Photosensitive Chiral Polyisocyanates

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SUMMARY: The dynamic polyisocyanate helix amplifies changes in the conformation of its side groups. Thereby it acts like a fast responding switch for optical properties. Here we show how the photoisomerization of chiral azo side groups can be used to induce large changes of chirooptical properties. These changes can be detected by CD measurements or by ORD measurements far from the absorption region. Large changes of the optical rotation can be induced reversibly in a multicycle process.

Introduction

Azo dyes are well known for their photochemical isomerization process. We used the sterical and polarity changes correlated with this process to induce different optical properties in chiral polyisocyanates.

Primary isocyanates can be polymerized anionically with sodium cyanide in dimethyl formamide yielding polymers with nylon-1 structure$^{1)}$. Recently we have synthesized several series of copolymers consisting of hexyl isocyanate and different amounts of chiral azo derivatives$^{2),3),4)}$. Due to the high cooperativity within the helical polymer chains, small amounts (less than 10%) of chiral photoisomerizable side groups are sufficient to favor one helical twist sense among the achiral hexyl side groups (so-called "sergeants and soldiers" copolymers)$^{5)}$. The necessary overall azo dye concentration is extremely low thus resulting in a transparent material. Due to the strong cooperative effect a small change in the azo side groups is amplified via the helical main chain (Figure 1), leading to significant changes in the chirooptical properties of the material. This response can be measured at many different wavelengths, even far from the absorption wavelengths of both the azo dye and the polymer chain.

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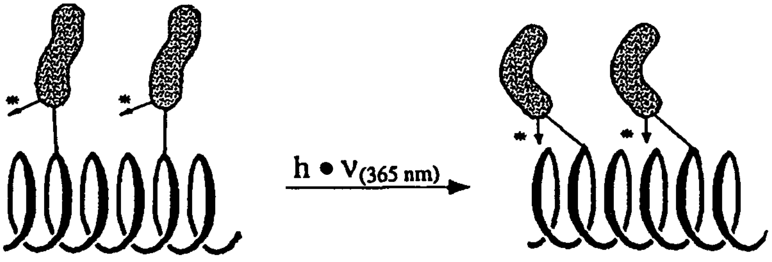

Figure 1. Schematic representation of the transition from M- to P-helical polyisocyanates initiated by a photochemical trans-cis isomerization of the azo dye

Results and discussion

For this investigation two polymers were chosen (see Figure 2), one with a chiral group located in the azo side group, at the phenyl ring in ortho position to the spacer (**P1**), and another with a stereocenter in the spacer (**P2**). Their synthesis is described elsewhere[3),4)].

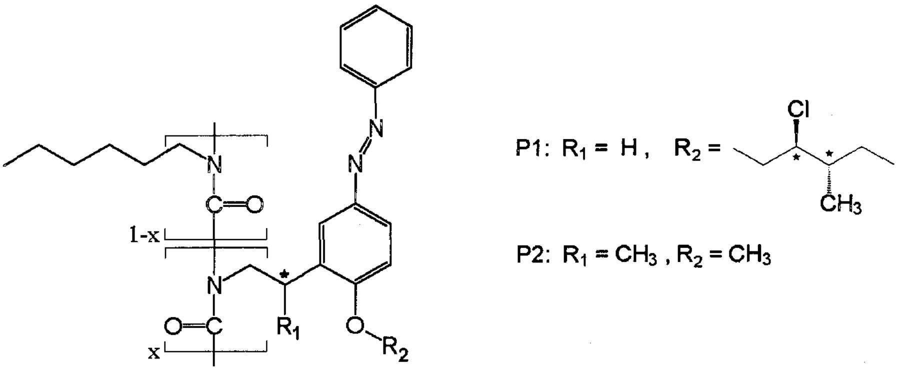

Figure 2. Copolyisocyanates with hexyl and x = 8 mol% azo side groups

In the azo groups a switching between the trans and the cis conformation by photochemical isomerization is possible because of the different absorption characteristics of the trans and the cis isomer. For the irradiation a 150W Xenon lamp was used. The trans→cis isomerization is performed at 365 nm (using an interference filter) thus irradiating at the π→π* transition of the trans isomer. Over 95% yield of cis isomer is achieved. The cis→trans isomerization is done with a cut-off filter (Schott GG 420) irradiating at the n→π* band of both isomers. Because of the much higher absorption coefficient of the cis isomer about 80% yield of trans isomer can be achieved (Figure 3). This is, however, less trans isomer as in the dark state (about 100% after 300 hours in the dark).

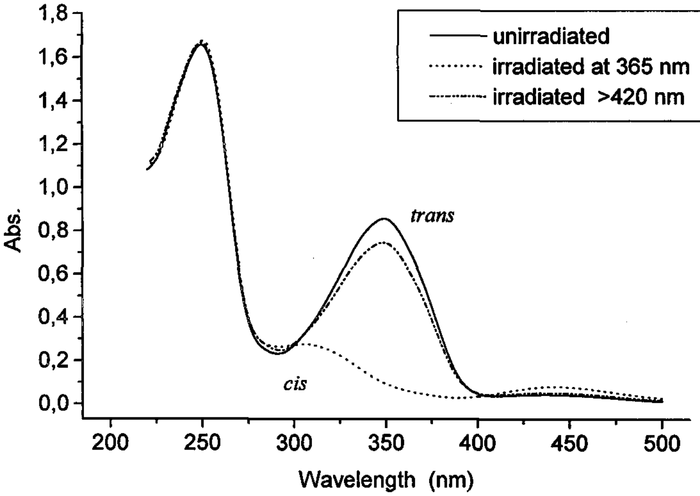

Figure 3. UV spectra of **P1** in THF

This absorption cycle can be repeated. After ten cycles the absorption spectra of the two isomeric states have not changed. After each cycle the absorption at the maximum of the π→π* transition of the trans isomer returns to the same value (Figure 4). The two isosbestic points at 300 nm and 404 nm remain, indicating the absence of degradation of the material or of other photoreactions.

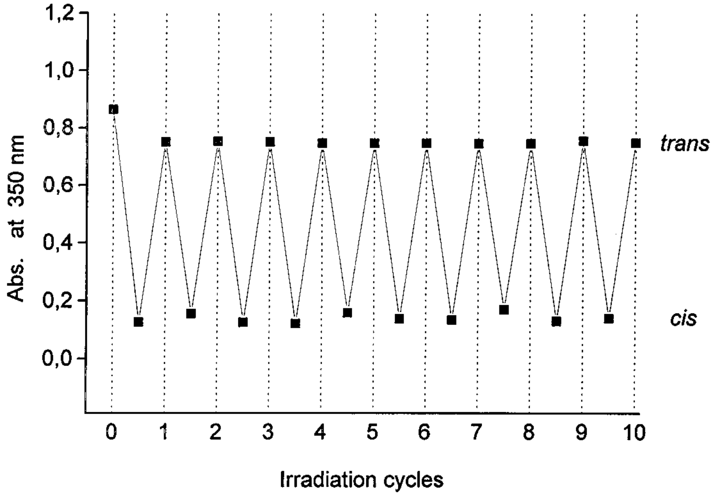

Figure 4. Absorption at 350 nm of **P1** during multiple irradiation cycles

By combination of the photoisomerizable side groups with the helical main chain of the polyisocyanate a chirooptical switch can be realized. The photoisomerization of the azo dye induces - due to the changes in conformation and polarity of the side group - a change in the main chain conformation. This change can be investigated by circular dichroism (CD) spectroscopy. The molar ellipticity at the absorption wavelength of the $n \rightarrow \pi^*$ band of the main chain amide chromophore (250 nm) is proportional to the excess of one helical species. A positive band means an excess of P-helix (right-handed), a negative band an excess of M-helix (left-handed).

The helix equilibrium of **P1** is shifted from an excess of M-helix to an excess of P-helix by trans→cis isomerization and back to an excess of M-helix by cis→trans isomerization (Figure 5a). **P2** already has a strong preference for the M-helical twist sense in the trans isomeric state, which is further increased by UV irradiation (Figure 5b).

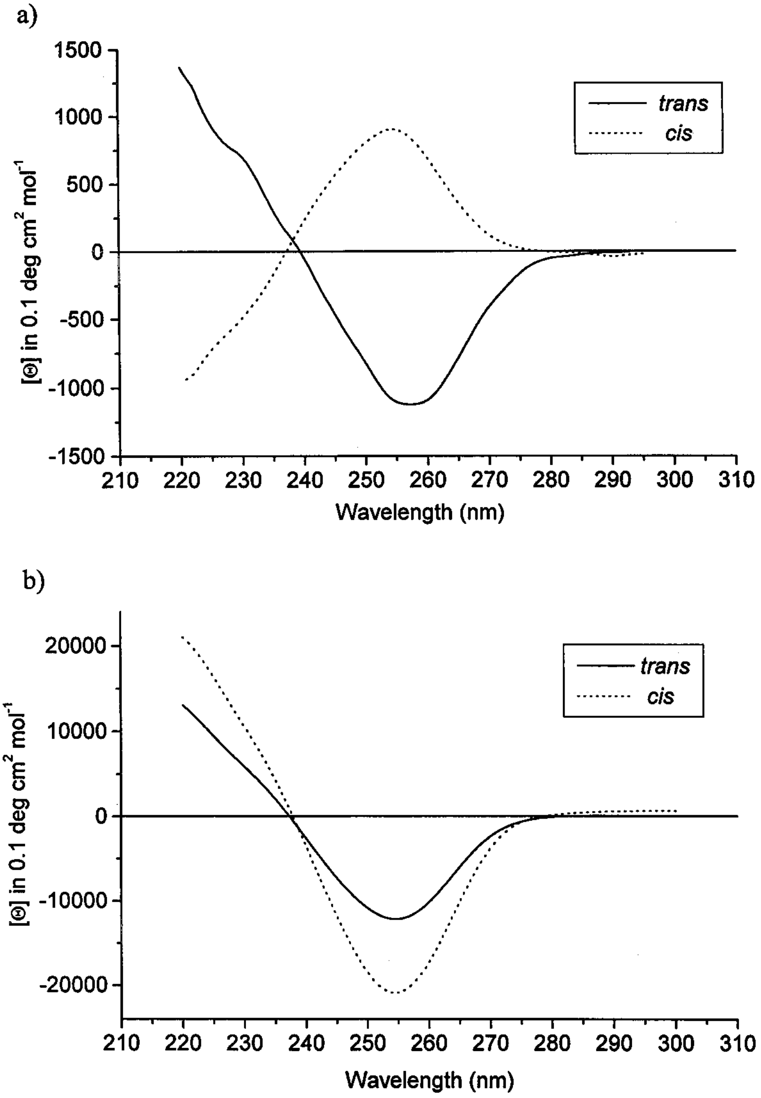

Figure 5. CD measurements before and after irradiation at 365 nm, 0.5 mg/ml in THF

a) **P1**

b) **P2**

The large changes in chirooptical properties during photoisomerization also make a readout far from the absorption wavelength possible. **P1** shows a reversal of sign of the optical rotation (Figure 6a), **P2** exhibits a large change in specific optical rotation between 410 and 550 deg dm^{-1} g^{-1} cm^{3} at 589 nm (Figure 6b).

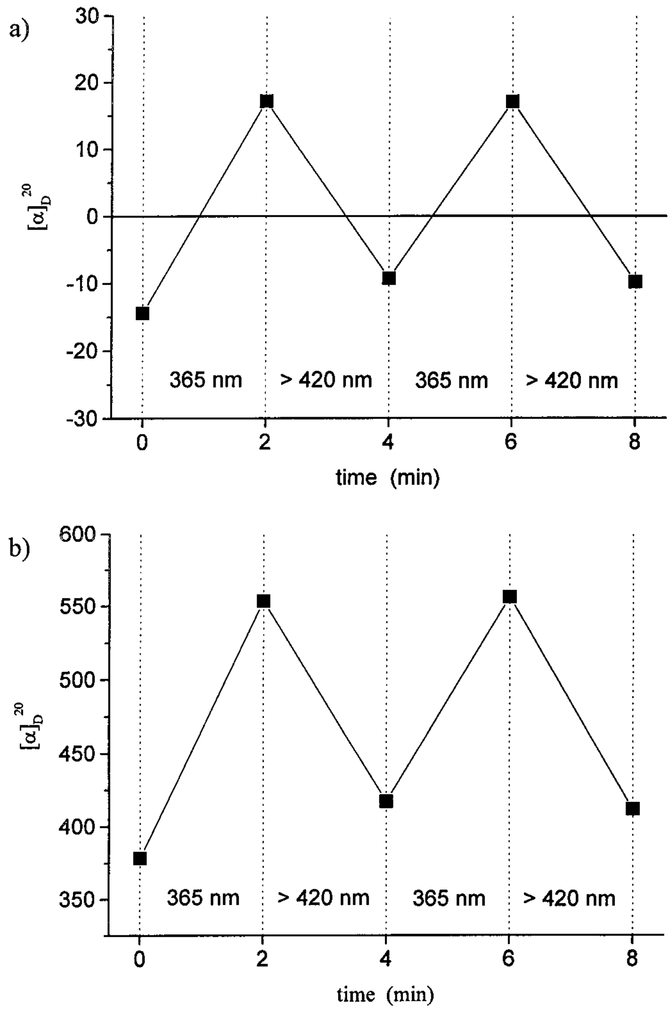

Figure 6. Optical rotation of a) **P1** and b) **P2**, after multiple irradiations at the indicated wavelengths

Each irradiation time was 2 minutes. The necessary irradiation time depends on the intensity of the lamp. The lamp we used had only a low intensity of 12 mW/cm^2. For technical use switching flashes of high intensity could be applied. It has been shown in another experiment that the system has the ability to react fast enough to follow changes in the azo configuration$^{6)}$.

Conclusion

The above results show that the dynamic polyisocyanate helices exhibit a fast responding switch induced by a change in their photoresponding side groups. The azo groups act as "remote control" for the chirooptical properties of the material. This is possible because of the close correlation between the azo structure and the helical configuration. Thus with a high intensity light source a fast switching cycle can be realized. In addition, the switching of the chirooptical properties makes an application as optical filters (circular polarizers) possible.

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