molecule. All four isomers have different physical properties.

Rubner, 2000) (in the case of ''weak'' polyelectrolytes) of the assembly solution, the polyelectrolyte chain conformation is modified, and hence the resulting film architecture is tuned. For instance, one can control thickness (Lösche et al., 1998; Dubas and Schlenoff, 1999), permeability (Rmaile and Schlenoff, 2003), morphology (Antipov et al., 2003; McAloney et al., 2003; Mendelsohn et al., 2000), and density (Dragan et al., 2003). Recently the technique has been modified to assemble the alternate layers using a spin-coater, which reduces the assembly times and adsorption solution volumes considerably (Chiarelli et al., 2001; Cho et al., 2001; Lee et al., 2003, 2001).

As a film preparation technique, this method has numerous advantages. The adsorption of the polymers is quasithermodynamic, with the chains adsorbing into a local minimum, which makes the films stable against many defects (dewetting, pinhole formation, etc.). Importantly, the technique is not limited to flat surfaces: any geometry that can be immersed in solution (or have solution flowed through) is suitable. Colloids have been efficiently coated with PEMs (Caruso, 2001; Sukhorukov et al., 1998b), and by dissolving the core one can also form hollow PEM microcapsules (Sukhorukov et al., 1998a). Multilayers can be formed on nearly any material (glass, quartz, silicon, most metals, etc.) and are robust against thermal and solvent treatment (Mermut and Barrett, 2001). One of the main interests in PEMs is due to their inherent biocompatibility (Richert et al., 2002): multilayers have been formed on enzyme microcrystals (Jin et al., 2001), used to encapsulate living cells (Diaspro et al., 2002) and coat arterial walls (Thierry et al., 2003). Perhaps the most useful feature of the multilayering technique is its ability to incorporate secondary functional groups into the thin film structure. The location of these functional units (which may be small molecules, pendants on the polyelectrolyte chains, or particles) within the multilayer stack can be controlled with subnanometer precision. A wide variety of functionalities have been demonstrated, including organic molecules (He et al., 2000a), synthetic polymers (Balasubramanian et al., 1998), biopolymers (Burke and Barrett, 2003b), natural proteins (Caruso and Möhwald, 1999), colloids (Lvov et al., 1997), inorganic nanoparticles (Kotov et al., 1995), clay platelets (Kleinfeld and Ferguson, 1994) (used as a nacre biomimic [Tang et al., 2003]), dendrimers (Watanabe and Regen, 1994), electrochemically active species (Knoll, 1996), functionalized C_{60} (Mattoussi et al., 2000), and even, counterintuitively, uncharged and nonpolar polymer chains (Rouse and Ferguson, 2002).

Many research groups have investigated the possibility of incorporating optically responsive azobenzene chromophores into the versatile PEM structures (examples presented in Fig. 1.8), including Advincula (Advincula et al., 2001, 2003; Advincula, 2002; Ishikawa et al., 2002), Kumar and Tripathy (Lee et al., 2000; Balasubramanian et al., 1998), Tieke (Ziegler et al., 2002; Toutianoush et al., 1999; Toutianoush and Tieke, 1998; ; Saremi and Tieke, 1998),

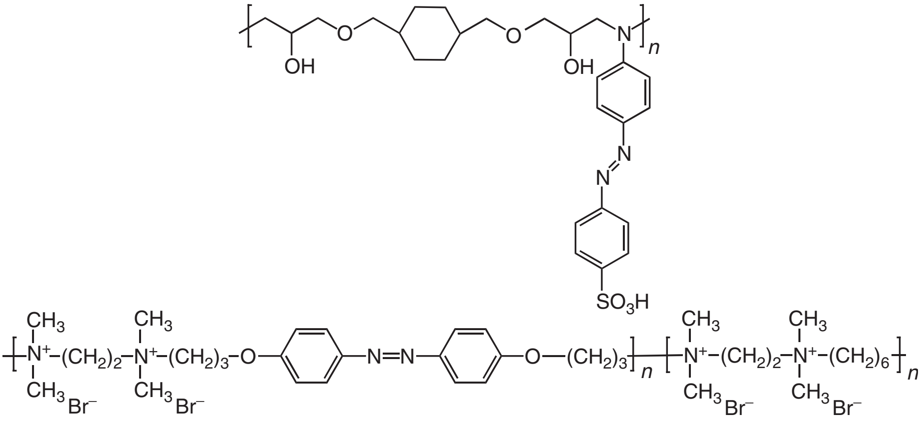

Figure 1.8. Examples of water-soluble azo polyelectrolytes, which can be used in the preparation of photoactive polyelectrolyte multilayers.

Heflin (Van Cott et al., 2002), and Barrett (Mermut and Barrett, 2003; Mermut et al., 2003). In some cases, copolymers are synthesized, where some of the repeat units are charged groups and some are azo chromophores (Suzuki et al., 2003; Wu et al., 2001a). These materials may, however, have solubility issues, as the azo chromophore is typically not water-soluble. Efforts have therefore gone into synthesizing azo ionomers (Jung et al., 2002; Hong et al., 2000), or polymers where the charge appears on the azobenzene unit (Wang et al., 1998, 2004; Wu et al., 2001a). The azobenzene chromophore may also be created by postfunctionalization of an assembled PEM (Lee et al., 2000). Azobenzene-functionalized PEMs have demonstrated all of the unique photophysics associated with the chromophore, including induced birefringence (Ishikawa et al., 2002; Park and Advincula, 2002) and surface mass transport (Wang et al., 1998) (which is described in more detail in Section 1.3). It should be noted, however, that in general the quality of the patterning is lower (Wang et al., 2004), presumably because of the constraints to chain motion that the ionic ‘‘cross-links’’ engender. There are many examples of performing the multilayering with a polyelectrolyte and a small molecule azobenzene ionic dye (Dragan et al., 2003). In contrast to conventional doped systems, the chromophores in these systems do not suffer from aggregation instabilities (Advincula et al., 2001), and the azo photomotions do couple to the matrix, as evidenced by birefringence (dos Santos Jr. et al., 2003; Bian et al., 2000) and surface patterning (He et al., 2000a,b). These effects can again be attributed to the fact that the ionic attachment points act as cross-links in a dry PEM sample. The aggregation and photochemical behavior of the azo chromophore (absorbance spectrum, isomerization rate, etc.) vary depending on the nature of the counterpolymer (Dante et al., 1999) (and of course, is affected by any ionic ring substituent). These may be viewed as undesirable matrix effects, or as a way to tune the chromophore response. The multilayering technique does not offer the precision and reproducibility of conventional inorganic film preparation techniques. It is, however, simple, versatile, and offers the possibility of combining unique structures and functionalities (for instance, it has been used to create superhydrophobic surfaces [Zhai et al., 2004], to make azo photochromic hollow shells [Jung et al., 2002], and is amenable to patterning [Nyamjav and Ivanisevic, 2004]). Although it is unlikely to replace established techniques for high performance devices, it may find applications in certain niches (coatings, disposable electronics, biomedical devices, etc.).

1.2. PHOTOINDUCED MOTIONS AND MODULATIONS

Irradiation with light produces molecular changes in azobenzenes, and under appropriate conditions, these changes can translate into larger scale motions and even modulation of material properties. Following Natansohn and Rochon (2002), we will describe motions roughly in order of increasing size scale. However, since the motion on any size scale invariably affects (and is affected by) other scales, clear divisions are not possible. In all cases, some of the implicated applications, photoswitching, and photomodulations will be outlined.

1.2.1. Molecular Motion

The fundamental molecular photomotion in azobenzenes is the geometrical change that occurs on absorption of light. In *cis*-azobenzene, the phenyl rings are twisted at 90° relative to the C–N = N–C plane (Naito et al., 1991; Uznanski et al., 1991). Isomerization reduces the distance between the 4 and 4′ positions from 0.99 nm in the trans state to 0.55 nm in the cis state (Brown, 1966; Hampson and Robertson, 1941; de Lange et al., 1939). This geometric change increases the dipole moment: whereas the trans form has no dipole moment, the cis form has a dipole moment of 3.1 D (Hartley, 1937). The free volume requirement of the cis is larger than that of the trans (Naito et al., 1993), and it has been estimated that the minimum free volume pocket required to allow isomerization to proceed via the inversion pathway (Naito et al., 1991; Paik and Morawetz, 1972) is $0.12\,\mathrm{nm}^3$, and $\sim 0.38\,\mathrm{nm}^3$ via the rotation pathway (Lamarre and Sung, 1983). The effects of matrix free volume constraints on photochemical reactions in general have been considered (Weiss et al., 1993). The geometrical changes in azobenzene are very large, by molecular standards, and it is thus no surprise that isomerization modifies a wide host of material properties.

This molecular displacement generates a nanoscale force, which has been measured in single-molecule force spectroscopy experiments (Holland et al., 2003; Hugel et al., 2002) and compared with theory (Neuert et al., 2005). In these experiments, illumination causes contraction of an azobenzene polymer, showing that each chromophore can exert pN molecular forces on demand. A pseudorotaxane that can be reversibly threaded–dethreaded using light has been called an ‘‘artificial molecular-level machine’’(Balzani et al., 2001; Asakawa et al., 1999). The ability to activate and power molecular-level devices using light is of course attractive since it circumvents the limitations inherent to diffusion or wiring. The fast response and lack of waste products in azo isomerization are also advantageous. Coupling these molecular-scale motions to do useful work is of course the next challenging step. Progress in this direction is evident from a wide variety of molecular switches that have been synthesized. For example, an azo linking two porphyrin rings enabled photocontrol of electron transfer (Tsuchiya, 1999). In another example, dramatically different hydrogen-bonding networks (intermolecular and intramolecular) can be favored on the basis of the isomeric state of the azo group linking two cyclic peptides (Steinem et al., 1999; Vollmer et al., 1999).

1.2.2. Photobiological Experiments

The molecular conformation change of the azo chromophore can be used to switch the conformation and hence properties of larger molecular systems to which it is attached. This is particularly interesting in the case of inclusion within molecular-scale biological systems. The bridging of biology and physical chemistry is an ever-expanding research domain. It is no surprise that the clean and unique azo photochemistry has been applied to switching biological systems (Willner and Rubin, 1996). One of the earliest investigations of azobenzene in a biological context involved embedding azobenzene molecules into a model membrane system (Balasubramanian et al., 1975). On isomerization, the lamellae were disrupted and rearranged, which also changed the enzymatic activity of membrane-bound proteins. The catalytic activity of a cyclodextrin with a histidine and azobenzene pendant was photocontrollable because the trans version of the azo pendant can bind inside the cyclodextrin pocket, whereas the cis version liberated the catalytic site (Lee and Ueno, 2001). Photoregulation of polypeptide structure has been an active area of research (Ciardelli and Pieroni, 2001), with the azobenzenes making significant contributions. Azo-modified poly (L-alanine) (Sisido et al., 1991a,b), poly(L-glutamic acid) (Houben et al., 1983; Pieroni et al., 1980), and poly(L-lysine) (Malcolm and Pieroni, 1990), among others, have been prepared. Depending on the system, photoisomerization may cause no change (Houben et al., 1983) or can induce a substantial conformational change, including transitions from ordered chiral helix to disordered achiral chain (Fissi et al., 1996; Yamamoto and Nishida, 1991; Montagnoli et al., 1983), changes in the α-helix content, or even reversible α-helix to β-sheet conversions (Fissi et al., 1987). Also, owing to the change in local electrostatic environment, the pK_a of the polypeptides can be controlled in these systems.

Covalent attachment of azobenzene units to enzymes can modify protein activity by distorting the protein structure with isomerization. This was used to control the enzyme activity of papain (Willner and Rubin, 1993; Willner et al., 1991a) and the catalytic efficiency of lysozyme (Inada et al., 2005). A different methodology is to immobilize the protein of interest inside a photoisomerizable copolymer matrix, which was used to control α-chymotrypsin (Willner and Rubin, 1993; Willner et al., 1991b, 1993). The azobenzene need not be directly incorporated into an enzyme of interest. In one case, the activity of tyrosinase could be modified by isomerization of small-molecule azo inhibitors (Komori et al., 2004). The photoselective binding of short peptide fragments into enzymes can be used to inhibit, thus control, activity (Harvey and Abell, 2000, 2001). Similarly, the binding of an azopeptide with a monoclonal antibody was found to be photoreversible (Harada et al., 1991). The photoresponse of azobenzene can thus be used to control the availability of key biomolecules. In one case, NAD^+ was modified with an azobenzene group, and introduced into a mixture with an antibody that binds to the trans form (Hohsaka et al., 1994). This binding makes NAD^+ unavailable, whereas irradiation of the solution with UV light induces the trans to cis isomerization, and thereby liberates NAD^+.

Bioengineering has more recently been broadened by expanding the natural protein alphabet with artificial amino acids. This enables novel and nonnatural protein sequences to be created, while still exploiting the highly efficient natural synthesis machinery. Chiral azobenzene amino acids have been synthesized and incorporated into protein sequences (Wang and Schultz, 2004). The introduction of artificial photoactive residues opens the possibility of photocontrol of biological processes. For instance, *Escherichia coli* variants were selectively evolved that would incorporate azobenzene amino acids into proteins, which enabled photocontrol of protein binding in that organism (Bose et al., 2006). For instance, photocontrol of the binding affinity of a transcription factor to its promoter, allowed for, in essence, light control of gene expression in the organism. In another case, a (negatively charged) hydrophilic azobenzene amino acid was incorporated into a restriction enzyme, and enabled control of activity with light (Nakayama et al., 2004, 2005). Specifically, the *trans*-azo residue was positioned at the dimer interface, and disrupted association, whereas in the cis state, the proteins could aggregate and exhibit normal biological activity. It has also been suggested that the rapid switching of azobenzene could be used as a "molecular shuttle" for electron transduction in enzyme systems (Voinova and Jonson, 2004). In effect, this would mean that light could be efficiently used to alter behavior in yet another class of enzymes. Incorporation of azobenzene into DNA is another interesting way to control biological systems. In one case, the duplex of modified DNA could be reversibly switched (Asanuma et al., 2001), since the *trans*-azobenzene intercalates between base pairs and helps bind the two strands of the double helix together, whereas the *cis*-azobenzene disrupted the duplex (Liang et al., 2003). By incorporating an azobenzene unit into the promoter region of an otherwise normal DNA sequence, it was possible to photocontrol gene expression (Liu et al., 2005). In this case, the trans versus cis states of the azo unit have different interactions with the polymerase enzyme.

These experiments suggest an overall strategy to control biological systems using light. A complex biochemical pathway can be controlled by photoregulating the activity or availability of a key biomolecule. This allows one to turn a biological process on and off at will using light. The use inside living organisms is obviously more complicated, but one can reasonably easily apply these principles to control biological processes in industrially relevant settings. The ability to quickly and cleanly switch biological activity using a short light pulse may find application in new microfluidic devices, which need to be able to address specific device regions and may rely on natural molecular machinery to carry out certain tasks. Azobenzenes present unique opportunities in the biological sciences for studying complex biological systems, in addition to controlling them. A bacteriorhodopsin analog with a central azobenzene molecule, rather than the retinal, was prepared as a model system for studying rhodopsin (Singh et al., 1996). As expected, the azobenzene molecule did not interact as favorably with the protein host as strongly as the natural retinal. Despite this, the azo molecules could be coupled into the protein (in the absence of retinal) and led to significant shifts in the physicochemical properties of the complex. Moreover, the azo molecule could be used as a probe of the inner protein domain (sensing pH, for instance). A particularly elegant experiment involved using azobenzenes to monitor protein folding (Bredenbeck et al., 2003; Spörlein et al., 2002). Femtosecond two-dimensional infrared (2-D IR) spectroscopy was used as a gauge of the distances between carbonyl groups in the peptide. An azobenzene chromophore, incorporated inside the polypeptide chain, acted as the photoswitch, initiating a conformational change, hence initiating protein folding, on demand. Simultaneous time-resolved measurements of the azo spectra allowed determination of the folding dynamics. This unique measurement of protein-folding behavior was possible because of the phototriggering nature of the azo unit. Ultrafast laser pulse experiments are used to study a large number of chemical reactions, providing detail not possible before. This technique is, however, obviously limited to systems where the chemical events can be phototriggered. By incorporating azobenzene units into new systems, one can generate a phototriggerable system from an otherwise photoinactive one. This strategy can thus be applied to a wide range of problems in chemical dynamics, with biological systems being obvious targets.

1.2.3. Photoorientation

Azobenzene chromophores can be oriented using polarized light (Yu and Ikeda, 2004; Ichimura, 2000) via a statistical selection process, described schematically in Fig. 1.9. Azobenzenes preferentially absorb light polarized along their transition dipole axis (long axis of the azomolecule). The probability of absorption varies as $\cos^2\phi$, where ϕ is the angle between the light polarization and the azo dipole axis.

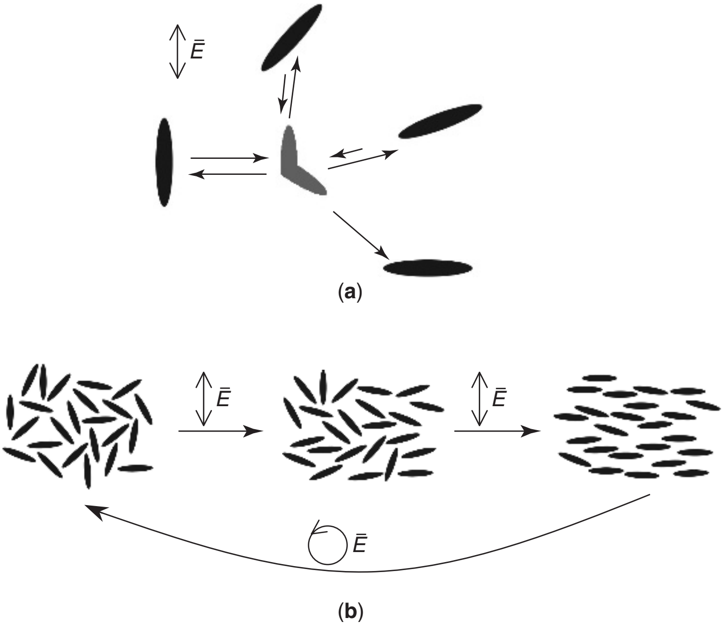

Figure 1.9. Statistical photoorientation of azomolecules. (**a**) The molecules aligned along the polarization direction of the incident light absorb, isomerize, and reorient. Those aligned perpendicular cannot absorb and remain fixed. (**b**) Irradiation of an isotropic samples leads to accumulation of chromophores in the perpendicular direction. Circularly polarized light restores isotropy.

Thus, azos oriented along the polarization of the light will absorb, whereas those oriented against the light polarization will not. For a given initial angular distribution of chromophores, many will absorb, convert into the cis form and then revert to the trans form with a new random direction. Those chromophores that fall perpendicular to the light polarization will no longer isomerize and reorient; hence, there is a net depletion of chromophores aligned with the light polarization, with a concomitant increase in the population of chromophores aligned perpendicular (i.e., orientation hole burning). This statistical reorientation is fast and gives rise to strong birefringence (anisotropy in refractive index) and dichroism (anisotropy in absorption spectrum) because of the large anisotropy of the azo electronic system. The process is especially efficient because of the mesogenlike cooperative motion that the azobenzene groups facilitate even in amorphous samples below T_g (Wiesner et al., 1991). Since the process requires cycling of the chromophores between the trans and cis states, the pseudo-stilbenes have the fastest response.

The orientation due to polarized light is reversible. The direction can be modified by using a new polarization angle for the irradiating light. Circularly polarized light will randomize the chromophore orientations. It must be emphasized, however, that there is another preferential alignment direction during irradiation: along the axis of the incoming light. It is unavoidable that chromophores will efficiently build up aligned along the irradiation axis, but this is often ignored in the literature, or characterized as ''photobleaching'' when in fact it is a reversible photoalignment (albeit one that reduces the absorbance as viewed by any photoprobe). Because unpolarized light can photoorient (along the axis of illumination) (Han and Ichimura, 2001), even sunlight is suitable. The motion of the sun through the sky over the course of a day can cause orientation at different tilt angles (Ichimura and Han, 2000). This causes chromophores at different depths to be oriented in different directions, which produces a net chiral helical ordering in the film of a particular handedness (on the basis of the hemisphere in which the experiment is performed). The implications of such results to the origin of absolute chirality in biological systems are intriguing.

1.2.3.1. Birefringence.

Irradiation with light polarized in the y-direction will lead to net alignment of chromophores in the x-direction. As a result, the refractive index probed in the x-direction, n_x, will measure the azo long axis, and will be larger than n_y. Birefringence is the anisotropy in refractive index: $\Delta n = n_x - n_y$. Photoalignment in azobenzene systems can achieve extremely high values of Δn, up to 0.3–0.5 at ~633 nm (Hagen and Bieringer, 2001; Natansohn et al., 1994). Importantly, very high birefringence values can be obtained far outside of the azo-absorption band, which means that the birefringence can be utilized/measured without disturbing the chromophores. An in-plane isotropic state ($n_x = n_y$) can be restored by irradiation with circularly polarized light, and a fully isotropic state can be obtained by heating above the T_g.

The exact nature of the orientation can be rigorously quantified using optical techniques. Using surface plasmon resonance spectroscopy or waveguide spectroscopy, the three orthogonal refractive indices in an oriented sample can be measured (Tawa and Knoll, 2002). Stokes polarimetry can be used to fully characterize the optical anisotropy, separating linear and circular components (Hore et al., 2002). The anisotropy of the cis population during irradiation can also be measured in some systems (Buffeteau et al., 2001; Sekkat et al., 1995b), where it is found that, as with trans, there is an enrichment perpendicular to the irradiation polarization. In some LC systems, however, it may occur that the cis population preferentially aligns with the irradiating polarization (which may be attributed to an optical Fréedericksz transition) (Hore et al., 2003).

The birefringence can be written and erased hundreds of thousands of times, which is important technologically (Holme et al., 1996). Amorphous polymer systems with relatively high T_g exhibit good temporal stability of any induced orientation. Upon heating, some order will be lost, with full isotropy restored after heating past T_g. A short spacer between the chromophore and the polymer backbone slows the growth of birefringence yet promotes stability, owing to hindered motion. Surprisingly, main-chain azos can achieve high levels of birefringence, indicating relatively high polymer mobility (Wu et al., 2001b; Xu et al., 2000; Lee et al., 1998). As might be expected, (nanosecond) pulsed experiments lead to thermal effects, which enhance chromophore motion and thereby induced greater birefringence at the same net dose compared with continuous-wave (cw) experiments (Cimrová et al., 2002; Hildebrandt et al., 1998). At very high pulsed fluence, the thermal effects were too great and erased the induced birefringence.

The easily inscribed and erased birefringence has a number of unique applications. Most readily, it can be used to create wave plates (Shi et al., 1991a) and polarization filters, which can be used to separate right-handed from left-handed circularly polarized light (Natansohn and Rochon, 1999). The strong refractive index contrast, if patterned into a line, can serve as a channel waveguide (Watanabe et al., 1996; Shi et al., 1991b). This offers the unique possibility of optical devices that can be patterned, erased, and reused. In principle, these photonic circuits could be altered during device operation, enabling optical routing of optical signals (i.e., optical computing). The switching of orientational order can thus be used as an all-optical switch (Shishido et al., 1997). By illuminating an azo sample with a spatially varying light pattern, birefringence gratings can also be formed (Eichler et al., 2001; Nikolova et al., 1996; Couture and Lessard, 1988). These are phase gratings, as opposed to amplitude gratings, and diffract light on the basis of spatial variation of the refractive index. This is the essence of holography: two interfering coherent beams generate a spatially varying light pattern, which is encoded into the material. Under illumination of the material with one of the beams, the diffraction reproduces the other encoded beam. In the case of liquid crystal samples, light induces a spatial pattern of nematic and isotropic zones (which have different refractive indices). These holographic phase grating can be rapidly formed, erased, and switched (Yamamoto et al., 2001).

1.2.3.2. Nonlinear Optics. The requirement for NLO response in any material is an asymmetric (strictly, anharmonic) response of the electronic system. Pseudo-stilbenes, which have push–pull substituents, have a strongly asymmetric electron distribution, which makes them ideal NLO molecules (see, for instance, Fig. 1.10). For a bulk NLO response, one requires an overall noncentrosymmetric material. This requirement is achieved in many inorganic crystals. In organic systems, the broken symmetry is typically obtained by applying an electric field at a temperature sufficient to allow for the molecular dipoles to align with the field. This process is called electric field poling and is accomplished using interdigitated or flat electrodes or a sharp charged needle (or grid) held above a grounded sample (called corona poling). The NLO response is typically quantified using second-harmonic generation (SHG; the emission of light at double the frequency of the incident beam), the electrooptic effect (change of refractive index on application of an electric field), or wave-mixing experiments (where various frequencies of light can be synthesized or enhanced). These also constitute the main applications of NLO materials: they can be used to synthesize new frequencies of light, to electrically switch a beam, or to allow two beams of light to interact and couple (which can form the basis of an all-optical switch) (Eaton, 1991).

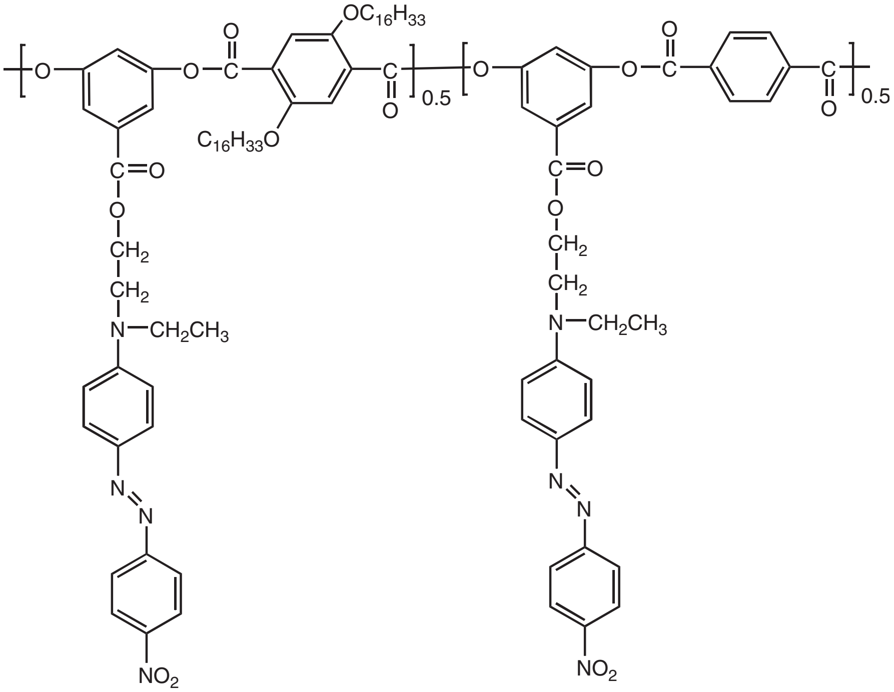

Figure 1.10. Example of a nonlinear optic azo polymer used for photoassisted poling.

Azo polymers have been shown to be excellent NLO materials (Yesodha et al., 2004; Delaire and Nakatani, 2000; Dalton et al., 1995; Burland et al., 1994). In azo systems, one has the additional advantage of using light to affect the chromophores. Although photoalignment orients the chromophore axis, it does not select out a preferred direction for the molecular dipole (thus, an equal number of dipoles point ‘‘left’’ and ‘‘right’’). In fact, evidence suggests that dipoles in these systems tend to orient antiparallel (H-aggregates) (Meng et al., 1996; Brown et al., 1995), thereby canceling polar order. Nevertheless, the photoalignment can be used to facilitate the electric poling, enabling it to be performed at room temperature and with a small DC field (Jiang et al., 1996; Sekkat et al., 1995a; Blanchard and Mitchell, 1993a,b). Furthermore, by using polarized light and its harmonic, a net noncentrosymmetry can be obtained in an all-optical process (Zhong et al., 2001; Nunzi et al., 1998). This occurs because the mixture of a primary beam and its second harmonic creates a directional electric field in the material.

Another interesting approach for NLO uses dendrons (‘‘half-dendrimers’’) with azo functionalities (Yokoyama et al., 2000). The dendritic architecture forces all the chromophores within the dendron to align, which strongly enhances the NLO response. The dendron had a first-order molecular hyperpolarizability 20 times larger than the monomer. With regard to applications, the azos have been shown to function as electro-optical switches (Yamane et al., 1999) and exhibit photorefraction (Iftime et al., 2002; Steenwinckel et al., 2001; Barrett et al., 1998; Ho et al., 1996), an NLO effect where photoconductivity permits light to establish a space charge grating, whose associated index grating refracts a probe light beam.

1.2.4. Domain Motion

The orientation and reorientation of LC domains has already been outlined. The azo chromophores act as mesogens and their photoalignment becomes transferred to the LC host. A very small azo content (a few mol% [Ikeda et al., 1990]) can lead to orientational control of LC domains. This is an excellent example of amplification of the azomolecular motion. The phase of a liquid crystal can also be switched with light. Irradiation produces cis isomers, which are poor mesogens and destabilize the nematic phase, thereby inducing a phase transition to the isotropic state. There are comparatively few examples of phototriggered increases in LC ordering. In one case, a nanoscale phase separation of the cis isomers led to a net increase in the order parameter of the LC phase (Prasad and Nair, 2001). In another system, a chiral azo was found to induce a cholesteric phase when it was in the cis state (Ruslim and Ichimura, 2001).

With LC (Nikolova et al., 1997) or preoriented amorphous samples (Ivanov et al., 2000), one can photoinduce a chiral domain structure. Incident circularly polarized light becomes elliptically polarized because of the first oriented layer. This ellipse subsequently reorients deeper chromophores, which in turn modify the ellipticity of the light. This reorientation continues throughout the film depth. Overall, a chiral ordering of the chromophore domains is established (Nikolova et al., 2000). Remarkably, one can switch between a right- and left-handed supramolecular helix at will, by changing the incident light handedness. There are many other examples of photocontrol of supramolecular order. The pitch of a cholesteric LC can be modified by isomerization (Sackmann, 1971). Biomacromolecular variants abound (Willner and Rubin, 1996). Azo-modified polypeptides can be photoswitched between ordered states (α-helix or β-sheet) and a random coil (Everlof and Jaycox, 2000; Fissi et al., 1996; Yamamoto and Nishida, 1991). The duplex of modified DNA can be reversibly switched (Asanuma et al., 2001), and the catalytic activity of histidine can be controlled (Lee and Ueno, 2001).

Photoisomerization can also affect self-assembly behavior at the domain level. On irradiation, one can induce a phase change (Aoki et al., 2000), a solubility change (Arai and Kawabata, 1995; Yamamoto et al., 1990), crystallization (Ebralidze and Mumladze, 1990), or even reversal of phase separation (Effing and Kwak, 1995). The critical micelle concentration (cmc) and surface activity can also be modified (Yang et al., 1995). In an amphiphilic polypeptide system, self-assembled micelles were formed in the dark and could be disaggregated with light (Higuchi et al., 1994). When allowed to assemble as a transmembrane structure, the aggregate could be reversibly formed and destroyed using light, which allowed for reversible photoswitching of ion transport (Higuchi et al., 1995a). Related experiments on methacrylates (Chen et al., 1997a; Angiolini et al., 1995) and polypeptides (Sisido et al., 1991b) showed that a polymer's chiral helix could be reversibly suppressed on irradiation. In a series of polyisocyanate polymers, it could be selected whether irradiation would suppress or increase chirality (Müller and Zentel, 1996; Maxein and Zentel, 1995).

1.2.5. Macroscopic Motion

It is interesting to study whether the azobenzene molecular conformational rearrangements can result in changes to bulk phenomena, or even to macroscopic motion. The first consideration is whether the material expands to an appreciable extent. In monolayers, it is well established that the larger molecular size of the cis isomer leads to a corresponding lateral expansion (Higuchi et al., 1995b), which can modify other bulk properties. For instance, this allows photomodulation of a monolayer's water contact angle (Siewierski et al., 1996) or surface potential (Stiller et al., 1999). Using fluorinated azo polymer, good photocontrol (Feng et al., 2001) and photopatterning (Moller et al., 1998) of wettability has been demonstrated. A monolayer of azo-modified calixarene, when irradiated with a light gradient, produced a gradient in surface energy sufficient to move a macroscopic oil droplet (Ichimura et al., 2000), suggesting possible applications in microfluidics. Modest photoinduced contact angle changes for thin polymer films have also been reported (Sarkar et al., 2001). Recently an azobenzene copolymer assembled into polyelectrolyte multilayer showed a modest 2° change in contact angle with UV light irradiation. However, when the same copolymer was assembled onto a patterned substrate, the change in contact angle upon irradiation was enhanced to 70° (Jiang et al., 2005). It is well established that surface roughness plays a role in contact angle and many systems can be optimized to give rise to a large change in surface properties.

In layered inorganic systems with intercalated azobenzenes, reversible photochanges in the basal spacing (on the order of 4%) can be achieved (Fujita et al., 1998, 2001). In polymer films, there is some evidence that the film thickness increases, as measured by ellipsometry (Shi et al., 1991b) (the refractive index certainly changes [Ivanov et al., 1995], but this is not an unambiguous demonstration of expansion–contraction). Experiments that show that external applied pressure tends to hinder photoisomerization (Kleideiter et al., 2000) are related. Photocontraction for semicrystalline main-chain azos has been measured (Eisenbach, 1980b; Agolini and Gay, 1970). This photomechanical response presumably occurs because of the shortening of the polymer chains upon trans → cis conversion. However, photoexpansion would seem to be contradicted by positron lifetime experiments that suggest no change in microscopic free volume cavity size during irradiation (Algers et al., 2004). More conclusive experiments are in order.

The most convincing demonstration of macroscopic motion due to azo isomerization is the mechanical bending and unbending of a free-standing polymer film (Ikeda et al., 2003; Yu et al., 2003). The macroscopic bending direction may be selected either with polarized light or by aligning the chromophores with rubbing. Bending occurs in these relatively thick films because the free surface (which absorbs light) contracts, whereas the interior of the film (which is not irradiated owing to the strong absorption of the upper part of the film) does not contract. Because the direction of bending can be controlled with polarized light, the materials enable full directional photomechanical control (Yu et al., 2005). This photomechanical deformation has also been used to drive macroscopic motion of a floating film (Camacho-Lopez et al., 2004). That these materials contract (rather than expand) appears again to be related to the main-chain azo groups and may also be related to the LC nature of the cross-linked gels. For a thin film floating on a water surface, a contraction in the direction of polarized light was seen for LC materials, whereas an expansion was seen for amorphous materials (Bublitz et al., 2000). A related amplification of azo motion to macroscopic motion is the photoinduced bending of a microcantilever coated with an azobenzene monolayer (Ji et al., 2004). One can also invert the coupling of mechanical and optical effects: by stretching an elastomeric azo film containing a grating, one can affect its wavelength-selection properties and orient chromophores (Bai and Zhao, 2001).

1.2.6. Other Applications of Azobenzenes

1.2.6.1. Photoswitches. As already pointed out, the azo isomerization can be used to photoswitch a wide variety of other properties (at numerous size scales). In addition to the optical changes already described, it is worth noting that the transient change in material refractive index (owing to the different n of cis and trans) can itself act as a photoswitch (Barley et al., 1991). The azo photochromism has even been suggested as a possible optical neural network element (Sumaru et al., 1999). Binding and transport properties can also be photoswitched (Weh et al., 1998; Anzai and Osa, 1994). In some systems the redox potential and ionic conductivity can be switched with light (Willner and Willner, 1997). Crown ethers (Zawisza et al., 1999; Tokuhisa et al., 1994) and calixarenes (Reynier et al., 1998) functionalized with azobenzene can be used as reversible ion-binding systems. Thus, ion transport can be photoregulated. In other cases, the transport properties can be photocontrolled not via binding but on the basis of changes in pore sizes (Sata et al., 2000; Abraham and Purushothaman, 1998; Kano et al., 1980). In a particularly elegant example, the size of nanochannels could be modified by irradiating azo ligands that decorate the channel walls (Liu et al., 2004). Azo-derivatized gramicidin ion channels represent a unique case where ion transport can be photocontrolled by the optical manipulation of a biomolecule (Lien et al., 1996). In addition to obvious applications in controlled transport, this offers the possibility of studying cells by controlling the timing of ion exchange processes. Photoinduced catalysis is also possible, for instance, using molecules where only the cis form is catalytically active (Wuerthner and Rebek, 1995). Extension of the molecular imprinting technique to azo polymers allows for photoswitching of binding activity with respect to the imprinted molecule (Minoura et al., 2004).

1.2.6.2. Photoprobes. The properties of an azo chromophore (spectrum, isomerization kinetics, etc.) depend strongly on the local environment. This enables the possibility of using the chromophore as a molecular sensing element: a photoprobe. For instance, it has been found that many azo properties depend on local H^+ concentration, to the extent that the azo can in fact be used as a pH meter (Uznanski and Pecherz, 2002; Mermut and Barrett, 2001). As mentioned earlier, the isomerization kinetics can also be used as a probe of free volume (Naito et al., 1993; Lamarre and Sung, 1983), local aggregation (Norman and Barrett, 2002), or phase transitions. The azo molecule is small and exhibits clean photochemistry, which makes it more versatile and robust than many other photoprobes. The rate of isomerization is also remarkably insensitive to temperature (Yamamoto, 1986), yet sensitive to local solvent conditions (Li et al., 2006; Norman and Barrett, 2002). This is an area of research that deserves considerably more attention.

In a more sophisticated example, azo chromophores were used to monitor protein folding (Bredenbeck et al., 2003; Spörlein et al., 2002). Specifically, femtosecond 2-D IR spectroscopy was used to monitor the distances between carbonyl groups in the peptide. An azo chromophore, incorporated inside the polypeptide chain, was used as a photoswitch to initiate a conformational change, hence initiate protein folding, on demand. Combined with time-resolved monitoring of the azo spectrum, this allows the deconvolution of folding dynamics. Pump-probe ultrafast laser pulse experiments are being used to study many different chemical reactions, but are obviously limited to reactions that can be triggered by light. Incorporating azobenzene into the experiment allows a wider range of reactions to be phototriggered.

1.2.6.3. Optical Data Storage. The azos have been investigated as optical storage media for some time. Early proofs of principle were on Langmuir–Blodgett films, using photochromism (Liu et al., 1990) or birefringence (Dhanabalan et al., 1999). Increasingly, amorphous polymer systems are being recognized as promising materials. In these easily processed systems, the birefringence is strong, stable, and switchable, making them ideal for optical memories. A single domain could encode one bit by either being isotropic or birefringent, a difference that is easily probed optically. The Δn values are large enough, in fact, that a gray-level algorithm could be used, where each domain stores more than one bit of data. On the negative side, the photoalignment generated in the direction of the read–write beam leads to an effective loss of material performance with time. Full anisotropy could be restored with heat, however (which can be local and photoinduced, with appropriate device setup). The feasibility of storing $\sim$30 GB of data on a single layer of a removable disk using this gray-level approach has been demonstrated (Hagen and Bieringer, 2001).

Even the fastest photoinduced birefringence in azo systems requires milliseconds and is slow compared with most computer timescales. However, optical data storage is amenable to gray-level read–write (Sabi et al., 2001) and to storing–retrieving full 2-D "pages" of data at a time. In principle, azo systems could achieve high data storage and retrieval speeds. The full 3-D volume of a material can be used by encoding many layers of 2-D data (pages) one on top of the other (Kawata and Kawata, 2000; Ishikawa et al., 1998). This is accomplished by moving the optical focal plane through the material.

An intriguing possibility for high density storage is to use angular multiplexing (Hagen and Bieringer, 2001). By storing multiple superimposed holograms in a single material, the data density is increased dramatically, and the whole 3-D volume of the material is exploited (Ramanujam et al., 2001). Volume-phase holograms in azo systems can have diffraction efficiencies greater than 90% (Zilker et al., 1998), making data readout robust. The hologram is encoded by interfering a reference beam and a writing beam inside the sample volume, at a particular angle. The write beam, having passed through a spatial light modulator (SLM), has a pattern corresponding to the data, which is then holographically encoded in the sample. The entire page of data is written at once. By selecting different angles, new pages of data can be written. To readout a page, the azo sample is set at the correct angle and illuminated with the reference beam. The resulting diffraction pattern is imaged on a charge-coupled device (CCD) array, which measures the encoded beam pattern (data). The volume of data and transmission rate is clearly large: projections of $\sim$1000 GB in a single disk have been made. Since the entire hologram image is stored throughout the material, the technique is fairly insensitive to dust, scratches, and pinpoint defects.

The use of azo-substituted peptide oligomers appears to enable control of the order, hence optimization for holographic applications (Berg et al., 1996). Optical memories would be considerably enhanced by using two-photon processes. This allows the addressable volume to be smaller and better defined, while reducing cross-talk between encoded pages. Some azo chromophores exhibit ‘‘biphotonic’’ phenomena, which could be employed to enhance optical data storage.

1.2.6.4. Surface Mass Transport. In 1995, a surprising and unprecedented optical effect was discovered in polymer thin films containing the azo chromophore Disperse Red 1 (DR1). The Natansohn–Rochon (Rochon et al., 1995) research team and the Tripathy–Kumar collaboration (Kim et al., 1995) simultaneously and independently discovered a large-scale surface mass transport when the films were irradiated with a light interference pattern. In a typical experiment, two coherent laser beams, with a wavelength in the azo-absorption band, are intersected at the sample surface. The sample usually consists of a thin spin-cast film (10–1000 nm) of an amorphous azo polymer on a transparent substrate. The sinusoidal light interference pattern at the sample surface leads to a sinusoidal surface patterning, that is, a surface relief grating (SRG). These gratings were found to be extremely large, up to hundreds of nanometers, as confirmed by atomic force microscopy (AFM). The SRGs diffract very efficiently, and in retrospect, it is clear that many reports of large diffraction efficiency before 1995, attributed to birefringence, were in fact due to surface gratings. The process occurs readily at room temperature (well below the T_g of the amorphous polymers used) with moderate irradiation (1–100 mW cm^{-2}) over seconds to minutes. The phenomenon is a reversible mass transport, not irreversible material ablation, since a flat film with the original thickness is recovered upon heating above T_g. Critically, it requires the presence and isomerization of azobenzene chromophores. Other absorbing but nonisomerizing chromophores do not produce SRGs. Many other systems can exhibit optical surface patterning (Yamaki et al., 2000), but the amplitude of the modification is much smaller, does not involve mass transport, and usually requires additional processing steps. The all-optical patterning unique to azobenzenes has been studied intensively since its discovery, yet there remains controversy regarding the mechanism. The competing interpretations are evaluated in Chapter 4, where they are discussed at length. Many reviews of the remarkable body of experimental results are available (Natansohn and Rochon, 2002; Delaire and Nakatani, 2000; Yager and Barrett, 2001; Viswanathan et al., 1999).

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