SMART LIGHT-RESPONSIVE MATERIALS

Azobenzene-Containing Polymers and Liquid Crystals

EDITED BY

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Kevin G. Yager and Christopher J. Barrett

PREFACE

Azobenzene and its derivatives are fascinating molecules display that the reversible photoisomerization between the more stable trans and the less stable cis isomers. Although photoisomerization can result in important changes of properties for azobenzene molecules on their own, such as a large change in molecular shape and dipole moment, changes that can be imparted to polymers and liquid crystals when azobenzene is part of their structures or is associated with them are more interesting. Indeed, reversible photoisomerization in azobenzene-containing polymers and liquid crystals enables the use of light as a powerful external stimulus to control or trigger the change of the properties of these two important classes of soft materials. For this reason, over the past two decades or so, there has been considerable worldwide research dedicated to azo polymers and liquid crystals-, ranging from fundamental studies to exploitation for applications. A number of important discoveries made in the 1990s have had a particular impact on this field. These include the surface relief grating that can readily be inscribed on azobenzene polymers using an interference pattern as a result of photoinduced mass transport and the isothermal photochemical liquid crystalline (LC)-to-isotropic (order-disorder) phase transitions because of the perturbation effect arising from the trans-cis photoisomerization. Today, the research field of azo-functional materials remains extremely active.

Although most research in the 1990s mainly dealt with the physical and optical properties of azo polymers and liquid crystals important for optical information storage and switching, the field has witnessed important new developments and directions over the past 6 to 7 years. Amazing new phenomena continue to be discovered, such as the light-controllable bending of cross-linked LC azo polymers, which, by showing how drastic the effect of azo photoisomerization can have on a material, offer new appealing opportunities. In recent years, there have been increasing efforts toward the development of diverse functional materials through rational molecular and material designs that make use of established knowledge, and newer applications other than information storage and switching have emerged. Convinced that ongoing and future research on azobenzene-based light-enabled smart materials will have great potential and impact on both fundamental and applied research, we think it is time to edit a book that, by reviewing recent developments and showing perspectives, provides a forum for discussions and exchange of new ideas. We would like to thank the great effort of all the contributors who have helped us put together a book that should not only benefit researchers who work on azo polymers and liquid crystals but should also be of interest to those who develop light-responsive materials without using azobenzene, as many of the discussed strategies and ideas about azobenzene could be adapted to other chromophores.

The vitality and sustained interest of this field can easily be noticed from the many research papers on azobenzene-based materials that continue to appear. Obviously, this book cannot cover all new, post-2000 developments. As editors, we have tried to ensure that all chapters are relevant to the theme of the book, with regard to research works that promise development of light-enabled smart materials based mainly on azo polymers and liquid crystals. Despite the apparent diversity of the topics covered in this book, the cohesion of all chapters and the link between the different chapters are solid. Chapter 1 (Yager and Barrett) introduces basic azobenzene photochemistry, photophysics, and the wide variety of azo materials. With Chapter 2 (Stumpe et al.) that reviews and discusses the photoinduced phenomena in supramolecular azo materials, the basic background is set to help the general readership understand the fundamental aspects involved in and the ideas and interests behind the various types of smart azo materials discussed in this book. This is followed by three chapters on photoinduced motion and the photomechanical effect of LC azo polymers (Chapter 3, Yu and Ikeda), amorphous azo polymers (Chapter 4, Yager and Barrett), and colloidal particles (Chapter 5, Wang). The conversion of photoenergy into mechanical energy is certainly a major new direction in the field. In contrast to the colloidal particles self-assembled by amphiphilic random copolymers, micellar aggregates are the subjects of Chapter 6 (Zhao) and Chapter 7 (Tribet) and involve the self-assembly of amphiphilic block copolymers and hydrophobically modified polymers, respectively. Solution self-assembled light-responsive micro- and nanostructures of azo polymers and their potential applications as discussed in these chapters represent another exciting new research direction. Likewise, the research works presented in Chapter 8 (Seki) and Chapter 9 (Watanabe) explore azo polymers in two dimensions and on surface. The next two chapters, Chapter 10 (Kurihara) and Chapter 11 (Zhao), mainly concern smart light-sensitive materials of small-molecule LCs. The last two chapters, Chapter 12 (Yu and Ikeda) and Chapter 13 (Liu and Brinker), provide excellent examples of new azo materials and architectures, with a focus on azo block copolymers in the solid state and azo hydride silica materials, respectively.

The state of research on azobenzene-based smart materials is progressing. We hope this book gives a critical review of the new developments and shows new directions. However, what we want most for this book is to really generate interest among graduate students and young researchers in this exciting field and help spark in them their imagination and ideas for creative research. This is essential to ensure further research and development and maintain the excitement in this field for many years to come.

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1

AZOBENZENE POLYMERS FOR PHOTONIC APPLICATIONS

Kevin G. Yager and Christopher J. Barrett

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.

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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

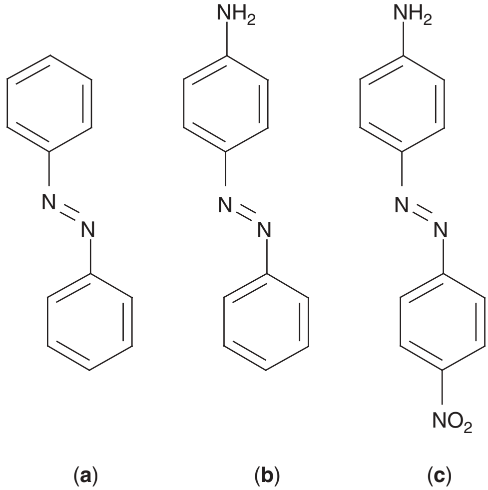

Figure 1.1. Examples of azomolecules classified as (**a**) azobenzenes, (**b**) aminoazobenzenes, and (**c**) pseudo-stilbenes.

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).

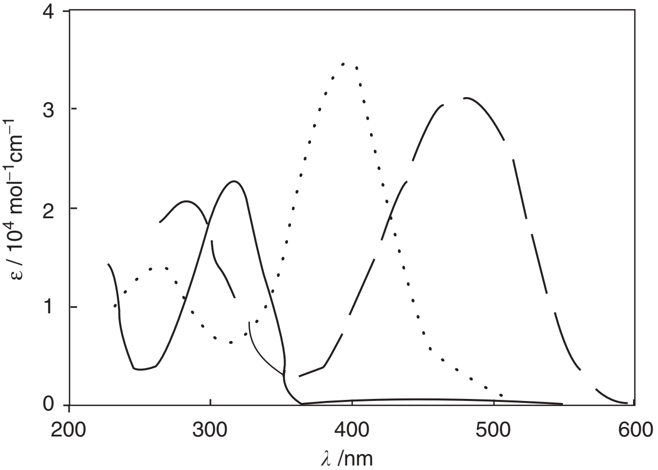

Figure 1.2. Schematic of typical absorbance spectra for *trans*-azobenzenes. The azobenzene-type molecules (*solid line*) have a strong absorption in the UV, and a low intensity band in the visible (barely visible in the graph). The aminoazobenzenes (*dotted line*) and pseudo-stilbenes (*dashed line*)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

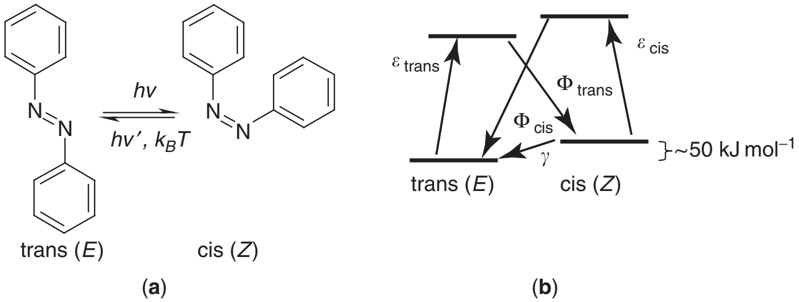

Figure 1.3. (**a**) Azobenzene can convert between trans and cis states photochemically and relaxes to the more stable trans state thermally. (**b**) Simplified state model for azobenzenes. The trans and cis extinction coefficients are denoted by $\varepsilon_{\text{trans}}$ and ε_{cis}. The Φ refer 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 $90\,\mathrm{kJ\,mol^{-1}}$ (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 $k = 2.8 \times 10^{-6}\,\mathrm{s}^{-1}$, at 3°C) (Lamarre and Sung, 1983), and an azobenzene parasubstituted with bulky pendants had a lifetime of 60 days ($k < 2 \times 10^{-7}\,\mathrm{s}^{-1}$, 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 ($k = 5.9 \times 10^{-7}\,\mathrm{s}^{-1}$) (Norikane et al., 2003), 1 year (half-life 400 days, $k = 2 \times 10^{-8}\,\mathrm{s}^{-1}$) (Rottger and Rau, 1996; Rau and Roettger, 1994), or even 6 years ($k = 4.9 \times 10^{-9}\,\mathrm{s}^{-1}$) (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 ($k = 2.9 \times 10^{-7}\,\mathrm{s}^{-1}$) 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 λ_{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

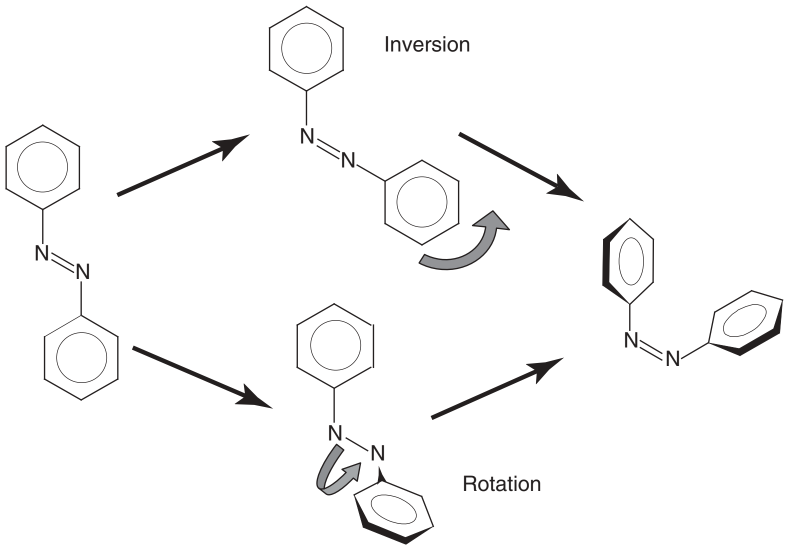

Figure 1.4. The mechanism of azobenzene isomerization proceeds either via rotation or inversion. The cis state has the phenyl rings tilted at 90° with respect to the CNNC plane.

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

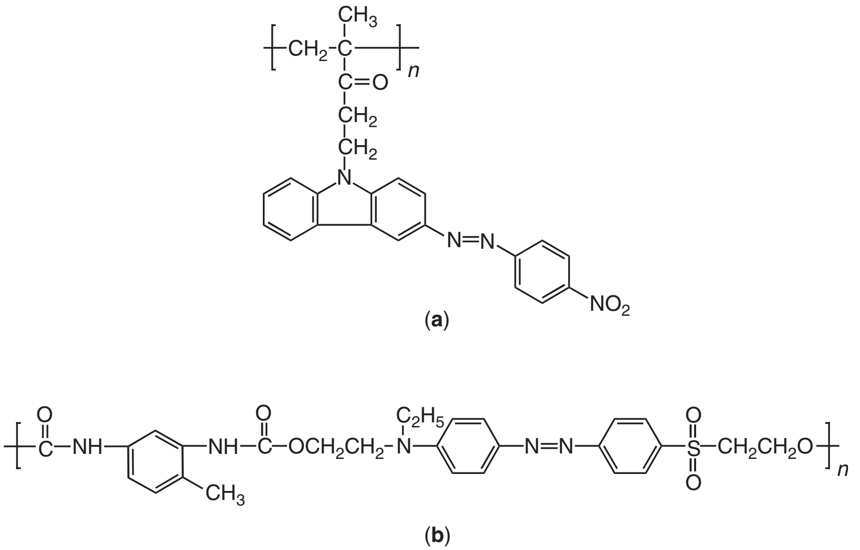

Figure 1.5. Examples of azo polymer structures, showing that both (**a**) side-chain and (**b**) main-chain architectures are possible.

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

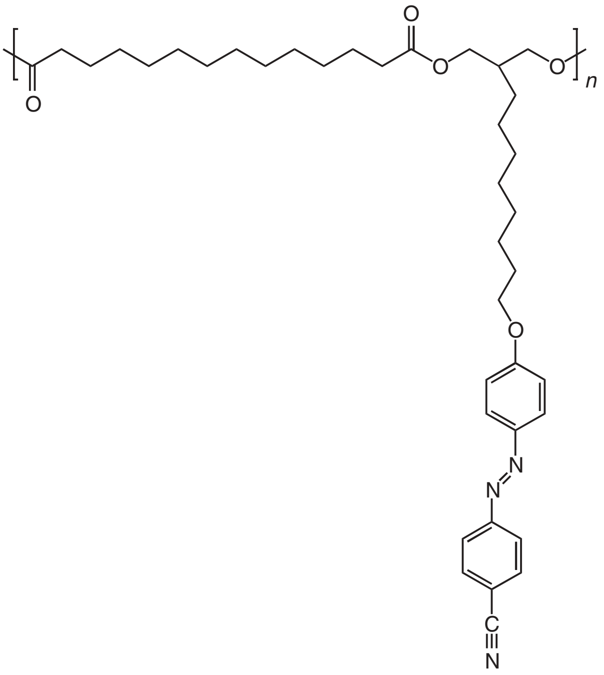

Figure 1.6. A typical liquid-crystalline side-chain azobenzene polymer.