Photochemical Control of the Macroconformation of Polystyrene Using Azobenzene Side Chains

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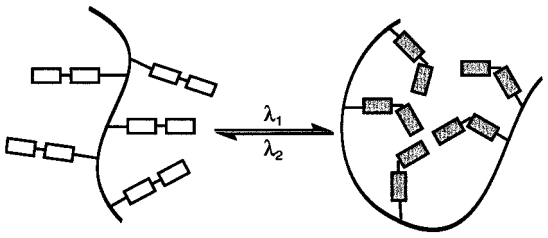
The dynamic control of macromolecular conformation is of fundamental importance in the fields of biology[1] and materials science.[2] In nature, protein structure is modulated by both receptor−ligand interactions[3] and through environmental changes.[4] In materials science, the ability to regulate macromolecular structure through external stimuli provides direct access to devices,[5] sensors,[6] and environmentally responsive materials.[7]

Supramolecular assembly is a powerful tool for the control of polymer structure.[8] Modulation of noncovalent interactions through external stimuli provides a means for regulating the structure of these systems, providing a starting point for device and materials design. In recent studies, we have demonstrated the use of side chain functionality to control polymer structure through aromatic stacking.[9] We report here the extension of this concept to the photocontrol of the polymer architecture through functionalization of a polystyrene backbone with photoswitchable azobenzene side chains.

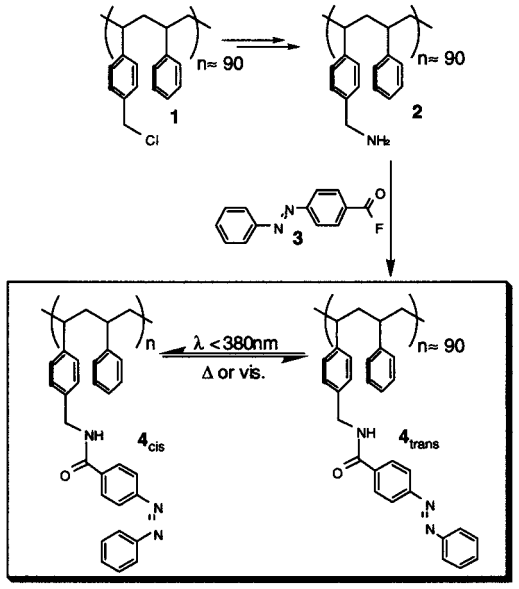
The azobenzene chromophore is a versatile tool for the creation of light-driven devices.[10] With the azobenzene system, UV irradiation results in isomerization from the more thermodynamically stable trans conformation to the less favored cis form.[11,12] This isomerization can be readily reversed either thermally, or through visible light irradiation. During this isomerization, there are large changes in both geometry and dipole of the chromophore,[13] making the azobenzene unit a potentially useful unit for the photocontrol of polymer structure (Scheme 1). Azobenzene functionality has been incorporated in wide variety of polymers as structural probes,[14] for optical storage,[15] for alignment of polymer in films,[16] and in liquid crystalline polymers,[17] and in dendritic polymers.[18] There have also been multiple investigations exploring the effects of photoswitching of mainchain azobenzenes on the hydrodynamic properties of polymers.[19] On the basis of our previous research on intrachain aromatic stacking, we hypothesized that photoswitching of *side chain* functionality could likewise modulate macromolecular structure. We report the use of photoswitchable azobenzene side chains to control the structure of a styrene-based random copolymer[20] in solution.

The desired random distribution of the azobenzene chromophore along the backbone of the polystyrene was achieved by starting with a 1:1 copolymer of styrene and *p*-chloromethylstyrene **1**, $M_w = 21\,800$ (Scheme 2). The chloromethyl sites were converted to amines;[21] subsequent reaction of polymer **2** with 4-phenylazobenzoyl fluoride (**3**) then afforded the fully substituted polymer **4**[22] featuring an average of 90 azobenzene-substituted

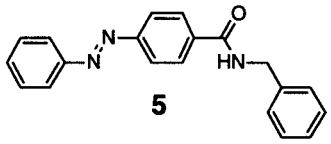
Scheme 1. Schematic Representation of the Photocontrol of Polymer Structure in Solution



Scheme 2. Synthesis of Azobenzene-Functionalized Random Copolymer 4 and Its Photochemical Behavior



side chains per polymer. To provide a control, monomeric amide **5** was synthesized in analogous fashion



through coupling of the acid fluoride **3** with benzylamine.

The absorption spectra of polymer **4** and the monomeric control **5** in $CHCl_3$ are similar,[23] with both possessing a band at 326 nm characteristic of the $\pi-\pi^*$ transition of the trans azobenzene. When the polymer solution was irradiated, the main band decreased rapidly (Figure 1), and as expected, a new weak band appeared at 446 nm characteristic of the $n-\pi^*$ transition for the cis isomer. After 10 min of irradiation, no further significant changes in the spectra could be detected, indicating that the photostationary state consisting of 79% of the cis isomer was reached. When the sample was kept in the dark, the back isomerization to trans was slow (less than 10% in 60 min) but was much faster when exposed to visible light.[24] Furthermore, during the transformation, isosbestic points could be detected at 288 and 382 nm, clearly indicating the effective and reversible conversion of the pendant azobenzene from

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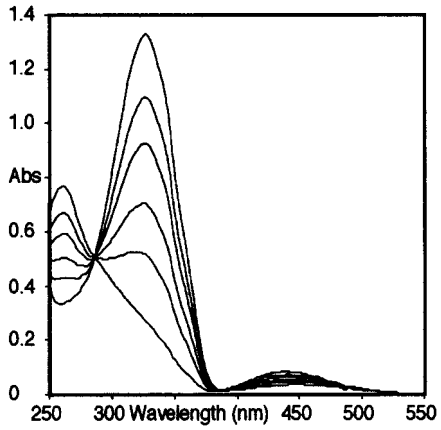

Figure 1. Variation of the absorption spectra of polymer **4** in $CHCl_3$ during the irradiation with UV light (top and lowest) and subsequent exposition to visible light. [**4**] = 5.5×10^{-7} M.

the trans to cis isomer. The monomeric azobenzene **5** possessed similar spectroscopic behavior to polymer **4**, with identical kinetics of photoisomerization. This indicates that the isomerization of the azobenzene units from both cis and trans states on the polymer **4** was accomplished efficiently and was not hindered by the polystyrene backbone. An identical study of the photochemical behavior of **4** was conducted in THF, indicating that a photostationary state of 75% cis isomer is achieved.

After establishing the efficiency of the photoisomerization, we then explored the effect of side chain geometry on the overall solution structure of polymer **4**. These studies were performed using gel permeation chromatography (GPC) through comparison of the retention time of $\mathbf{4}_{trans}$, $\mathbf{4}_{cis}$, and precursor **1** with polystyrene standards.[6,7] The variation in relative radius of gyration[25] (r_g) of these three species was estimated using the relationship

$$\frac{r_g^{\mathbf{1}_{cis}}}{r_g^{\mathbf{1}_{trans}}} = \left(\frac{M_{\mathbf{1}_{cis}}^{\,a+1}}{M_{\mathbf{1}_{trans}}^{\,a+1}} \right)^{1/3} \qquad (1)$$

where M represents the molecular weight of the polystyrene standards at the center of the respective GPC peaks for the polymers, and a is the viscometric exponent (0.73 for polystyrene in $CHCl_3$[26]). Using this method, we observed that irradiation of polymer $\mathbf{4}_{trans}$ at 365 nm in $CHCl_3$ and THF resulted in a decrease in the relative r_g (Figure 2a), reaching a limiting value after 20 min corresponding to $\mathbf{4}_{cis}$. In chloroform, the r_g of $\mathbf{4}_{cis}$ is 60% that of $\mathbf{4}_{trans}$, but in tetrahydrofuran, a smaller 20% decrease in relative size was observed. Those results indicate that isomerization of the side chains to the more compact cis isomer relaxes the polymer structure,[27] allowing enhancement of the side chain-side chain aromatic stacking and dipole−dipole interactions[28] in apolar solvent.[29] This isomerization process is reversible, and directly linked to the UV−vis behavior (Figure 2b): repeated cycling in $CHCl_3$ showed clean conversion between $\mathbf{4}_{trans}$ and $\mathbf{4}_{cis}$ using both UV−vis and GPC methods.

In summary, we demonstrated the control of polymer solution structure via photoisomerization of pendant azobenzene units. This structural modulation arises from the changes in side chain−side chain interactions that occur upon photoisomerization of the side chains.

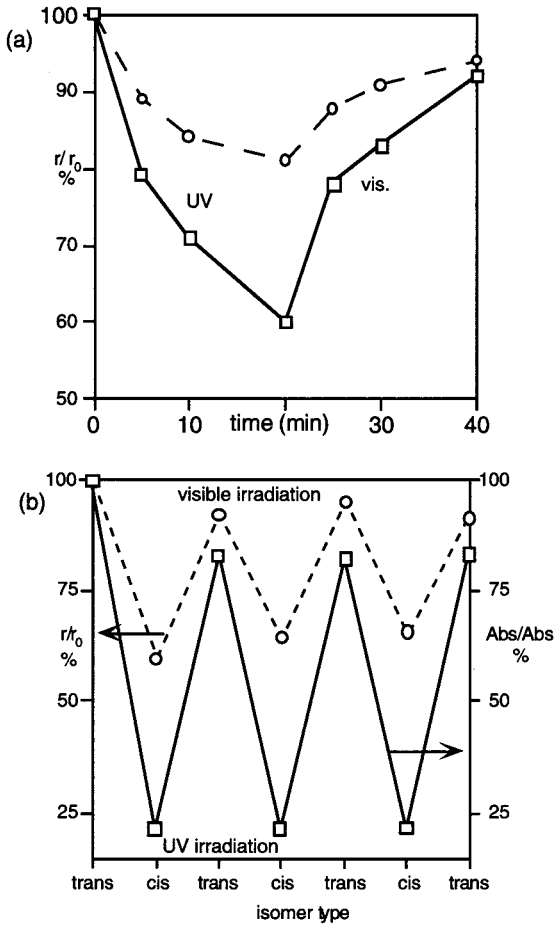

Figure 2. (a) Variations in the relative radius of gyration (as defined in eq 1, with r_0 being the polymer in the all trans conformation) of polymer **4** during irradiation in $CHCl_3$ (□) and THF (○) with UV light (from 0 to 20 min) and visible light (from 20 to 40 min). [**4**] = 1 mg/mL. (b) Changes in the relative radius of gyration (○) and absorbance (□) of polymer **4** during irradiation in $CHCl_3$.

We are currently applying this strategy to explore photoswitchable control of polymer properties such as diffusion rate and viscosity, as well to the creation of more sophisticated folded polymer systems for device construction.

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Supporting Information Available: Figures showing UV−visible spectra of **4** and **5** and GPC traces of **1**, $\mathbf{4}_{cis}$, and $\mathbf{4}_{trans}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) NMR confirmed the quantitative conversion of the amine group: the peak at 3.75 ppm for the benzylic protons in polymer **2** was undetected and was replaced by a new peak at 4.50 ppm.
(23) The concentrations of polymer **4** and the corresponding monomer **5** were adjusted to obtain an absorbance of 1.35.
(24) The trans isomer could not be totally recovered; the absorbance at λ_{max} reached a lower value after 30 min, and remained constant, indicative of reaching a photostationary state (82% of trans isomer).
(25) In the text, the variation of the relative r_g is denoted r/r_0 and expressed in percent relative to polymer **4** fully trans.
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