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Reviews

Recent Developments in Aromatic Azo Polymers Research

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The photochemical and thermal cis-to-trans isomerization of aromatic azo groups covalently bonded within polymers and its practical consequences as well as some other recent applications are reviewed. The kinetics and mechanism of the isomerization of azo polymers are briefly presented, and then several recent developments in azo polymers research are discussed. They include liquid crystallinity, nonlinear optical properties, monolayer assemblies, and the light-induced birefringence and dichroism. Some of the phase transitions of liquid-crystalline azo polymers can be induced photochemically by the azo groups isomerization. Second-order optical nonlinearity can be obtained in polymers with donor- and acceptor-substituted azo groups. Using the Langmuir-Blodgett technique, azo polymer monolayers can be built and used as "command surfaces" of liquid-crystal films. The light-induced birefringence is a reorientation phenomenon which is a consequence of the trans-cis-trans isomerization. Future possible applications for a variety of practical devices, such as display devices, optical modulators, optical waveguides, holography, and reversible optical storage are mentioned.

I. Introduction

Azo polymers (azo-containing polymers) are polymers that have —N=N— (azo) groups within the polymer structure. According to the position of the —N=N— group, they can be broadly classified as main-chain and side-chain azo polymers. Depending on other functionalities of the polymer backbones, azo aromatic groups can be present in polymers such as polyesters, polyamides, polyureas, polysilicones, polycarbonates, polyphosphazenes, polysilanes, polysiloxanes, etc. The synthesis of some azo polymers as well as their applications were reviewed elsewhere.¹ The synthesis and structures of different azo polymers will be mentioned in this review when necessary.

Azo polymers are receiving increasing attention because of their special properties and their potential applications. The literature on azo polymers grows by an average of 10 articles per month. In particular, many studies have been done on the trans-cis isomerization of the —N=N— groups and the literature on isomerization of azo aromatic compounds in solution or in the solid state was reviewed recently by Rau.² Various azobenzene derivatives have been utilized as dopants for conventional polymers to form polymer composites and change the polymer properties. In this case, the effects are usually governed by the concentration of the azo dopants and the compatibility of the mixture. Recently, there has been an increase in interest about azo polymers which have the azo groups covalently bound within the polymers. The influence of

the polymer properties on the photochemical and thermal isomerization has been demonstrated by kinetic studies on different azo polymers and the rate of isomerization of the azo groups attached covalently to the polymers depends on the structural properties of polymer matrix.^{2,3}

Azo polymers can be liquid crystalline, have nonlinear optical properties, and show light-induced dichroism and birefringence. This review concentrates mainly on these special properties of the azo polymers. The conformational changes induced by photochemical trans-cis isomerization of the azo groups and their effects on polymer properties or polymer solution properties have been reviewed in 1989 by Kumar and Neckers.⁴ In the following, the trans-to-cis and cis-to-trans photochemical and thermal isomerizations of the azo polymers are briefly discussed. Then some of the effects of isomerization on polymer properties are presented. Potential applications of the azo polymers are also discussed.

II. Isomerization in Azo Polymers

It is well-known that the azo aromatic group can exist in two configurations, the trans or "E" form and the cis or "Z" form as illustrated in Figure 1. The trans form is generally more stable than the cis form. The energy difference between the ground state of the trans and cis isomers is about 50 kJ/mol in the case of azobenzene.² The cis-trans interconversion can be affected by light and heat. When exposed to light of a certain wavelength, the stable trans form can be photoisomerized to the cis form. Cis-to-trans isomerization can occur thermally or/and pho-

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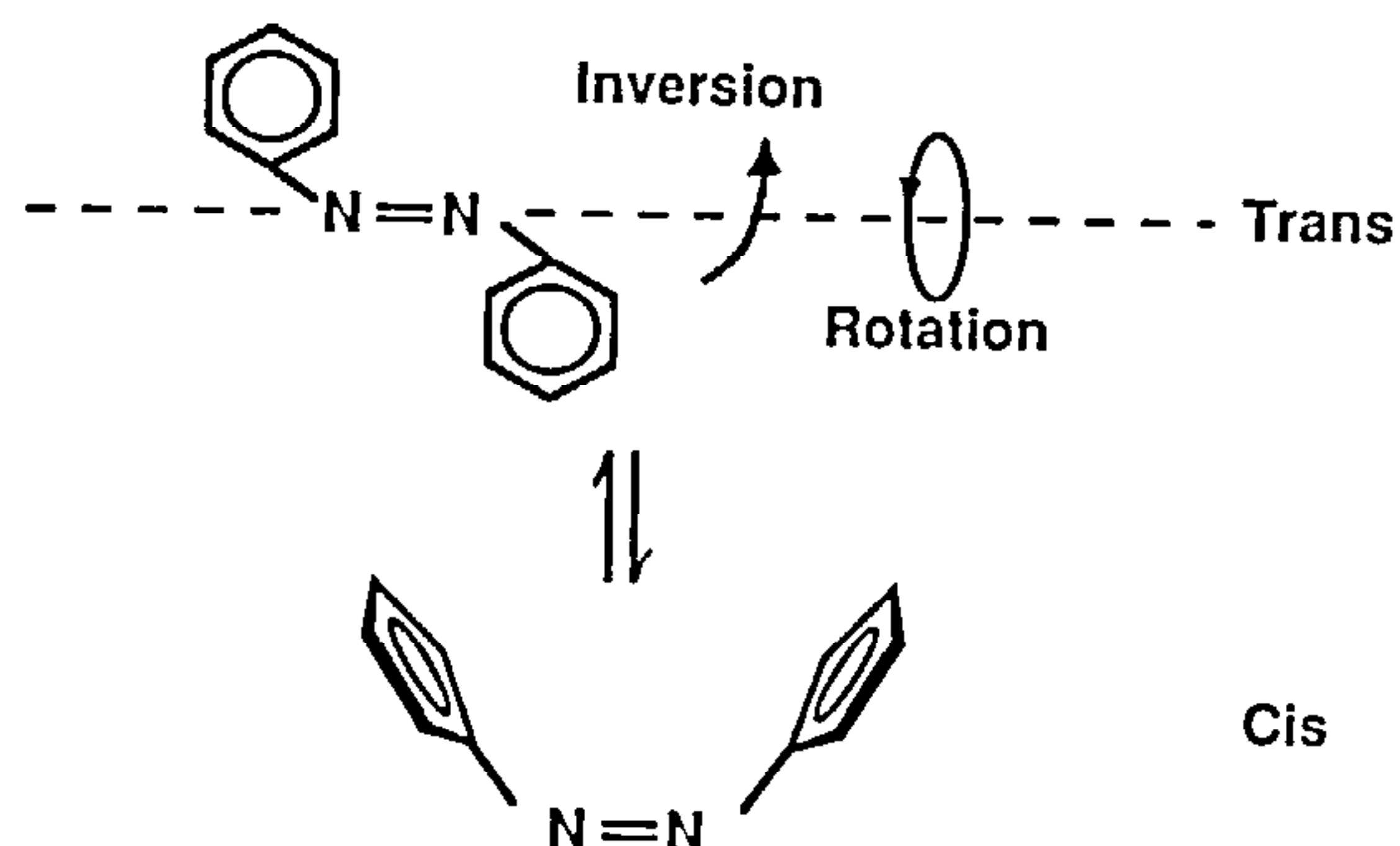


Figure 1. Trans-cis isomerization of azobenzene.

tochemically. This phenomenon was first studied with azo dye molecules in solution or dispersed in a variety of polymers, as recently reviewed.⁴ This subject continues to be investigated.⁵⁻⁹

Previous studies demonstrated that *cis*-azobenzene molecules obtained from the transformation of the planar *trans* form have globular geometry with the phenyl rings twisted perpendicular to the plane determined by C—N=N—C as shown in Figure 1.⁵ The distance between the 4 and 4' positions of the *trans*-azobenzene is 1.0 nm and the same distance is 0.56 nm for *cis*-azobenzene.² The dipole moment increases from 0.5 to 3.1 D from *trans* to *cis*. Azo aromatic molecules are characterized spectroscopically by $n-\pi^*$ and $\pi-\pi^*$ bands in the electronic spectra. The differences between the *cis* and *trans* isomers are revealed by the λ_{\max} of these absorbances. Thus, the *cis*-*trans* isomerization of some azo groups can be monitored by intensity changes in the electronic spectra.

The isomerization mechanism has been under investigation since the early 1950s.² It was first suggested that the azo aromatic groups isomerized by rotation about the —N=N— bond. An alternative mechanism was later proposed where isomerization occurred via the inversion of one or both of the nitrogens through a linear sp²-hybridized transition state in which the double bond was retained (Figure 1). It is generally accepted that the inversion mechanism is involved in the thermal isomerization of azo aromatic groups, and both mechanisms are possible in the photochemical isomerization process. The rotation vs inversion controversy is still not settled. It was suggested in earlier studies that an additional energy to rearrange the polymer conformation was involved during the isomerization process.^{10,11} Further experiments and calculations are being carried out in this area for a better understanding of the mechanism of the isomerization reaction.

It is generally recognized that almost any isomerization in polymers requires a minimum, critical size of local free volume in the vicinity of the chromophore. A free volume of 0.12 nm³ is estimated to be necessary for isomerization of azobenzene in polymers in the cases where inversion is the isomerization mechanism.^{9,10} Furthermore the quantum yield for the *trans* to *cis* isomerization depends on the size of the azo dyes, temperature, and other factors. Thus

photochemical and thermal isomerization of the azo dyes with different sizes are valuable in the study of the free volume and the morphology of the polymers.^{12,13}

The kinetics of thermal and photochemical isomerization of different kinds of azo compounds is well investigated. The results from small azo dye molecules dispersed in polymers and dissolved in solutions can be used as a comparison basis for the study of the azo polymers that have the azo groups covalently bound within the polymer structure.⁶⁻¹⁰

According to Rau,² azo compounds are classified into three classes based on the relative energetic order of their (n,π^*) and (π,π^*) states: molecules of the azobenzene type, molecules of the aminoazobenzene type, and molecules of pseudo-stilbenes type. The azobenzene type molecules are characterized spectroscopically by a low-intensity $n-\pi^*$ band in the visible region of the spectrum and a high-intensity $\pi-\pi^*$ band in the UV. With this type of molecule, it is possible to isolate the *cis* isomer because the *cis*-to-*trans* thermal isomerization is relatively slow. Aminoazobenzene type molecules are characterized spectroscopically by a close proximity of $n-\pi^*$ and $\pi-\pi^*$ bands, while pseudo-stilbene type molecules have a long wavelength $\pi-\pi^*$ band and the sequence of (n,π^*) and (π,π^*) states is reversed on the energy scale, which is similar to stilbene. Aminoazobenzene and pseudo-stilbene type molecules with the pull/push substituents isomerize back very quickly (of the order of several milliseconds) at room temperature. These important differences in the kinetics of *cis*-to-*trans* thermal isomerization of different azo groups are critical in the interpretation of the properties of the azo polymers and in the design of azo polymers. For example, two kinds of optical information storage can be envisaged using the azo polymers either with relatively stable *cis* isomers or with unstable *cis* isomers.

The kinetics of the isomerization reactions of an azobenzene or a derivative bound in the main chain or attached to the side chain of polymers have been extensively investigated since Paik and Morawetz^{10,11} and Eisenbach¹⁴ followed the photoinduced *trans*-to-*cis* isomerization and thermal *cis*-to-*trans* isomerization by UV-vis spectroscopy to extract the kinetic parameters in bulk as well as in dilute solutions. The isomerization of rubbery azo polymers exhibited a first-order rate constant similar to that of small azo compounds in dilute solution. In the glassy state, the photochemical *trans*-to-*cis* isomerization was found to be slower than in solution and a sufficiently flexible matrix was necessary for the isomerization reactions to take place.¹⁵ Two rates for the thermal *cis*-to-*trans* isomerization were found below the glass transition temperature.¹⁶ A portion of the azo groups reacted anomalously fast while the remainder proceeded with the normal first order rate. The fractional amount of the fast process increased slowly with temperature and exhibited a sudden increase around the glass transition temperature of the polymer. The two relaxation processes were further studied recently by Wiesner et al. using forced Rayleigh scattering with some liquid-crystalline side-chain azo

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polymers in the glassy state.¹⁷ The faster process was attributed mainly to the reorientation of the dye in contact with the glassy matrix. The slower process was attributed to the relaxation of the azobenzene back to its trans conformation.

These results led to the assumption that the isomerization with a relatively high activation energy, $E_a \sim 80$ kJ/mol did not take place in a single step as it did in solution. The overall activation energy E_a is the sum of activation energies of rotation of the dye and of the translation of the neighboring groups, i.e. the process is controlled by the nature of the neighboring groups and is sensitive to the environment around the azo groups, thus it is strongly influenced by the free volume.^{15,16} The minimum free volume of a sphere of 4.5 Å in radius (about 0.38 nm³) is estimated to be required for the isomerization of the azobenzene groups in a polymer, considering rotation as the dominant mechanism.¹⁶ (The calculation based on inversion as dominant mechanism showed a smaller volume as discussed before.)

New azo polymers including polymers containing aliphatic azo groups and cross-linked polymers were synthesized recently.¹⁸⁻²¹ The isomerization is found to be possible for both types of polymers but is significantly depressed when cross-linking is present.²⁰ The photochemical trans-cis isomerization and the thermal cis-trans isomerization of the azo groups have been studied under different microenvironments, such as in amphiphilic polyelectrolytes, in a nonpolar solvent and under hydrophobic microdomains.²¹

The kinetic studies of the trans-cis isomerization of the azo groups have provided information on the structure, morphology and segmental mobility of the azo polymers.⁴ For example, the azo labels on different sites of polymers were used as molecular probes to detect the free volume distribution and physical aging of the polymers.^{4,22-23} Further studies were carried out using other methods such as electrochemistry,²³⁻²⁶ where it was reported that the accuracy of the kinetic analysis could be greatly increased by the electrochemical identification of the cis isomers. In the electrochemical approach, the cis isomer was electrochemically reduced to a hydrazine compound (-NH-NH-) at substantially more anodic potential than the trans isomer, and the hydrazine compound produced was exclusively oxidized to the trans isomer.

III. Some Properties Resulting from Isomerization in Azo Polymers

Interest in the study of polymers containing azo aromatic groups increased because of their bright color and

high stability of the dye. Apart from the good mechanical and thermal properties and low flammability, which were established from the beginning,¹ azo polymers have many other special properties. Among these liquid-crystalline properties and/or nonlinear optical properties are gaining importance. As well, the trans-cis isomerization reactions are always accompanied by significant changes of polymer properties, such as the phase, conformation and optical properties. The photoinduced trans-cis isomerization of the azo groups leads to photochromism and optical dichroism. Most of the properties have been studied only recently and are receiving an increased interest due to their potential applications.

(1) **Liquid-Crystalline Azo Polymers: Photochemically Induced Phase Transitions.** Liquid crystallinity is a known property of some azo polymers. Liquid-crystalline (LC) polymers are an important area of research because of their highly anisotropic optical, electrical, and mechanical properties. They are a class of polymers which have been intensively investigated for more than a decade.^{27,28} Liquid crystallinity of a polymer generally requires rigid mesogenic groups and sufficient conformational freedom to allow the mesogenic units to form stacks or organized domains. The aromatic azo groups can be used to provide the mesogenic units. Liquid-crystalline polymers can then be prepared in two ways. First, the aromatic azo groups can be linked to a polymer chain through some flexible connector groups to give side-chain liquid-crystalline polymers. The polymer backbone could be simple hydrocarbons,²⁹⁻³⁷ esters,³⁸ amides,³⁹ phosphazenes,⁴⁰ etc. Examples of different kinds of side chain LC azo polymers are shown in Figure 2. Second, the aromatic azo groups can be bound into the backbone with some flexible spacers, in methylene units, for example, between the mesogenic units. This gives main-chain liquid crystalline polymers,⁴¹⁻⁴⁵ the most common of these found in the literature are polyesters, as shown in Figure 3. A variety of LC azo polymers with new architectures have been synthesized recently. One such example is a com-

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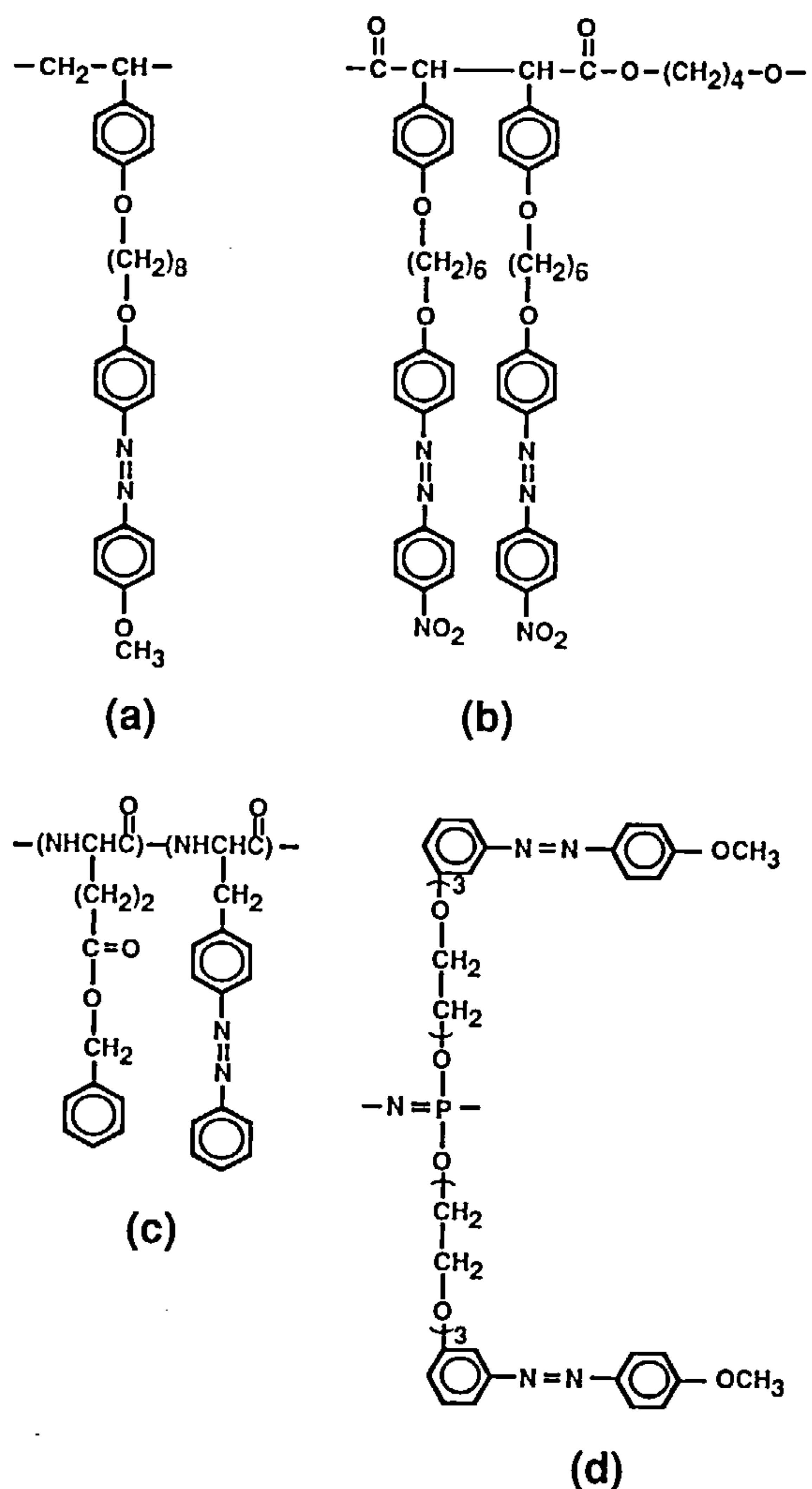


Figure 2. Side-chain LC azo polymers.^{35,58-60}

bined LC azo polymers, where azo groups and flexible spacers can be found both on the main chain and side chain.⁴⁶ LC polymers may have better mechanical properties and processability.⁴⁷ They can be used as passive optical elements, controlled optical and photooptical media, optical storage media, nonlinear optical media, etc.^{27,28,36}

The liquid-crystalline polymers containing azo aromatic mesogenic groups in the side chain or in the main chain offer the possibility to modify the order state by external fields and/or light. Photochemically induced isothermal phase transitions of some side chain liquid crystalline polymers were studied by Ikeda et al. using calorimetry, FT-IR dichroism, polarizing microscopy, etc.³⁰⁻³³ When a liquid-crystalline azo polymer sample is examined on a polarizing microscope equipped with a hot stage and irradiated with a linearly polarized laser beam, the nematic-to-isotropic phase transition can be successfully induced by the photoisomerization of the azo groups in the polymer. The reverse process, the cis-trans isomerization occurs in dark and restores the polymer to the initial nematic state. The thermodynamic data and order parameters were investigated for different polymer systems, such as homopolymers,^{31,32} copolymers,³⁰⁻³³ and azo-doped poly-

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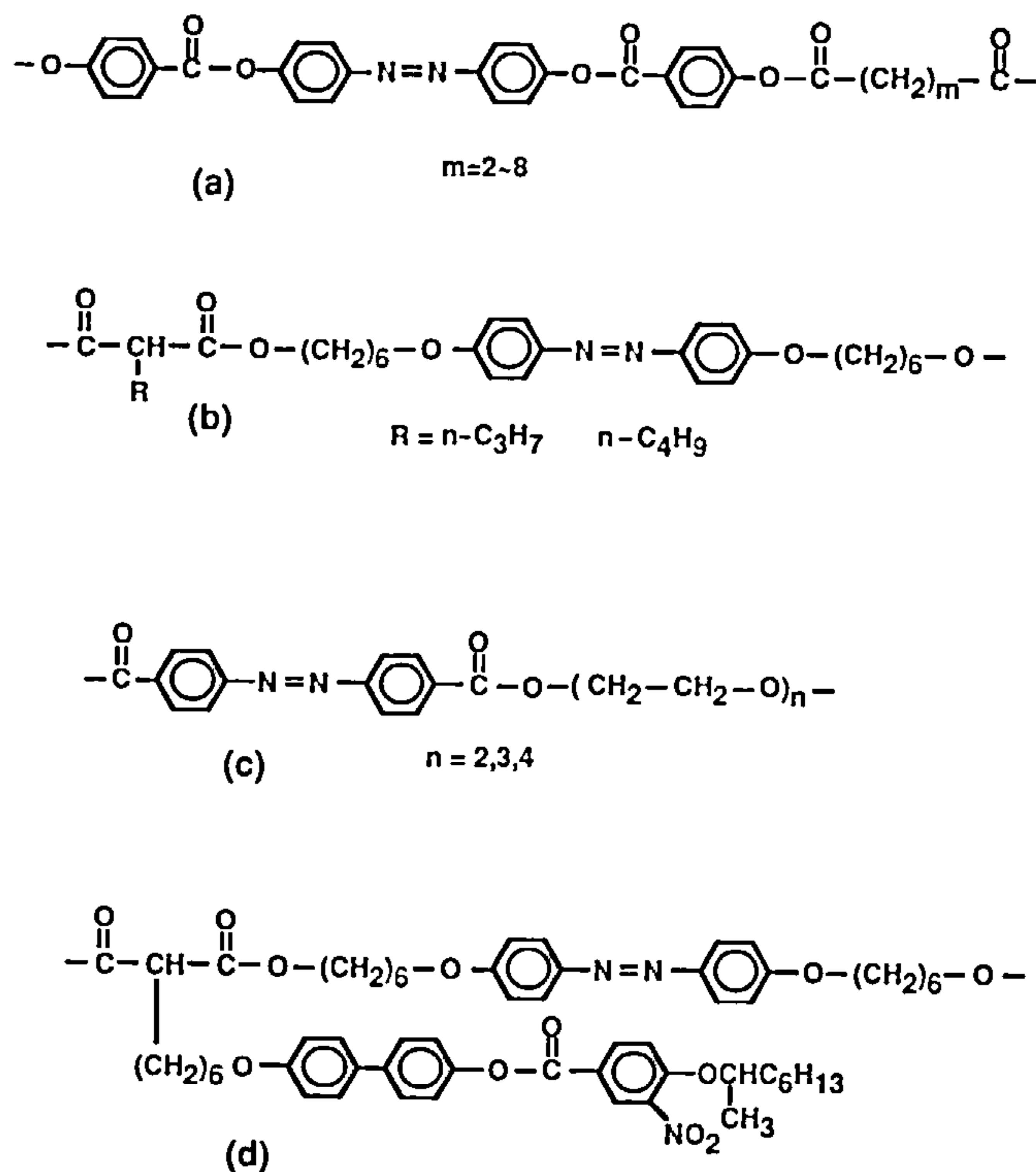


Figure 3. Main-chain LC azo polymers.^{41-43,46}

mers.^{31-33,48,49} The efficiency of the photochemically induced isothermal phase transition was found to be closely related to the orientational ordering of the initial polymer and the photoinduced nematic-to-isotropic isothermal phase transition took place more effectively in a system with a less ordered nematic state. The order depends on the spacer length between the main chain and the mesogenic group and on the molecular weight of the liquid-crystalline polymer.

The photochemical phase transition behavior could be understood when the different molecular shape of the cis and trans isomers is considered, as shown in Figure 1. The trans configuration of the azo aromatic group possesses a rodlike shape, while the cis configuration has a bent shape. The rod-shaped trans configurations are amenable to the formation of a liquid-crystalline phase. The cis isomer is formed during light exposure and these bent configurations act as impurities which disrupt the orientational order.⁵⁰

(2) **Nonlinear Optical Properties.** A variety of practical devices, including modulators, optical frequency doublers and switches, may be produced from materials which exhibit second-order nonlinear optical (NLO) properties.⁵¹ While both organic and inorganic crystals with good transparency and high nonlinear susceptibility have been developed, their practical applications may be limited due to the difficulties in processing them into the required physical forms. One solution to this problem is to include optically nonlinear organic chromophores into polymer structures. Azo polymers are suitable for this purpose.

In general, organic molecules bearing electron-donor and -acceptor groups separated by conjugation have been shown to possess large values of the second-order molecular hyperpolarizability. However, efficient nonlinear optical

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properties can be achieved only in materials having both a large second-order hyperpolarizability at the molecular level and a noncentrosymmetric bulk ordering. Oriented polymer systems provide an attractive possibility for NLO properties because of their processability, good optical properties, wide variety, and low cost. An example, the statistical centrosymmetry of the chromophores can be disrupted when the nonlinear optical chromophores bound in the polymers are poled in an electrical field.⁵¹

Nonlinear optical polymer materials may be subdivided into two systems depending on whether the nonlinear optical chromophores are covalently bonded to the polymer or are dissolved as guests in the host polymer matrix. The guest/host nonlinear optical polymer systems usually contain a low concentration of guests because of the limited solubility and have rather poor stability of the nonlinear coefficients owing to thermal relaxation of the alignment of the guest in the processed polymer material. Stupp et al. discussed the increase of the second harmonic signal and the thermal stability using polymers with nematogenic backbones as a solvent for azo dye solutes by magnetically induced order.⁵² However, a better arrangement is to connect the optically active NLO species covalently to or within the polymer backbone.

Using azo aromatic groups to provide the long conjugation between the donor and acceptor groups, both main-chain^{50,51,53,54} and side chain polymers⁵⁴⁻⁷⁵ have been synthesized and their NLO properties have been tested. Examples of NLO azo polymers are shown in Figure 4. Different polymers with a variety of polymer backbones, such as polyesters,⁵³ polyacrylates,^{56,57,63} polyphosphazenes,⁵¹ polysilanes,⁷⁴ and polysiloxanes⁷⁵ have been synthesized and investigated.

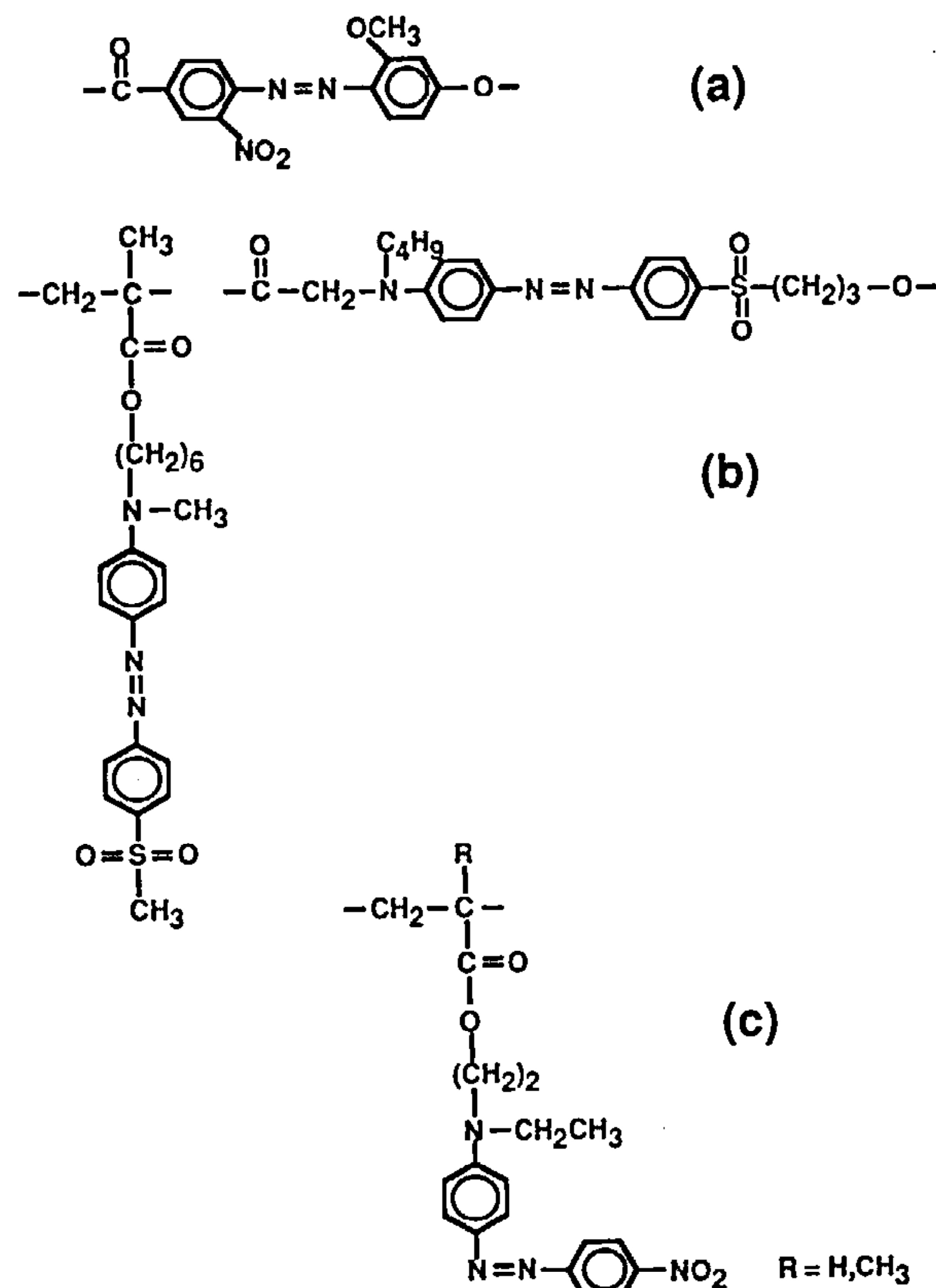


Figure 4. NLO azo polymers.^{53,55,57}

In most cases, the electron donor groups are amines ($-N-$) or oxygen ($-O-$). The acceptor groups are cyano ($-CN$), nitro ($-NO_2$), or sulfone ($-SO_2-$). It is known from theoretical and experimental considerations that extended conjugation between the donor and acceptor enhances the nonlinear optical properties. However, complications such as insolubility, instability, or the inability to process the polymer can be created by adding conjugating units to the chromophore in order to further separate the donor and acceptor groups.⁵³ Liquid-crystalline properties can be obtained by changing the flexibility around the azo aromatic mesogenic groups. It was reported that NLO polymers with six methylene units between the main chain and the azo aromatic mesogenic side chain displayed LC properties.^{56,62,70} By using some copolymers with different concentrations of azo nonmesogenic structural units and mesogenic structural units, it has been shown that liquid crystallinity enhanced the nonlinear optical properties upon poling under similar conditions.⁷⁰ Liquid-crystalline polymers are interesting for nonlinear optical device materials because of the easier poling process and better results.

The optical nonlinearities of the polymers are induced by poling, a process of applying an electric field at the temperature above the glass transition of the polymer. After a few minutes, the polar groups of the nonlinear optical material are aligned under external electrical fields because of their dipole moments. The polymer is cooled below the glass transition temperature with the electric field on. The electrical field can then be removed, and the second-order nonlinear optical properties of the polymer are achieved. Below the glass transition temperature of the polymer, the segmental motion of the polymer chains is frozen in, and thus the orientation of the azo groups can be kept stable for a long period of time. In an alternative processing method, carbon dioxide has

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been used in amorphous polymer films during the poling process. By using a supercritical CO₂ polymer solution, the glass transition temperature of the solution is depressed below room temperature. It is then possible to align the chromophore in an applied electric field with ambient temperature processing. After poling, with the electric field on, the CO₂ is removed thus freezing the orientation.⁷⁶

Investigations on second-order nonlinear optical polymers containing azo chromophores revealed that the electrooptical figure of merit could exceed that of LiNbO₃.⁷⁷ Already these materials are promising for practical applications. It was reported that using a poling field strength of 20 V/μm, poly{2-[(4-((4-nitrophenyl)azo)phenyl)ethylamino]ethyl acrylate} (PDR1A) (Figure 4c) achieved an electrooptic coefficient (r_{33}) of about 3 pm/V which is comparable with other nonlinear optical materials.⁵⁷

High chromophore density will favor the increase of the nonlinear optical susceptibility, but the high probability of aggregation, caused by the strong polarity of the chromophore, requires longer poling time and higher poling temperatures.⁵⁸ The liquid-crystalline properties of some azo polymers enhance the efficiency of the dipole moment reorientation upon poling. This means that the overall poling time and the applied voltage can be reduced for liquid-crystalline polymers.

The relaxation of electric-field-induced orientation is a problem in azo polymers for NLO applications. It was found that the relaxation of a side-chain azo polymer occurs through local reorientation of the chromophores. For main-chain azo polymers, both a local orientation and the reorientation of the end-to-end vectors of the chains could be detected.^{59,60} The stability of the poled sample can be improved by cross-linking between the chains since cross-links between the polymer chains further restrict the molecular motion of the segments and hence prevent the reorientation of the ordered NLO molecules. In addition, the cross-linked system is expected to possess enhanced thermal stability due to the network structure. This approach was first reported by Eich et al.⁷⁸ However, the cross-linked polymers are not as easily processed under an electric field. Thermosetting or photo-cross-linkable polymer systems which can be poled first and then cross-linked may be a solution for this problem.⁶³⁻⁶⁷

Azo aromatic groups in polymers can be reoriented by polarized light, which will be discussed in detail in the following chapter. Poling can then be done by photochemically reorienting the molecules in the presence of an electric field without heating above T_g of the polymers.⁷⁹ The orientational order obtained is stable below T_g .

Polar orientation of the azo polymers can also be achieved by Langmuir-Blodgett procedures, in which monomolecular layers at the air-water interface are mechanically transferred to a solid substrate.^{80,81} This technique allows the chromophore to align without a poling

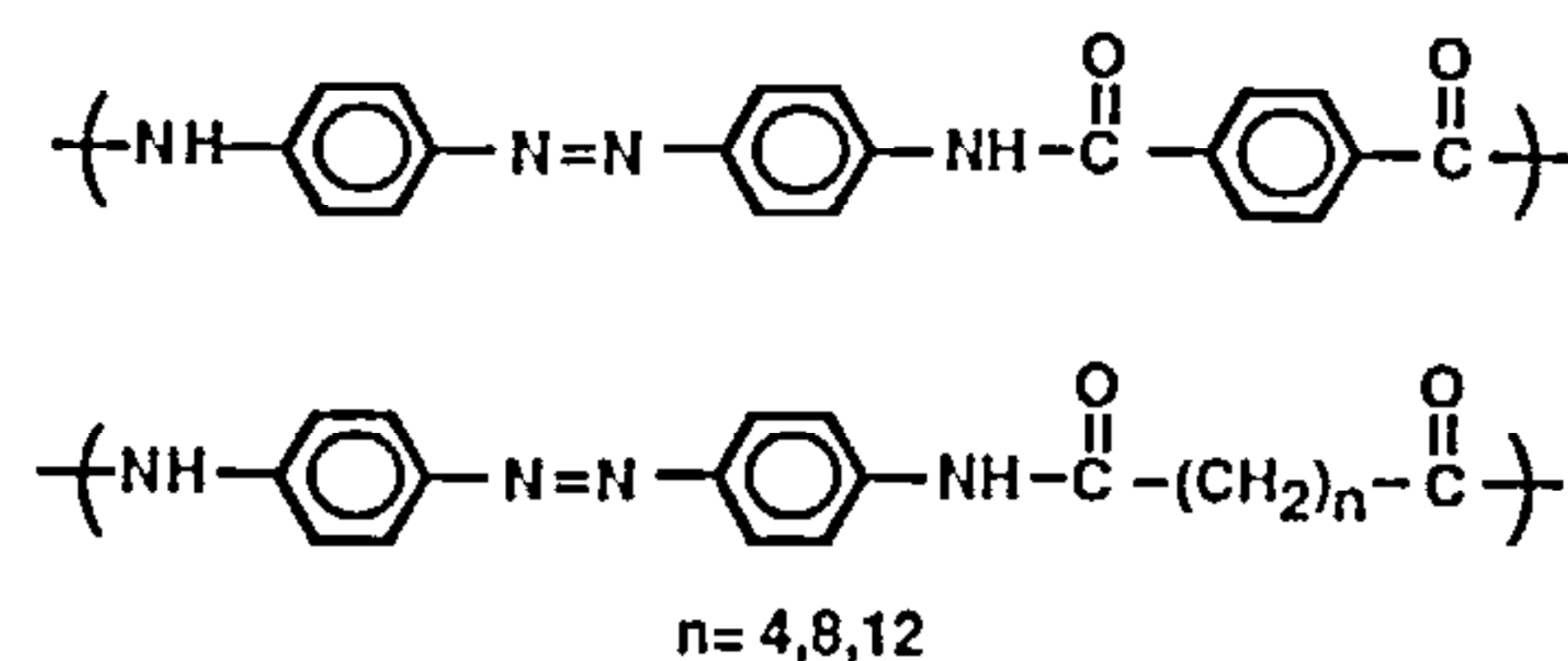


Figure 5. Main-chain azo polyamide.⁴

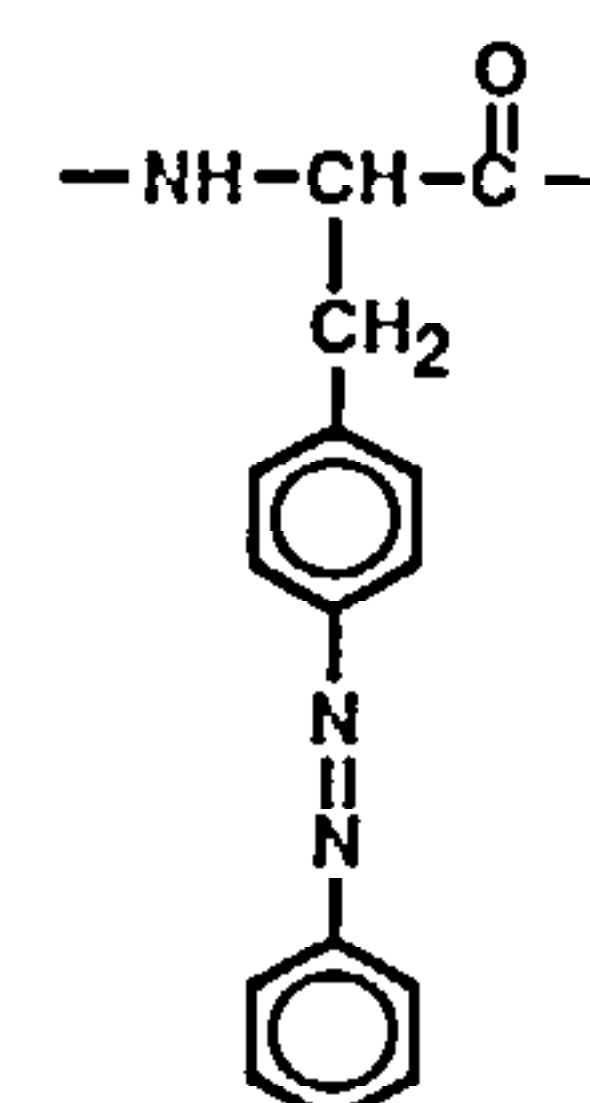


Figure 6. Side-chain azo polyamide.⁸³

process. The multilayered film of copolymer of PMMA-co-DR1A obtained by horizontal deposition showed a large second-order susceptibility, 9.8 pm/V.⁸¹ As well, the stability of the polar structure can be enhanced by the irreversible chemisorption of molecules from homogeneous solutions. There is a continuing interest in developing the LB method and exploring its utility for making practical materials for nonlinear optics.⁶⁰

(3) Photocontrolled Reversible Property Changes: Azo Polymers with Relatively Stable Cis Isomers. The photochemistry of the azo groups plays an important role in controlling the properties of azo polymers. Cis isomers of azo aromatic groups without amino or push-pull substituents have relatively good thermal stability.² For polymers with stable cis azo groups, the light energy can be stored as a chemical structure change of the chromophore. Because of the differences in the structure and properties of the cis and trans isomers of the azo groups, the polymer properties can be changed by the isomerization.

Most of the studies on conformational changes involve optically active polymers, for example, azo-containing polypeptides or polyamides which are shown in Figures 5 and 6.^{4,82-85} The conformation change upon irradiation with light is attributed to the interaction between the azo chromophore and the optically active centers in the polypeptides main chain. Concurrent with conformational changes are changes of various polymer physical properties as well as polymer solution properties, such as intrinsic viscosity,^{4,86} solubility,^{4,87,88} mechanical properties,⁸⁹ bioactivity,⁹⁰ and refractive index.⁹¹ These effects of trans-cis isomerization were discussed by Rabek and reviewed

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by Kumar and Neckers.^{3,4} They were useful in the control of polymer properties, regulation of life processes of plants and other biological processes. The photocontrol of surface wettability, adsorption, pH, conductivity, membrane properties, and equilibria has received much attention and is finding practical applications.^{4,18,92}

The Langmuir-Blodgett-Kuhn (LBK or LB) technique has been used recently to study azo polymers with thermally stable cis isomers.⁹³⁻¹¹¹ It is one of the most powerful tools for the construction of organic thin films in which the molecules are assembled properly. Studies of LB films of azo polymers provide information on the structure of photoisomerization at the molecular level. Polymers containing amphiphilic side groups are found to form stable monolayers at the air-water interface and bilayer membranes in aqueous media. These monolayers have been used to monitor formation of polyion complex, promote structural change of a thin film by cis-trans isomerization, provide an electrical field source in the LB film, and indicate molecular miscibility in mixed monolayers.¹¹¹

Photochemical transformation of molecules could induce a drastic structure change of the neighboring organized molecular system. Ichimura et al. treated the surface of some liquid crystals using side-chain azo polymer monolayer.⁹³⁻¹⁰⁰ The LC cell is constructed by setting the liquid crystals between two glass plate substrates. The surface of the glass substrate is modified by silylation with reagents having photochromic units or by spin coating or deposition of an LB membrane of azo polymers.⁹⁷⁻¹⁰⁰ They found that the liquid-crystal alignment changes were governed by the photoisomerization of the azobenzene groups as shown in Figure 7. The trans-to-cis isomerization of the azo groups occurs upon exposure to UV light, and the cis-to-trans isomerization is induced by visible light. Induction and modulation of the LC molecular alignment axis have been performed by using linearly polarized UV

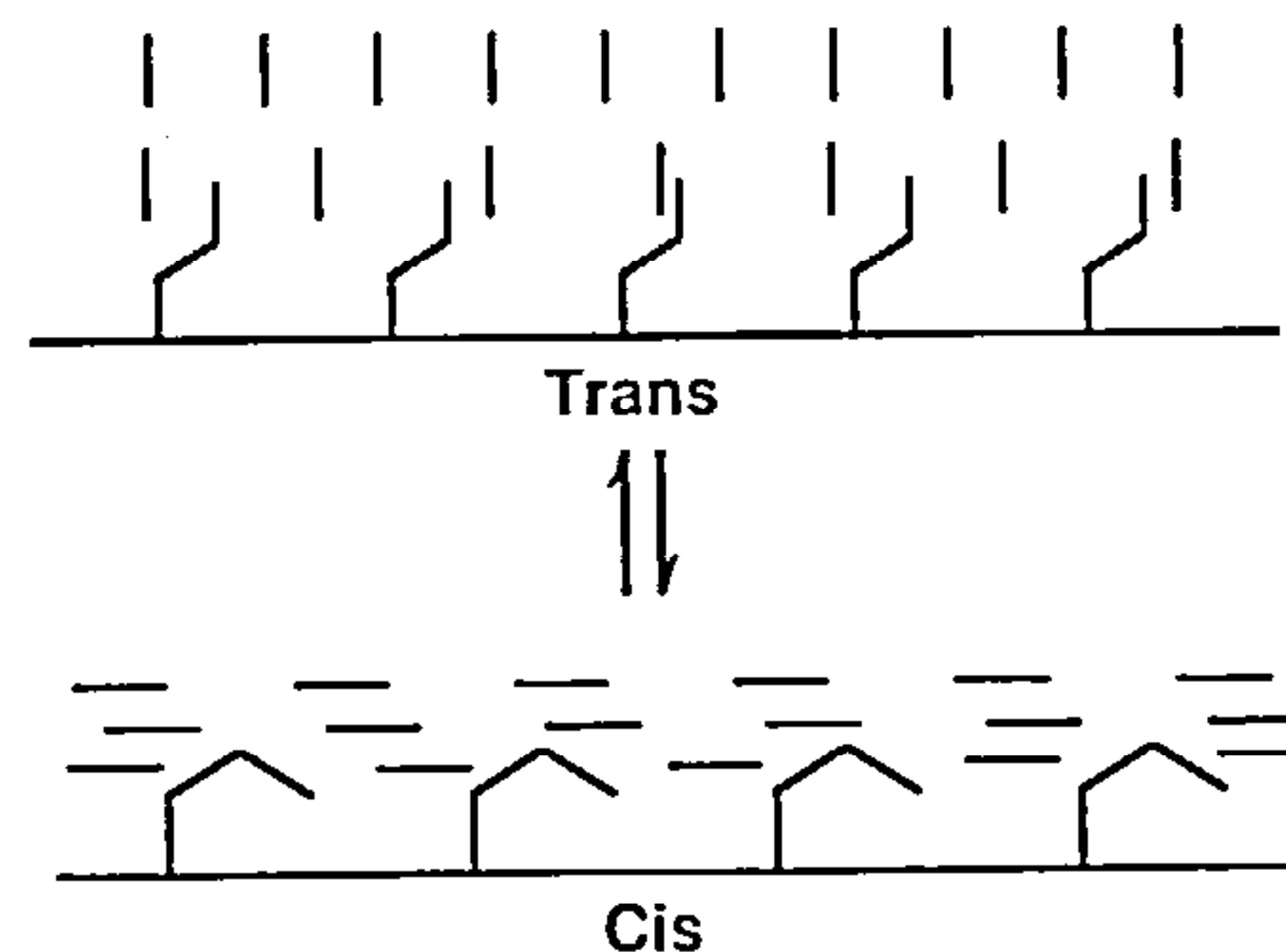


Figure 7. Reversible changes of LC alignment induced by photoisomerization of side chain azo polymers.⁹⁴⁻¹⁰⁰

light.⁹⁷ The fact that two azobenzene units bring about 15 000 LC molecules to change the alignment can be used as an effective amplification of optical information. The surfaces modified with azo polymer monolayers have been referred to as "command surfaces" and have been investigated from a practical point of view for constructing LC display and recording devices.

The efficiency of the "command surfaces" is crucially affected by various factors including the molecular structure of the azobenzene moiety, the occupied area per azo group on substrate surface, cell thickness, and the number of repeating cycles.^{99,100} This phenomenon is related to the cooperative motion of the azo group and neighboring liquid-crystal molecules. Further knowledge of the orienting mechanisms on a molecular level at the LC/photochromic layer interface is necessary in order to characterize the phenomenon.

Knoll et al. demonstrated the use of LB films of azo side-chain LC polymers in reversible optical data storage.¹⁰¹⁻¹⁰⁴ Writing is done through trans-to-cis isomerization and the optical information is being stored as refractive index changes when cis isomers predominate. By illumination with visible light, the LB films could be transformed from isotropic to uniaxial structures that exhibited dichroism and birefringence of $\Delta n = 0.21$.¹¹⁰ The cis isomers are stable for more than 3 months and the lateral resolution is better than 4 μm .

It is noteworthy that the reversible photoisomerization of azobenzene derivatives can be restricted in the case of pure LB films.¹⁰⁸⁻¹¹⁰ Copolymers with only a certain percentage of azo side groups are used in most cases. The irreversible isomerization occurring in homopolymers is attributed to the high energy of repacking the molecules in the monolayers.

(4) Optically Induced and Erased Birefringence and Dichroism. The research on optical storage systems has become a subject of extensive scientific and industrial interest. Polymers with high optical sensitivity, high storage densities, short switching and access time, reversibility, and high signal-to-noise ratio after many write-erase cycles are being developed for use as optical recording media. Azo polymers were found to be such materials. These could be used in erasable optical memory disks and tapes, as erasable holographic information storage materials, and as optical sensors usable over a wide range of temperatures.

The possibility of using a polymer system containing an azo molecule as optical recording medium was first suggested in 1983 with azo dyes (methyl red and methyl orange) dispersed into a polymer matrix (poly(vinyl

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alcohol)).^{112,113} When the polymer system is irradiated with a linearly polarized laser beam with a wavelength of 488 nm (close to the maximum of the absorbance of the azo dye), the optical transmission for light polarized along the polarization direction of the writing light increases and that for light perpendicular to the direction of the writing light decreases.¹¹² Optical dichroism as well as birefringence is induced. However, the photoinduced optical anisotropy can only be maintained for a short time even when the material is stored in the dark.

Since Wendorff demonstrated reversible optical storage properties on some liquid-crystalline azo polymer films in 1987,¹¹⁴ there has been a lot of interest in this area.¹¹⁵⁻¹²³ It was reported that optical anisotropy can be achieved by irradiation with a linearly polarized laser beam. The isomerization of the azo group affects the liquid-crystal orientation, giving rise to a reorientation of the mesogenic groups. The orientational order is proven using spectroscopic methods.

A homopolymer containing a *p*-nitroazobenzene bound as side chain in a polyester through an oxygen atom and a spacer of six methylene units was used in the earlier studies (Figure 2a).¹¹⁴ Other examples of LC azo polymers were polyacrylates containing the same azo side groups as shown in Figure 2b. The spacer provides the flexibility and allows the mesogenic azo aromatic groups to move about for reorientation and to form the liquid-crystalline phase. Liquid-crystal copolymers with both photosensitive and nonphotosensitive side groups were also used in these studies. The writing procedure consists of a first step of orientation of the liquid-crystalline film by an external field, followed by irradiation with the polarized laser light in the liquid crystalline state or in the glassy state. It was shown that the optical axis of the preoriented liquid-crystalline polymer changes to be perpendicular to the polarization direction of the irradiating laser light.

The study on some copolymers containing azo groups and other mesogenic groups showed that reorientation of the azobenzene moieties actually affects the neighboring nonphotosensitive mesogenic groups either below or above the glass transition temperature.^{117,123} This is due to the cooperative motion of the neighboring groups. The reorientation of the liquid-crystalline non-chromophores can be achieved by laser irradiation in the fluid nematic state of the copolymers or by rubbing the surface with a nylon cloth.^{124,125} However, it was also reported that the

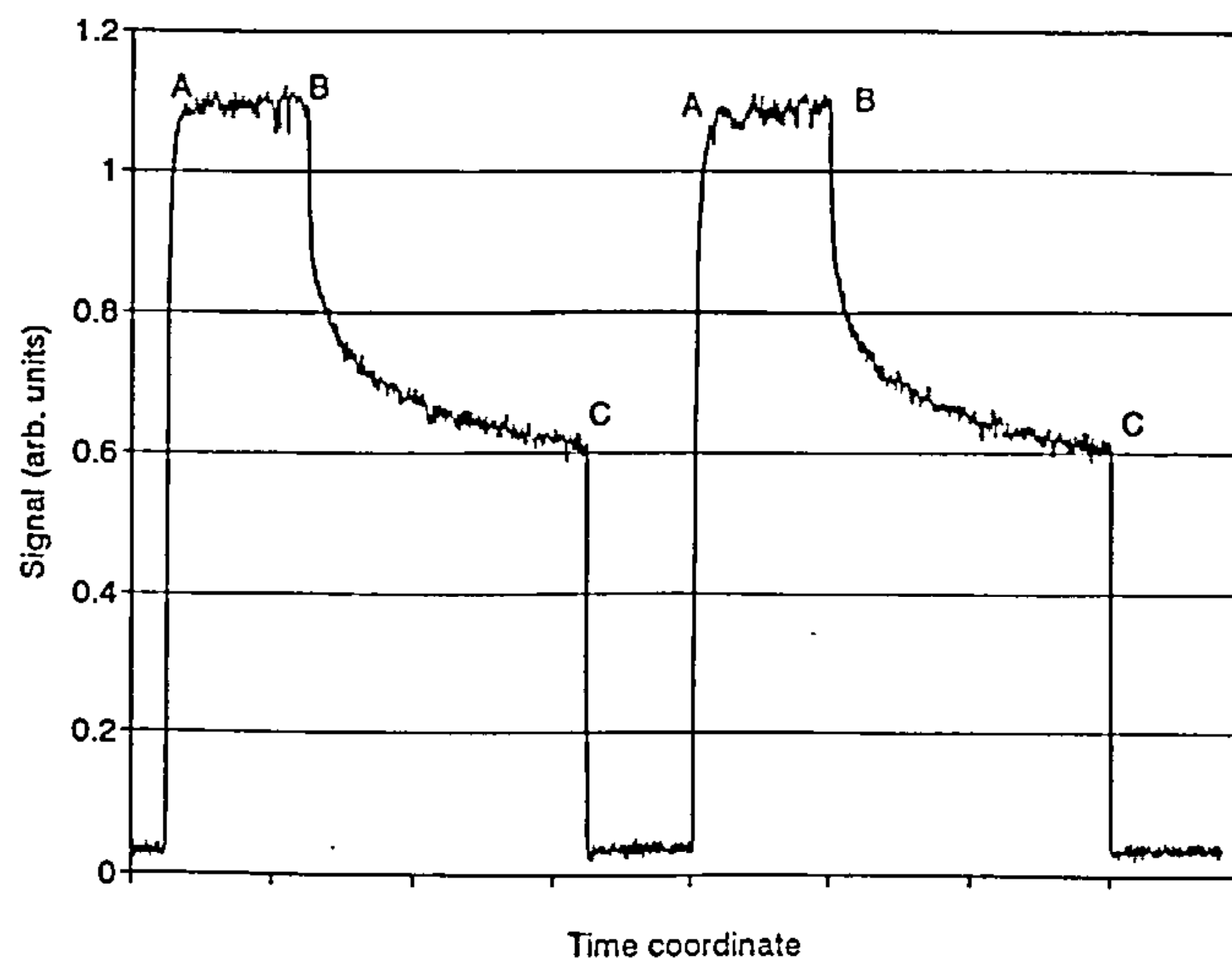


Figure 8. Writing and erasing sequence on an amorphous azo polymer: (A) Writing beam on; (B) Writing beam off; (C) Erasing beam on.

reorientation of the azobenzene moieties did not influence the neighboring groups when the film was below its T_g . This phenomenon was called molecular addressing.¹¹⁷ The experimental evidence in a few recent papers suggests that reorientation may occur below T_g as well.¹²³⁻¹²⁶

All these liquid-crystalline azo polymers have glass transition temperatures slightly higher than room temperature because of the requirement of flexibility. In principle, the higher the glass transition temperature of the polymer, the greater the stability of the writing at room temperature when this is well below the glass transition temperature.^{127,128} This can be clearly seen by performing the orientation experiment at different temperatures for a series of polymers with different glass transition temperatures.¹²⁶

Some amorphous azo polymers with high glass transition temperatures have been synthesized and tested recently for reversible optical storage processes.¹²⁷⁻¹²⁹ High glass transition temperatures are obtained by using very short or no spacers between the main chain and the azo side groups. This results in a significant increase in the stability of the written material. It has thus been proven that liquid crystallinity is not a necessary condition for a material to exhibit reversible optical storage properties. The writing using polarized laser light with wavelength of the absorbance of the azo group can be performed at room temperature in the glassy state. The birefringence can be monitored by a light beam whose wavelength is out of the region of absorbance of the azo polymer. The written information can be erased either by heating the polymer above its glass transition temperature or by irradiating with circularly polarized light. Figure 8 shows a typical writing-erasing sequence obtained by measuring the birefringence-induced transmission of a sample placed between crossed polarizers.¹²⁹ The time required to reach saturation depends on a few factors, such as sample

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thickness and type of the azo groups. The fastest time was about 10 ms in our laboratory.

It should be noted that a higher birefringence was generated in some cases when writing on crystalline azo-containing polymers.^{65,66,110} This happens probably because the nonphotoactive mesogens undergo a reorientation in concert with the azo mesogens.^{110,130} The cooperative effect is strongly influenced by the packing of the mesogens. On the other hand, the time for the storage process increases significantly because the cooperative motion is much slower than the photochemically activated reorientation of the azo groups.

The laser-induced optical birefringence and dichroism is a result of induced molecular reorientation. The mechanism postulated for the laser-induced reorientation phenomena is related to the trans-cis-trans isomerization processes of the azo groups in the polymers. Different azo polymer systems have been used to investigate the mechanism.^{117,128} Subjecting the azo group to light of wavelength close to its own absorbance induces the trans to cis isomerization of the group. The azo group will be inert to photochemical excitation by the laser beam if its orientation is perpendicular to the polarization direction, because the trans-to-cis photochemical transition rate can be described by a $I \cos^2(\phi)$ term, in which I is proportional to the laser beam intensity and ϕ is the angle between the azobenzene orientation and the laser polarization direction.¹²⁸ With a polarized laser beam, the groups parallel to the polarization direction of the light beam have the highest isomerization probability. The thermally excited cis-to-trans isomerization is spontaneous, and the resulted trans azo group may fall in any direction. But those groups with a component parallel to the polarization direction of the incoming light will be continuously subjected to this trans-cis-trans isomerization process while those azo groups which fall perpendicular to the laser polarization direction at the end of one of the cis-trans isomerization processes, will remain in this position, because they cannot be reactivated when $\cos^2(\phi) = 0$. The final state of the material is the state with an excess of azo groups perpendicular to the direction of the laser polarization.¹²⁷ Using circularly polarized light, the orientational order is destroyed because of the random trans-cis-trans isomerization.

This phenomenon of photoinduced birefringence in azo polymers has been investigated in applications such as polarization holography, birefringence diffraction grating, and opto-optic switching.^{68,110,112,113} Dalton et al. reported a large photoinduced birefringence in a polyester con-

taining disperse red 19 bound on the side chain.^{68,69} They explained it as the relaxation of the excited state of trans isomer to the ground state of the cis isomer. This is the only case mentioned in the literature of a relatively stable cis isomer of the pseudo-stilbene type with pull-push substituted azobenzene.² The authors claimed that the cis isomer was formed and prevented from isomerization to trans by a high degree of cross-linking. Various applications were discussed, such as fabrication of channelized wave guides and other integrated optical components. One can control the direction of optic axis by changing the write beam polarization direction, the amount of birefringence by changing the write beam energy dose, etc. It should be noted however that the presence of the cis isomer is not necessary for forming channel wave guides.⁷⁹

The writing-erasing can be performed reversibly for many times without substantial changes. In the case of prolonged writing with a high-energy laser beam, bleaching of the sample has been noted. This is possibly the result of an increased number of azo groups being oriented along the propagation direction of the beam (i.e., perpendicular to the film surface). These groups no longer participate in the absorption of light. This bleaching effect can be removed by heating the sample above T_g and restoring the randomness of orientation. Thus this is a reversible fading. Irreversible fading is more complicated, and it appears to be dependent on the total energy absorbed at a particular spot.^{129,130} Previous studies revealed that the photofading rate is inversely related to the rate of the thermal cis-trans reaction.⁶ The chemistry of photofading reaction of azo dyes in polymers was reviewed by Griffiths.¹³²

IV. Conclusions

Since the discovery of the azo dyes in 1863, a wide variety of properties has been found. In recent years, a number of new applications of azo dyes were developed, extending their use beyond that of coloring agents. In conjunction with different polymers, more and more properties have been studied for practical applications as discussed in this review. The combination of many special properties of azo polymers offers the possibility for multi functionalization of the material and the possibility of practical use in electro optics and image recording.

Azo polymers described in this review represent a new field of specialty polymers. It is hoped that future research will help bring closer together theoretical studies and practical uses.

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