

Review

Incorporation of Azobenzene in Polymers: Photo switchable Architectures, Synthetic Strategies, and Emerging Applications

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Abstract:

Azobenzene and its derivatives represent one of the most intensively studied classes of photo responsive molecules, primarily because of their clean, reversible photoisomerization between the thermally stable trans (E) and the metastable cis (Z) configurations. When grafted onto or integrated within polymer matrices whether as pendant side groups, main-chain segments, or crosslinking nodes these molecules impart light-responsiveness to macroscopic materials in ways that purely synthetic analogs rarely achieve. This review consolidates current understanding of the chemistry underlying azobenzene incorporation into polymers, examines the structural diversity of the resulting materials, and surveys the broad spectrum of applications that have emerged over the past two decades, including photoresponsive liquid-crystal networks, drug-delivery platforms, optical data storage, soft actuators, surface-relief gratings, and stimuli-responsive coatings. Challenges still facing the field — such as fatigue resistance, wavelength tunability, and process ability are critically assessed, and an outlook on future directions is offered.

Keywords: azobenzene; photoisomerization; stimuli-responsive polymers; liquid crystal elastomers; photo actuation; side-chain polymers; trans–cis isomerism; smart materials

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Introduction:

The quest for materials that can change their properties on demand — responding to heat, electricity, pH, or light — has been a defining theme of polymer science over the past three decades. Among the available stimuli, light occupies a uniquely attractive position: it can be delivered remotely, with exceptional spatial and temporal precision, at intensities that do not mechanically disturb delicate specimens, and across a wide wavelength range that can be matched to specific chromophoric transitions. Azobenzene, the simplest diaryl diazene, emerged early as the photochromic

unit of choice for building light-responsive polymeric systems, and that standing has not been seriously challenged since. The photochemistry of azobenzene has been studied since Hartley first reported the photoisomerization of the molecule in 1937.[1] The trans isomer is planar, aromatic-conjugation stabilized, and roughly 0.9 kcal mol⁻¹ more stable than the cis form. Irradiation with UV light around 320–365 nm triggers conversion to the bent cis isomer, which reverts to the trans form either thermally or photochemically upon visible (430–530 nm) irradiation. The geometric change is dramatic: the distance between the para carbons of

the two phenyl rings contracts from approximately 9.0 Å in the trans state to around 5.5 Å in the cis state.[2] This molecular-scale actuation becomes macroscopically useful only when azobenzene units are embedded in a polymer that can transduce the individual conformational events into a collective mechanical or optical response. The earliest polymer-azobenzene conjugates were largely exploratory — azo dyes incorporated into poly(methyl methacrylate) hosts for non-linear optical applications and holographic recording[3] Over time, the field diversified enormously. Today one encounters azobenzene-decorated dendrimers, hyperbranched architectures, polyelectrolytes, block copolymers that self-assemble into photoresponsive nanoscale domains, supramolecular networks held together by reversible hydrogen bonds, and crosslinked liquid crystal elastomers that bend, twist, or oscillate under steady light. Each architecture embodies a different strategy for harnessing the same fundamental photochemical event. The purpose of the present review is therefore not to catalogue every azobenzene-polymer system that has ever been synthesized several excellent treatments already exist for that purpose [4,5,6] but rather to illuminate the design principles that govern how azobenzene units are incorporated, how the architecture of the host polymer shapes the photophysical and mechanical response, and where the most compelling application spaces currently lie. Section 2 addresses the photochemistry of azobenzene and its derivatives. Section 3 surveys synthetic strategies for incorporation. Sections 4 through 7 cover structural architectures and their specific properties. Section 8 reviews applications, and Section 9 offers a critical perspective on remaining challenges and future opportunities.

2. Photochemistry of Azobenzene: Fundamentals and Substituent Effects

2.1. The trans–cis Photoisomerization

Azobenzene exhibits two well-resolved absorption bands: the intense $\pi \rightarrow \pi^*$ transition near 330 nm and the much weaker $n \rightarrow \pi^*$ band around 450 nm. The relative oscillator strengths of these two transitions change markedly on going from trans to cis, a diagnostic feature that is routinely used to monitor the isomeric composition of solutions and films by UV–Vis spectroscopy. The quantum yield for

trans→cis photoisomerization is typically 0.10–0.25, while the reverse process has a somewhat higher quantum yield of 0.40–0.60 when driven photochemically.[7] The mechanism of photoisomerization has been a matter of active debate. Two limiting pathways — in-plane rotation about the C–N=N bond and inversion through a planar transition state — have both found experimental and computational support.[8] Modern ultrafast spectroscopic studies suggest that the S1 state relaxes on a sub-picosecond timescale and that both pathways may be operative simultaneously depending on excitation wavelength and the degree of steric congestion around the azo group. From a polymer design standpoint, the mechanistic subtleties matter less than the macroscopic outcome: a large, fast, reversible change in molecular geometry that is robust to thousands of switching cycles under mild conditions. 2.2. Tuning Photoswitching Behaviour Through Chemical Substitution The three conventional sub-classes of azo compounds — azobenzenes, aminoazobenzenes, and pseudo-stilbenes — differ primarily in the position of their $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands and in the thermal half-life of the cis isomer.[9] Parent azobenzene has a cis half-life on the order of hours to days at room temperature. Push-pull systems bearing electron-donating groups (e.g., amino, alkoxy) at the 4-position and electron-withdrawing groups (e.g., nitro, cyano) at the 4'-position — the so-called pseudo-stilbenes — exhibit greatly accelerated thermal relaxation (half-lives of seconds to minutes), which limits their usefulness for applications requiring a stable switched state but makes them attractive for actuation cycles that need to be rapid. A particularly important recent development has been the design of ortho-fluorinated azobenzenes, where steric interactions between fluorine atoms at the 2,2',6,6'-positions enforce a perpendicular geometry on the cis form, dramatically extending the thermal half-life to weeks or even months in some cases.[10] These 'slow-switching' azo compounds are invaluable in applications such as optical data storage and shape-memory polymers, where the written state must persist without continuous irradiation.

3. Synthetic Strategies for Incorporating Azobenzene into Polymers

3.1. Post-polymerization Functionalization

One of the most operationally straightforward approaches involves first synthesizing a reactive polymer backbone and then attaching azobenzene moieties in a subsequent step. Reactive handles commonly exploited include pendant hydroxyl groups (for esterification or etherification with azo acid chlorides or tosylates), amine groups (for amide bond formation), and activated esters such as N-hydroxysuccinimide esters.[11] The advantage of post-polymerization functionalization is that well-established living polymerization methods — RAFT, ATRP, ring-opening metathesis polymerization — can be used to define molecular weight and dispersity precisely, after which the azo loading can be tuned through stoichiometry. A practical limitation is that large azo substituents can hinder reaction with nearby backbone sites, capping maximum loading well below 100%.

3.2. Polymerization of Azo-Containing Monomers

An alternative strategy is to incorporate the azobenzene unit directly into the monomer before polymerization. Azo-methacrylates, azo-acrylates, azo-styrenes, and azo-norbornenes have all been prepared and polymerized by free-radical, anionic, cationic, and ring-opening metathesis mechanisms.[12,13] This route generally affords higher azo loading and more uniform substitution than post-functionalization, at the cost of somewhat more demanding monomer synthesis. Side-chain liquid crystalline polymers with mesogenic azobenzene groups have been prepared by ATRP of 6-(4-cyanobiphenyl-4'-oxy)hexyl methacrylate and related derivatives to achieve well-defined block copolymer architectures.[14]

3.3. Incorporation into the Polymer Main Chain

In main-chain azobenzene polymers, the photoswitch becomes a structural element of the backbone itself, so that isomerization directly modulates the end-to-end distance of the chain. Such architectures were pioneered using step-growth polycondensation of azo diols with diacid chlorides or diisocyanates.[15] More recently, copper-catalyzed azide-alkyne cycloaddition chemistry (CuAAC) has been used to couple azobenzene bis-alkynes or bis-azides with complementary

difunctional oligomers, yielding main-chain azo polymers in a modular fashion.[16] The photomechanical response of main-chain systems is generally larger per azo unit than that of sidechain polymers because each isomerization event directly propagates a conformational change through the backbone.

3.4. Azobenzene as a Crosslinker

Incorporating difunctional azobenzene derivatives as crosslinking points in polymer networks is a strategy that combines network topology with photoswitchability. Upon UV irradiation, the crosslink geometry changes from the planar trans to the bent cis configuration, locally straining the network and, if the azo content is high enough, producing macroscopic deformation. This principle underlies much of the work on azobenzene-crosslinked liquid crystal elastomers (LCEs) and hydrogels that can perform work against external loads.[17]

3.5. Supramolecular and Host-Guest Approaches

Beyond covalent strategies, azobenzene has been exploited as a guest in host-guest supramolecular assemblies. Cyclodextrin (CD) host-guest chemistry is particularly elegant in this context: the trans isomer binds selectively inside the β -CD cavity with a binding constant of 10^3 – 10^5 M⁻¹, whereas the bulkier cis isomer is expelled upon irradiation.[18] This reversible association/dissociation event has been used to build self-healing polymer networks, lightcontrollable hydrogels, and surfaces whose wettability can be toggled optically.

4. Side-Chain Azobenzene Polymers

Side-chain architectures represent the largest and most thoroughly characterized family of azobenzene polymers, partly for historical reasons and partly because they allow independent optimization of the backbone (for mechanical properties, glass transition temperature, solubility) and the chromophore (for absorption wavelength, switching speed, thermal stability). The most studied systems are poly(methacrylate)s and poly(acrylate)s carrying azo pendant groups separated from the backbone by flexible alkyl spacers. A critical parameter is the spacer length. Short spacers impose cooperative coupling between backbone motions and azo reorientation, which can be beneficial for

cooperative switching but imposes steric congestion that lowers quantum yield. Longer alkyl spacers (typically C4–C8) decouple the chromophore from the backbone sufficiently to allow efficient photoisomerization in solid films, a property that is important for optical storage and non-linear optics applications.[19] A striking collective phenomenon observed in dense azo side-chain systems is mass migration: continuous irradiation with a light intensity gradient causes material to flow from bright to dark regions, inscribing a surface-relief grating (SRG) with amplitude in the range of hundreds of nanometers to several micrometers.[20] The mechanism of SRG formation remains somewhat debated, but most accounts assign a key role to the anisotropic pressure exerted by the repeated trans–cis–trans cycling of aligned azo groups. SRGs formed by holographic two-beam interference are potentially useful as diffractive optical elements, waveguide couplers, and templates for Nano patterning.

5. Azobenzene-Containing Liquid Crystal Polymers and Elastomers

The synergy between liquid crystallinity and azobenzene photoswitching has been one of the most fertile areas of the entire field. Azobenzene groups are themselves mesogenic — they are rodshaped molecules capable of forming nematic and smectic phases — and the cooperative nature of liquid crystalline order amplifies the response to individual photoisomerization events.[21] When a small fraction of trans→cis conversion disrupts the orientational order of a liquid crystal polymer (LCP) film, an isothermal phase transition from ordered to isotropic can be triggered, producing large-amplitude bending or contractile deformation. Liquid crystal elastomers (LCEs) crosslinked with azobenzene units — or containing azobenzene groups aligned along the director — can perform macroscopic mechanical work under light. A thin LCE film prepared with a splayed director orientation (homeotropic on one surface, planar on the other) bends toward the light source upon UV irradiation and recovers upon visible light or in the dark.[22] The bending arises because the illuminated face contracts (as the trans → cis transition disrupts local order) while the shadowed face retains its ordered, contracted state. Particularly

dramatic demonstrations of LCE photoactuators include millimeter-scale robotic swimmers that propel themselves forward under oscillating UV/visible illumination,[23] artificial cilia arrays that generate directed fluid flow,[24] and light-driven grippers capable of picking up and releasing small objects.[25] The energy conversion efficiency remains modest by the standards of electroactive actuators, but the wireless addressability and compatibility with biological environments are compelling differentiators.

6. Azobenzene in Block Copolymers and Self-Assembled Nanostructures

Block copolymers bearing an azobenzene-containing block and an inert block spontaneously microphase-separate into lamellar, cylindrical, or spherical nanodomains whose characteristic periodicity falls in the range of 10–100 nm. Photoisomerization of the azo block changes the effective volume fraction and interaction parameter of the blocks, providing a photochemical handle to reconfigure the microdomain morphology.[26] Such light-driven order–order transitions and order–disorder transitions have been documented in poly(styrene-*b*-methacrylate) diblock copolymers with azobenzene side chains on the methacrylate block. In solution, amphiphilic block copolymers containing azo groups self-assemble into micelles, vesicles, or wormlike aggregates whose structure can be altered photochemically. The change in polarity and geometry upon trans→cis isomerization shifts the hydrophilic–lipophilic balance and may trigger disassembly of micelles or vesicles, releasing any encapsulated cargo. This principle has been explored extensively for photocontrolled drug delivery, as discussed in Section 8.2.[27]

7. Azobenzene-Functionalized Hydrogels and Biocompatible Systems

The interest in azobenzene-polymer systems for biological applications has driven significant effort toward hydrogel matrices. Polyacrylamide and poly(ethylene glycol) hydrogels crosslinked with azobenzene units can undergo light-induced volume changes, provided that the azo content is sufficient to perturb chain conformation collectively.[28] In practice, the swelling changes achievable with purely photochemical driving are modest compared to temperature- or pH-driven volume transitions in

responsive hydrogels, but the spatial and temporal precision of optical control compensates for this limitation in many biomedical scenarios. An influential design strategy uses azobenzene–cyclodextrin host–guest pairs within the hydrogel network as dynamic, light-responsive crosslinks. In the trans state, azo–CD complexation maintains crosslink density; UV irradiation disrupts the complex and reduces crosslink density, causing swelling and softening. The gel effectively 'melts' locally where the light beam is focused. This approach was used to demonstrate lithographic patterning of hydrogel mechanics — creating soft inclusions within a stiffer matrix with potential relevance to 3D cell culture platforms and tissue engineering scaffolds.[29]

8. Applications

8.1. Optical Data Storage and Holographic Recording

The anisotropic photoinduced birefringence and the ability to inscribe surface relief gratings in azobenzene polymer films made optical data storage one of the first serious application targets.[30] Holographic gratings are recorded by two-beam interference and read out by diffraction, offering high storage density and, in principle, non-destructive readout. The key material requirements — high photoinduced birefringence, low scattering loss, negligible spontaneous relaxation at the operating temperature — have been addressed through careful molecular engineering of the azo side chain and backbone. Despite early optimism, the application has not yet reached commercialization, partly because competing phase-change and flash memory technologies have moved so rapidly.

8.2. Drug Delivery and Theranostics

Light-triggered release from azobenzene-polymer vehicles offers the prospect of spatiotemporally precise drug administration, reducing systemic side effects. Several delivery geometries have been explored: hollow polymersomes with azo-functionalized membranes whose permeability increases upon UV illumination, dendrimer hosts whose guest-binding affinity is photochemically modulated, and mesoporous silica nanoparticles gated with azobenzene– β -cyclodextrin nanovalves.[31,32] A practical concern is that UV

light (360 nm) penetrates biological tissue poorly, limiting in-vivo applicability. This has spurred work on red/near-IR-absorbing azo systems achieved either by direct synthesis of donor–acceptor azobenzenes with red-shifted absorption or by two-photon excitation using near-IR pulses.[33]

8.3. Photoresponsive Coatings and Wettability Control

The change in dipole moment from trans (near zero) to cis (approximately 3 D) translates into measurable changes in surface energy and contact angle when azobenzene groups are oriented at a polymer surface. Water contact angles can shift by 10–30° upon UV irradiation of azobenzene-modified surfaces, enabling light-driven droplet transport and switchable adhesion.[34] These effects have been demonstrated on self-assembled monolayers, spin-coated polymer films, and electrospun fiber mats.

8.4. Soft Robotics and Mechanical Actuators

The translation of molecular photoisomerization into macroscopic mechanical output is perhaps the most visually striking application of azobenzene polymers. In addition to LCE-based actuators described in Section 5, azobenzene-crosslinked glassy polymers exhibit photoinduced stress generation that can be harnessed in constrained geometries.[35] Shape-memory polymers with azobenzene switches allow shapes to be written thermally and selectively erased or restored photochemically, adding a second addressable state beyond the thermal one. Multi-material 3D-printed structures incorporating azo-elastomer inks have demonstrated light-driven crawling locomotion and shape morphing.[36]

8.5. Non-Linear Optics

Push-pull azobenzene chromophores possess large molecular hyperpolarizabilities (β values), making them candidates for electro-optic polymer waveguides and second-harmonic generation materials. The challenge is achieving stable non-centrosymmetric poling in glassy polymer matrices; the azo groups must be oriented electrically at temperatures above T_g and the orientation must be frozen in on cooling.[37] Photoinduced anisotropy can supplement or replace electric-field poling in certain geometries, and the combination of photoisomerization and orientational hole-burning gives rise to a rich diversity of optical functions.

9. Challenges and Outlook

Despite the maturity of the field, several persistent challenges continue to constrain the translation of azobenzene polymer systems from laboratory demonstrations to deployed technologies. First, the UV irradiation requirements for most classical azobenzene systems are a genuine barrier to biomedical use and to outdoor applications where UV exposure would cause uncontrolled switching. The development of visible- and NIR-activated systems is therefore a high priority, with promising approaches including donor-acceptor azobenzenes, bridged azo architectures, and sensitized triplet-state isomerization. Second, photofatigue — the degradation of photoswitching performance over repeated cycles — remains incompletely solved. The primary degradation pathway involves side reactions of the cis isomer, particularly hydrazone or azoxy formation under ambient conditions. Encapsulation strategies, oxygen exclusion, and the design of sterically protected azo cores have all been shown to extend operational lifetimes, but the design rules are not yet fully general. Third, scaling up synthetic procedures for azo monomers and polymers to multi-gram or kilogram quantities introduces challenges around the handling of diazonium salt intermediates, which are energetically unstable and require careful temperature control. Green chemistry Review Article | Azobenzene-Incorporated Polymers Page 10 approaches using electrochemical diazonium generation and flow reactor technology have been reported but have not yet become standard practice. Looking forward, several emerging directions appear particularly promising. The integration of azobenzene switching with molecular motors and other mechanically interlocked molecules opens pathways to materials with amplified, directional mechanical output. The use of azobenzene as a photoresponsive element within metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) combines the porosity and structural precision of framework materials with light-driven actuation at the angstrom scale.[38] Machine-learning-assisted inverse design of azo chromophores with targeted absorption spectra and thermal relaxation rates promises to accelerate materials discovery considerably. Finally, the

convergence of azobenzene polymer photonics with optogenetics — using polymer coatings to modulate the light environment experienced by engineered cells — represents a frontier that is just beginning to be explored. In summary, the incorporation of azobenzene into polymers has evolved from a curiosity of photochemistry into a rich platform technology spanning optics, robotics, medicine, and materials science. The continuing invention of new synthetic strategies, the deepening understanding of photomechanical transduction mechanisms, and the broadening of responsive wavelength ranges collectively ensure that the field will remain vibrant and consequential for years to come.

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