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Communications to the Editor

Photochemical Amplification of Chiral Induction in Polyisocyanates

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Chirooptical properties like optical rotation and circular dichroism increase usually with the size of the chiral entity. They are comparably small for molecules with a single chiral center (usually a carbon atom with four substituents), but they can be very large for systems with a (chiral) helical superstructure, like chiral liquid crystalline phases (e.g. cholesteric)[1] or helical polymers.[2,3] In, e.g., helical polymers the optical rotation can increase from values ($[\alpha]_D^{20}$) of about 1 to 500 deg dm^{-1} g^{-1} cm^3 on transforming a monomer into a polymer.[4,5] Helical polymers and liquid crystalline phases can thus act as amplification media, which increase the chirooptical properties primarily derived from single chiral centers. It was the aim of this investigation to test if the amplifying effect of helical polymers can be triggered by a reversible photochemical isomerization in such a way that it is enhanced for one isomer. To perform this task, we combined a reversible photochemical switch with—a priori racemic—polymer helices such that the chiral inductions from the chiral center (the primary source of chiral information) to the polymer helices should be very different for both photochemical isomers (see Figure 1).

For the helical polymers we selected polyisocyanates,[6–8] which are known to possess a dynamic helix conformation with very few helix reversals.[9] Since the polyisocyanate chain has no chiral center, these polymers exist as a racemic mixture of P (right handed) and M (left handed) helices (or helical segments within one long polymer chain), as long as there is no chiral center in the side chain. However, due to the high cooperativity within the helical polymer chains, small amounts (about 0.1%) of chiral side groups in copolymers are sufficient to favor one twist sense of the helical segments in sergeant and soldier copolymers[4] (P and M helices become diastereomers in the presence of chiral side groups). The induced chiral conformation of the polymer backbone can be detected directly by CD measurements in the absorption range of the polymer backbone (280 to <200 nm).[4,10–12]

We have now prepared polyisocyanates with chiral azo chromophore side groups, in which the chiral center is a separated by seven σ-bonds from the polymer backbone. The reversible cis–trans isomerization of the azo chromophores should vary the distance—and thereby the interaction—of the chiral center in the side group and the racemic polymer chain. If the interaction is weak, a nearly racemic mixture of P and M helices should exist, whereas an increase of the population of helices of one twist sense is expected for stronger interactions. This concept is different from that in helical polypeptides with achiral photoisomerizable side chains,[13] for which the chiral groups are located within the polymer main chain.

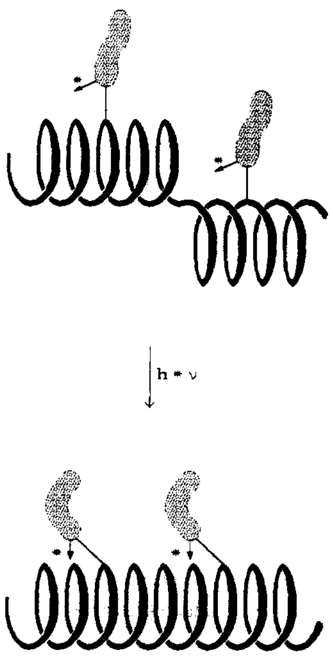

Figure 1. Schematic representation of the shift in the equilibrium between P and M helices of polyisocyanate by the use of chiral photoisomerizable side chains.

Synthesis of Monomers. To realize this concept, a new isocyano functionalized chiral azo dye has been synthesized as described in the Scheme 1.

3-(1-Hydroxy-4-(phenylazo))-2-phenyl)propionic Acid (3). Dihydrocumarin (29.6 g, 200 mmol), 24.0 g (600 mmol) of sodium hydroxide, and 200 mL of water were heated under reflux for 3 h to open the lactone. After cooling to 5 °C, the solution was diazotized according to the standard procedure. The raw product was dissolved in 1.9 L of boiling ethanol/water (1:1 v/v). After cooling to room temperature and filtration, the volume of the solution was decreased by distillation to one-third. The product precipitated as orange crystals. Yield: 50.9 g (93%). Mp: 140–142 °C.

3-(1-((*S*)-2-Methylbutoxy)-4-(phenylazo)-2-phenyl)propionic Acid (7). Compound 4 (29.4 g, 99 mmol), 4.25 g (103 mmol) of (*S*)-2-methyl-1-butyl tosylate, 14.3 g (103 mmol) of potassium carbonate, 1.7 g of potassium iodide, and 150 mL of dry acetone were stirred and heated under reflux for 4 days by the procedure of a Claisen etherification.[14] The precipitate was filtered off and extracted with acetone. After evaporation of the solvent the ester **6** remained in the form of 28.1 g of red crystals. When the crude compound **6** was heated in a solution of 5 g (125 mmol) of sodium hydroxide in 90 mL of water and 90 mL of ethanol under reflux for 1 h, the ester was saponified to the sodium salt of the carboxylic acid **7**. The product was precipitated by neutralization with hydrochloric acid and separated by vacuum filtration. After recrystallization from 170 mL of ethanol and 70 mL of water the product was obtained as orange crystals. Yield:

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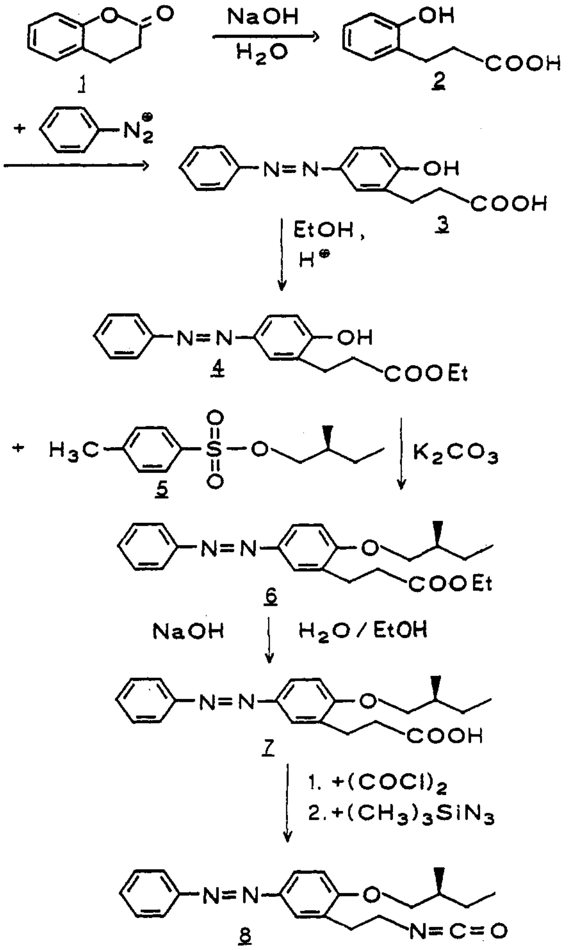
Scheme 1



18.5 g (75%). Mp: 88–94 °C. $[\alpha]_D^{20}$ = 9.8 deg dm^{-1} g^{-1} cm^3 (20 mg/mL, $CHCl_3$).

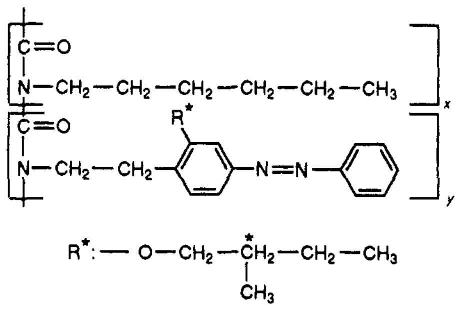
3-(1-((*S*)-2-Methylbutoxy)-4-(phenylazo)-2-phenyl)propionyl Chloride. Oxalyl chloride (5 mL, 58 mmol), was added to a solution of 4 g (12 mmol) of compound **7** in 20 mL of dry benzene. The solution was stirred under dry nitrogen for 2 h at room temperature and for 30 min at 50 °C. After the solvent and excess oxalyl chloride were removed, the product was collected as a deep red oil. The acyl chloride was used without further purification in the same flask. IR (neat): 1800 cm^{-1} (vs, CO).

2-(1-((*S*)-2-Methylbutoxy)-4-(phenylazo)-2-phenylethyl isocyanate (8). Trimethylsilyl azide[15] (2.4 mL, 18 mmol), was added to the solution of the acid chloride in 15 mL of dry toluene. After stirring for 1 h in an oil bath at 90 °C, the solution was refluxed for a further 20 min. The volatile compounds of the mixture were evaporated. The remaining product was a deep red oil. The product was purified by Kugelrohr distillation (ca. 210 °C at 0.1 mbar). It was a deep red oil, which did not crystallize. Yield: 3.2 g (80% from 7). $[\alpha]_D^{20}$ = 10 deg dm^{-1} g^{-1} cm^3 (16 mg/mL, $CHCl_3$). IR (neat): 2260 cm^{-1} (vs, NCO). ^1H NMR ($CDCl_3$): δ 0.8–1.1 (multiplet; methyl, 6H), 1.2–1.7 (multiplet; $-CH_2-$, 2H), 1.7–2.1 (multiplet; methine, 1H), 2.9–3.1 (tripplet; Ar$-CH_2-$, 2H), 3.4–3.7 (tripplet; $-CH_2-$NCO, 2H), 3.7–2.0 (quartet; O$-CH_2-$, 2H), 6.8–8.0 (multiplet; Ar-H, 8H).

Synthesis and Characterization of the Polymers. From monomer **9** and hexyl isocyanate, commercially available from Kodak, a series of copolymers was prepared. The properties of these copolymers are listed in Table 1. The polymerizations were carried out in DMF at about −60 °C using a sodium cyanide initiator.[5,6] The dye concentrations of the copolymers were analyzed by UV and ^1H NMR spectroscopy. For the first method the absorbance of the π–π* transition was used. The extinction coefficient (ϵ = 24 800, λ = 251 nm) of this transition was determined from the UV spectrum of monomer **8**. To obtain well resolved ^1H NMR spectra, the polymers had to be decomposed to trimers, as described in refs 4 and 5. Both methods gave the same results and show the dye concentrations in the monomer mixture and in the resulting copolymers to be identical.

In order to determine the helicity of the polymer backbone (seven σ-bonds away from the chiral center), the chirooptical properties were investigated. The copolymers exhibited higher specific rotations, than the chiral monomer **9** ($[\alpha]_D^{20}$ = 10 deg dm^{-1} g^{-1} cm^3). The decomposition of the copolymers to trimers led to a drastic

Table 1. Characterization of Copolymers 9a–k



polymer	Y/mol %	M^a/1000	$[\alpha]_{600}^{20}$/ deg dm^{-1} g^{-1} cm^3	$[\alpha]_{600}^{20\,b}$/ deg dm^{-1} g^{-1} cm^3	[Θ] (at λ = 250 nm)/ 0.1 deg cm^2 mol^{-1}	[Θ]^b (at λ = 250 nm)/ 0.1 deg cm^2 mol^{-1}
9a	0.6	>400	+11	+9	400	400
9b	1.4	>400	+23	+26	800	1100
9c	2.3	>400	+34	+42	1200	1600
9d	4.5	>400	+72	+95	3100	3900
9e	7.6	>400	+91	+114	4000	4800
9f	10	>400	+99	+132	3900	5100
9g	15	240	+130	+165	6700	8400
9h	26	140	+157	+181	8300	10600
9i	33	130	+170	+178	8800	11500
9j	46	77	+141	+135	8600	11000
9k	55	66	+115	+108	8900	11300

[a] Peak maxima, calibrated against polystyrene standards. [b] After irradiation.

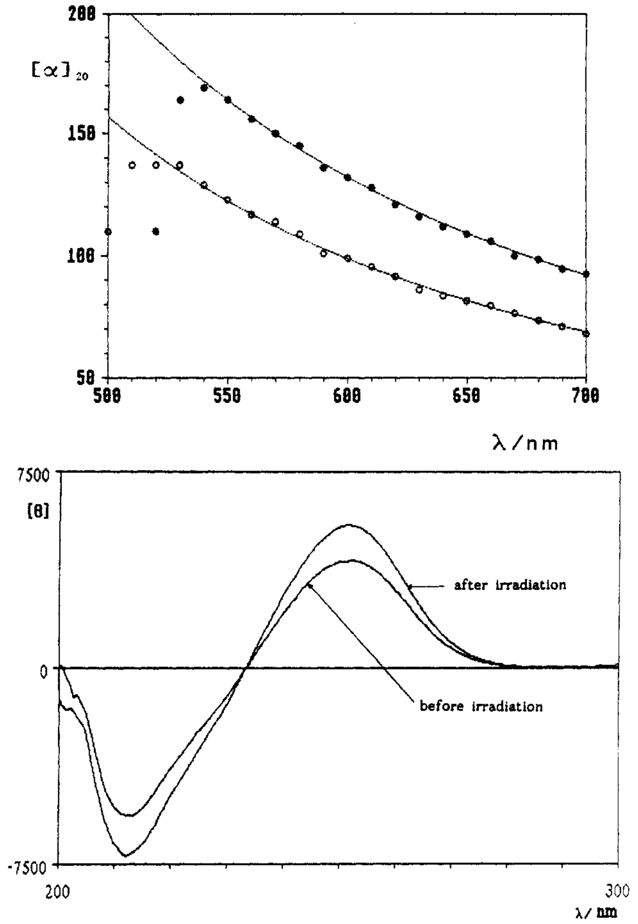


Figure 2. (a, top) ORD spectra of copolymer **9f** recorded before (□) and after (■) the photoisomerization. (b, bottom) CD spectra of copolymer **9f** recorded before and after the photoisomerization.

decrease of the specific rotations. For example polymer **9i** has a specific rotation of $[\alpha]_{600}^{20} = +141$ deg dm^{-1} g^{-1} cm^{3}, while the value of its trimer is only $[\alpha]_{600}^{20} = +4.7$ deg dm^{-1} g^{-1} cm^{3}. This indicated a chiral helical conformation of the polymer backbones.

A more direct proof was obtained from CD and ORD measurements. The CD spectra had extrema typical for chiral polyisocyanates[4,10,11] at wavelengths of the main chain absorption (Figure 2b). In addition the long wavelength of the ORD spectra (Figure 2) can be calculated by the Drude equation[16] using the absorption of the main chain. They are found to be analogous to poly((*R*)-2,6-dimethylheptyl isocyanate.[5] This all shows that the chiral center of the dye in the side chains influences the twist sense of the polymer helix. The signs of the chirooptical properties show that P helices predominate (poly((*R*)-2,6-dimethylheptyl isocyanate), which is known to exist mainly as an M helix,[9] has the opposite chirooptical signs).

Photoisomerization. Photoisomerization of the azo groups was carried out in solution (1–3 mg/mL; THF) using a polychromatic light source (Osram Ultra Vita Lux, 300 W) and a filter solution (0.16 M $CuSO_4$ + 1.2 M $NiSO_4$ + 2.13 M $CoSO_4$ + 0.42 *m* KNO_3) with a maximum transition at 340 nm. Thereby yields of at least 90% of the cis isomer could be obtained. The yields were estimated from the decrease of the absorption at 360 nm after irradiation. The conversions are probably higher as there is also some absorption of the cis isomer at this wavelength.

Changes in the population of P and M helical segments by the photoisomerization should show up in the ORD and CD spectra. The ORD spectra presented in Figure 2 were recorded before and after the irradiation. They show an increase of the specific rotations (see Table 1) for almost all polymers. The long wavelength spectra can again be fitted by the Drude equation. Since the influence of the side chain absorption is ignored in these fits, they are only functions of the chiral conformations of the main chain. The enlargements in the ORD spectra indicate an increase of P helices after the photoisomerization. The CD spectra in Figure 2 and the values in the table also show increases of the molar ellipticities after photoisomerizations. While the shape of the CD spectra measured in the range of the main chain absorption is unaffected by the photoisomerization, their absolute values increase. This corresponds to a shift of the population of P and M helical segments. Between 300 and 500 nm weak Cotton effects of the dye side chains are observed.

Both measurements show that the population of P helices can be increased by the photoisomerization of the chiral side chains. This acts as a switch, whose effect is amplified in the polymer backbone.

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