Photochemical Inversion of the Helical Twist Sense in Chiral Polyisocyanates

Georg Maxein and Rudolf Zentel*

Institut für Organische Chemie, Johannes Gutenberg-Universität, J.-J. Becher-Weg 18-20, D-55099 Mainz, Germany

Received June 6, 1995

Revised Manuscript Received September 16, 1995

Helical polymers[1] (e.g., DNA or helical polypeptides) are well known for their importance in nature. In proteins, helical rigidity acts to stabilize the three-dimensional structure. Changes in the helical structure[2] (e.g., helix–helix or helix–coil transitions) can be triggered by temperature or pH changes. In polypeptides, for example, which are close to one of these conformational transitions, it has long been known to be possible to induce this transition photochemically.[3]

Synthetic helical polymers (e.g., polyisocyanides,[4–6] poly(tritylmethacrylate)s,[7] and polychloral[8]) can be prepared by polymerisation reactions using chiral initiators or, in one example, via racemic separation.[9] In these synthetic systems, helix–coil transitions are not seen. Their helical structures are not stabilized by H-bonds as in the native polymers. Certain of these synthetic polymers are of special interest for their use as materials for racemic separation[10] and because they allow a defined geometric orientation of substituents.[4]

Polyisocyanates[11] prepared from chiral monomers play a special role in this context, because of the fact that a reversible shift of the equilibrium between *P* and *M* helices can be induced, e.g., by a temperature change in aprotic solvents.[12] Since the polyisocyanate backbone has no chiral center, these polymers, prepared from achiral monomers, exist as a racemic mixture of *P* (right handed) and *M* (left handed) helices (or helical segments within one long polymer chain). However, due to the high cooperativity within the helical polymer chains,[13] small amounts (about 0.1 mol %) of chiral side groups in copolymers are sufficient to favor one twist sense of the helical segments. In these so-called "Sergeants and Soldiers" copolymers,[12] (*P* and *M* helices become diastereomers in the presence of the chiral side groups. We recently succeeded—for the first time—in inducing photochemically a reversible shift of the equilibrium between *P* and *M* helices in polyisocyanates.[14] In this case, the sign of the optical activity did not change; i.e., in both states, the same helix sense was favored.

Stimulated by these results, we have now discovered a copolyisocyanate that is capable of a reversible shift of the preferred helical twist sense from *M* to *P* helices initiated by a photochemical isomerization of the chiral azo dye side chains (Figure 1).

The synthesis of the chiral azo chromophore **3** (Scheme 1) is carried out by an etherification of **1**[14] with (2*S*,3*S*)-2-chloro-3-methylpentan-1-ol (**2**)[15] analogous to ref 16 followed by a Curtius rearrangement.[14]

The anionic copolymerization (NaCN, DMF, −65 °C[17]) of **3** with hexyl isocyanate in various monomer feed concentrations leads to polymers **P1**–**P5** (Table 1).

The photochemical trans–cis isomerization of the azo chromophores in polymers **P1**–**P5** was accomplished by irradiation of the THF solutions with 365 nm light (source: low-pressure mercury lamp (Osram HQV 125 W) with an integrated filter). The photoisomerization leads to a concentration of more than 90% of the cis isomer. The thermal reisomerization in THF (cis → trans) occurs with a halftime of about 25 h.

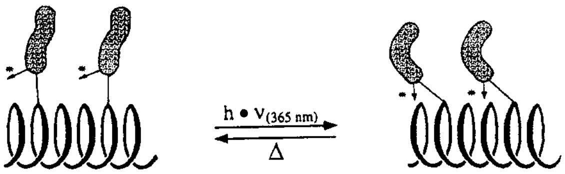
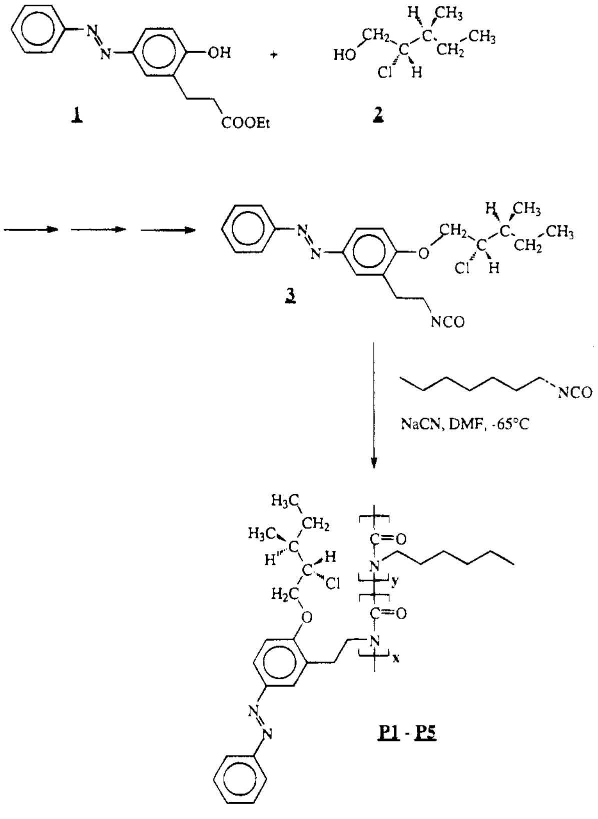


Figure 1. Schematic representation of the transition from *M*- to *P*-helical polyisocyanates initiated by a photochemical trans–cis isomerization of the azo dye. Both helical conformations (enantiomers) become diastereomers for the case that the side chains have chiral centers. Differences in the interactions between the asymmetric centers in the side chains and the polymer backbone (depending on the isomerization status of the azo chromophore) lead to a preference for the *M*- or *P*-helical conformation.

Scheme 1



Discussing the properties of the copolyisocyanates **P1**–**P5**, it has to be mentioned first that the specific rotation of the polymers (Table 1) is much higher than what would be expected from the monomer rotation ($[\alpha]^{20}_D = +15.7$ deg·dm^{-1}·g^{-1}·cm^3; in $CHCl_3$). A comparable model compound, the isocyanate trimer obtained via decomposition[12] of copolymer **P5**, has a rotation of $[\alpha]^{20}_D = +6.1$ deg·dm^{-1}·g^{-1}·cm^3. This means the two asymmetric carbon atoms, which are 7 and 8 covalent bonds away from the polymer backbone, lead to a preference of one twist sense corresponding, in kind, to the expectations of the "Sergeants and Soldiers" experiment[12] (Figure 3).

Figure 2 shows the drastic influence of the photoisomerization of the azo chromophores on the optical rotatory dispersion (ORD). Polymers with small amounts of azo dyes (8.0 mol %) show a change of sign in the ORD spectra for the trans–cis isomerization. The slightly differing shapes of the ORD curves (unirradi-

0024-9297/95/2228-8438$09.00/0

Table 1: Characterization of Copolymers P1–P5

polymer	Y (mol %)	$M_w{}^a$ ($\times 10^3$)	$[\alpha]^{20}{}_{600}$ (deg·dm^{-1}·g^{-1}·cm^3)	$[\alpha]^{20}{}_{600}{}^b$ (deg·dm^{-1}·g^{-1}·cm^3)	$[\Theta]$ (255 nm) (0.1 deg·cm^2·mol^{-1})	$[\Theta]$ (258 nm)^b (0.1 deg·cm^2·mol^{-1})
P1	8.0	490	−13.2	16.27	−1132	918
P2	12.5	251	−43.0	19.0	−3195	961
P3	15.1	89	−66.2	13.5	−5156	737
P4	18.2	183	−82.1	6.0	−7188	≈0
P5	20.2	114	−97.6	5.4	−8452	≈0

[a] Weight-average molecular weight determined by GPC versus polystyrene standards. [b] Irradiated species (cis isomer).

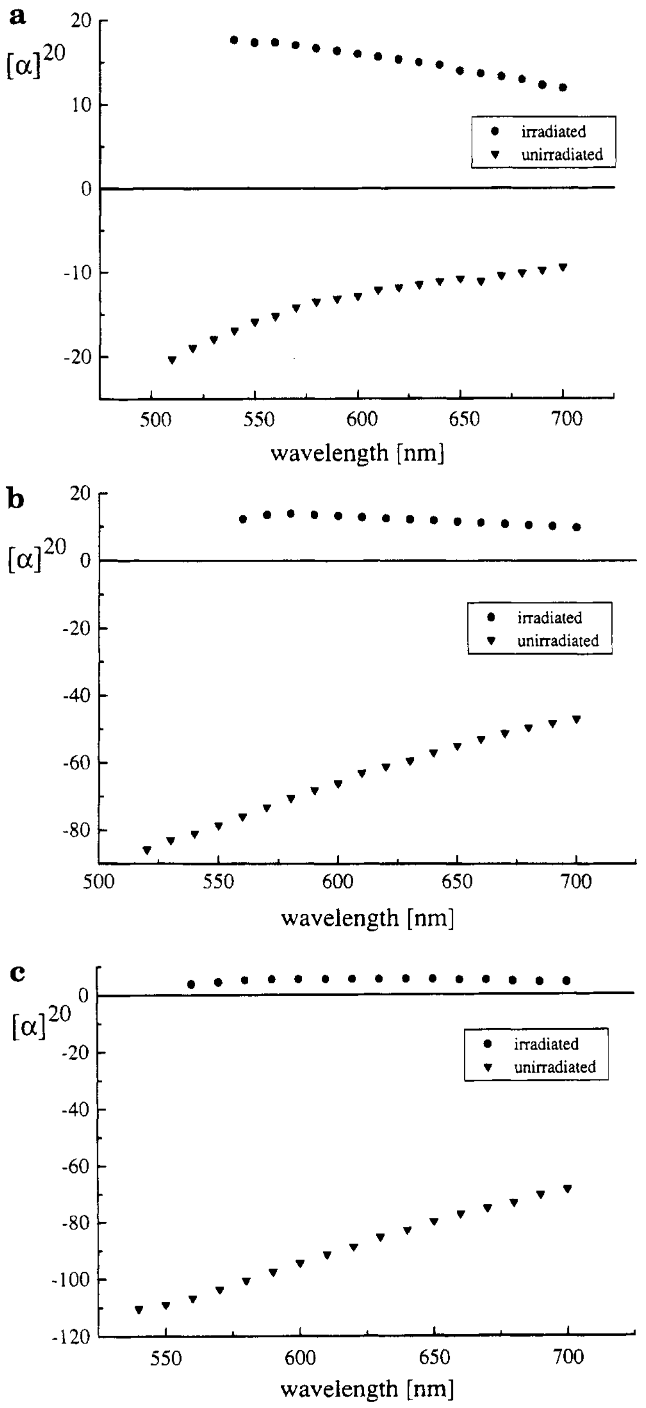


Figure 2. ORD spectra in THF (3 mg/mL) for **P1** (a), **P3** (b), and **P5** (c), which show the specific rotations (deg·dm^{-1}·g^{-1}·cm^3). The measurements were carried out with a Perkin-Elmer 241MC polarimeter.

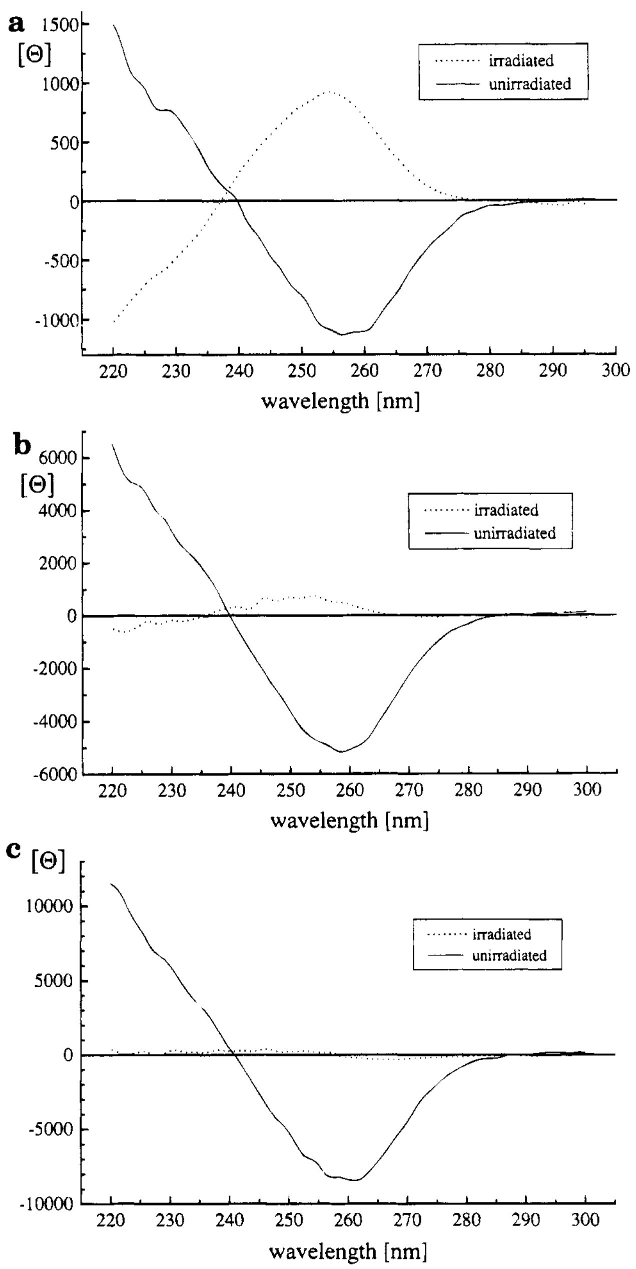


Figure 3. CD measurements in THF (0.5 mg/mL) for **P1** (a), **P3** (b), and **P5** (c), which show the molar ellipticities (0.1 deg·cm^2·mol^{-1}) based on the average molecular weight of a repeating unit. The measurements were performed with a computer-supported Jasco J-500A spectro polarimeter.

ated–irradiated) are presumably due to different Cotton effects of the azo chromophore (300–400 nm).[17, 19] An increasing concentration of the chiral comonomer leads to a continuous increase of the ORD signal for the *trans*-azo dye containing copolymers. This is what one would expect for an increasing preference for one helical twist sense (Figure 2a–c).

In contrast to this, the *cis*-azo dye containing copolymers show a decrease in their ORD signals with increasing dye concentration. As a result, the highly dye loaded copolymers undergo a shift from high negative ORD signals (trans) to signals close to zero (cis).

In addition to the ORD measurements and for a better understanding, circular dichroism (CD) investigations were made. With CD measurements at wavelengths smaller than 300 nm, it is possible to detect directly the chiral conformation of the polymer backbone, which is the helical twist sense. Although azo chromophores have strong UV absorption bands in this region, previous experiments[14] on polyisocyanates with achiral azo chromophores have shown that they do not contribute significantly to CD spectra in this wavelength range. The results obtained in this way (Figure 3) correspond to the ORD measurements. Even for a small dye concentration, there is a significant preference for one helical twist sense. From a comparison with other chiral polyisocyanates,[14] an excess of *M* helices can be concluded for the trans dye isomers. It is obvious that through the photochemical *trans*–cis isomerization, the equilibrium is shifted from an excess of *M* helices to an excess of *P* helices (Figure 3a). After the thermal reisomerization, the system recovers completely. An increasing dye concentration leads again to a continuous increase of the molecular ellipticity for the *trans*-azo dye containing copolymers, which means the excess of *M*-helical segments in the polymers increases continuously. However, for the polymers containing the *cis*-azo dye isomer, the molecular ellipticity first stays constant (Figure 3b) and decreases for higher dye concentrations within the measuring accuracy down to zero. Therefore after the photoisomerization, polymer **P5** consists of a racemic mixture of *M*- and *P*-helical segments.

To summarize: The CD measurements show that these synthetic copolymers can undergo reversibly—depending on the copolymer composition—both a transition from an excess of *M* to *P* helices and a transition from an excess of *M*-helical segments to a racemic situation. The question of how this depends on the concentration of the chiral azo dye of the copolymers is still unanswered. Investigations on other azo chromophore-containing copolyisocyanates support this in showing[19] that an increasing azo dye concentration leads to an increasing interaction between the azo dyes as evidenced from the appearance of exciton couplets.

Acknowledgment. Financial support from the DFG is highly appreciated.

References and Notes

(1) Lehninger, Albert L. *Prinzipien der Biochemie*; Walter de Gruyter: Berlin, 1987; p 168ff.

(2) Vogel, O.; Jayox, D. G. *Polymer* **1987**, *28*, 2179.

(3) For leading references, see: Ciardelli, F.; Pieroni, O.; Fissi, A.; Carlini, C.; Altomare, A. *Brit. Polym. J.* **1989**, *21*, 97.

(4) Nolte, R. J. M. *Chem. Soc. Rev.* **1994**, *23*, 11.

(5) Green, M. M.; Gross, R. A.; Schilling, F. C.; Zero, K.; Crosby, Ch., III. *Macromolecules* **1988**, *21*, 1839.

(6) Kollmar, Ch.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 8230.

(7) Okamoto, Y.; Honda, S.; Okamoto, I.; Yuki, H. *J. Am. Chem. Soc.* **1981**, *103*, 6971.

(8) Abe, A.; Tasaki, K.; Inomata, K.; Vogl, O. *Macromolecules* **1986**, *19*, 2707.

(9) Nolte, R. J. M.; van Beijnen, A. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1974**, *96*, 5932.

(10) Okamoto, Y.; Hatada, K. Helical Polymers as Chiral Stationary Phases for HPLC: Optically Active Poly(triphenylmethylmethacrylate) and Poly(diphenyl-2-pyridylmethylmethacrylate). *Chiral Separations by HPLC*; Krstolovic, A. M., Ed.; Ellis Horwood, Chichester, 1988; p 316.

(11) Bur, A. J.; Fetters, L. J. *Chem. Rev.* **1976**, *76*, 727.

(12) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Willson, G. *J. Am. Chem. Soc.* **1989**, *111* (16), 6452.

(13) Lifson, S.; Felder, C. E.; Green, M. M. *Macromolecules* **1992**, *25*, 4142.

(14) Müller, M.; Zentel, R. *Macromolecules* **1994**, *27*, 4404.

(15) Kloppenhöfer, B.; Schurig, V. *Org. Synth.* **1988**, *66*, 160.

(16) Zentel, R.; Reckert, G.; Bualek, S.; Kapitza, H. *Makromol. Chem.* **1989**, *190*, 2869.

(17) Müller, M.; Zentel, R. *Makromol. Chem.* **1993**, *194*, 101.

(18) Green, M.; Andreola, Ch.; Muñoz, B.; Reidy, M.; Zero, K. *J. Am. Chem. Soc.* **1988**, *110*, 4063.

(19) Müller, Manfred Ph.D. Thesis, Mainz, 1995. Müller, M.; Zentel, R. *Macromolecules*, submitted.

MA950799C