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Correlation between the Isomerization of Side Groups and the Helical Main Chain in Chiral Polyisocyanates

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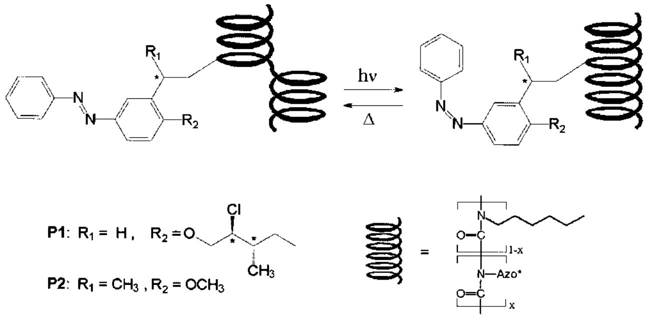
ABSTRACT: In polyisocyanates with chiral azo chromophores a change of the helical conformation can be triggered photochemically. In this investigation we studied the correlation between the isomerization of the main chain and the photoisomerizable side groups by CD measurements. A few minutes of irradiation are enough to reach a new helix equilibrium of the polymer chain. Also during slow thermal back-relaxation, the helical conformation of the polymer chain follows the isomerization of the side groups reversibly. The relation between the ratio of cis and trans isomer and the preference for one helical conformation can be linear or nonlinear. For low concentrations/inductions of the chiral side groups a linear relation is found. For higher concentrations/inductions the stronger inducting species dictates the helical conformation in accordance with the “sergeants and soldiers” principle.

Introduction

Helical polymers have been attracting attention due to their chiral structure which is common in naturally occurring polymers and due to their interesting chiro-optical properties[1−3]. For helical acrylate polymers, their screw sense is fixed kinetically during polymerization according to chirality in the monomer or catalyst, and this conformation is locked by high inversion barriers[3] between the helical senses. Polyisocyanates have much lower helix inversion barriers[3−5], which allow transformations from the P- to M-helical conformation. It is believed that their helical conformation is controlled thermodynamically in a dynamic equilibrium between P- and M-helical segments[4] through the movement of helix reversals along the chain axis. Nothing is, however, known about the kinetics of this process. Novak[5,6] has shown for structurally similar polycarbodiimides that the introduction of sterically demanding groups near the polymer chain can increase the inversion barrier. In this case annealing at elevated temperature was necessary to reach equilibrium.

We have been working with polyisocyanate copolymers, where a change of the helical conformation can be triggered photochemically.[7−10] Copolymers were made from hexylisocyanate and a chiral azo dye. Small amounts of these chiral groups are sufficient to induce a preferred helical twist sense due to the unique chiral amplification in polyisocyanates (so-called “sergeants and soldiers” copolymers).[11,12] Photoisomerization of the azo dye into the cis isomer alters the chiral induction of the chiral side groups thus triggering a change in the dynamic equilibrium between P- and M-helical segments, a switching of the polymer backbone conformation by irradiation (Scheme 1). When the sample is allowed to stand in the dark, thermal re-isomerization to the trans isomer occurs and the preirradiation state of dye absorption is restored. While the re-isomerization process of the azo side groups has been examined before,[10] we investigate now the time dependence of the helix equilibrium, i.e., how the main chain conformation follows the change in chiral induction caused by the isomerization of the chiral side groups.

Scheme 1. Schematic Representation of the Photochemical Isomerization and Thermal Back-Relaxation of the Chiral Azo Side Groups and the Induced Change between P- and M-Helical Polymer Backbone Conformation.



General Part

For this investigation two polymers were chosen (see Scheme 1), one with a stereocenter in the azo side group (**P1**) and another with a stereocenter in the spacer (**P2**). Their properties are listed in Table 1. Their synthesis is described elsewhere.[8,10] According to previous studies their structure is random. The isomerization of the azo dye can be followed by UV spectroscopy at the $\pi \rightarrow \pi^*$ absorption band, changes in the helix conformation equilibrium can be observed by circulardichroism (CD) spectroscopy measuring the molar ellipticity at the $n \rightarrow \pi^*$ transition of the amide chromophore in the polymer chain. The CD spectrum of **P1** (Figure 1) shows that the M-helix is favored with side groups in the trans form. After irradiation to the cis isomer it switches to an excess of P-helix. For **P2** (Figure 2) the negative sign of the molar ellipticity shows an excess of M-helix, which increases upon irradiation. After irradiation **P2** also shows strong Cotton effects in the

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Table 1. Properties of the Copolyisocyanates

polymer	x^a (mol %)	M_w (PS)^b ($\times 10^3$)	M_w (PIC)^c ($\times 10^3$)
P1	8.0	490	
P2	7.8	800	150

[a] Mole fraction of dye side groups, determined by UV spectroscopy. [b] Weight-average molecular weight, determined by GPC with polystyrene standards. [c] Weight-average molecular weight, determined by GPC with polyisocyanate standards.

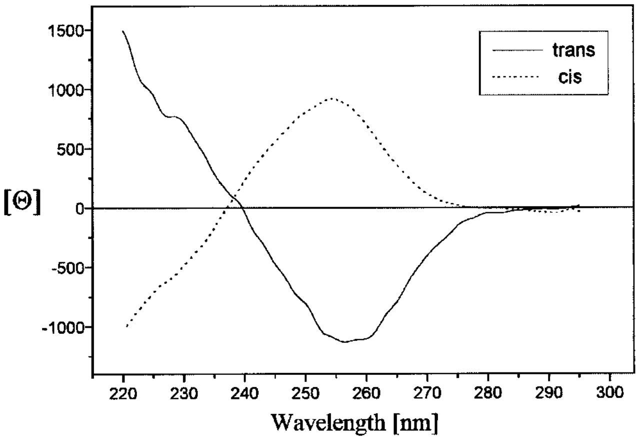

Figure 1. CD measurements for **P1** before and after irradiation. Molar ellipticities [Θ] (in 0.1 deg·cm^2·mol^{-1}) are based on the average molecular weight of the repeat unit.

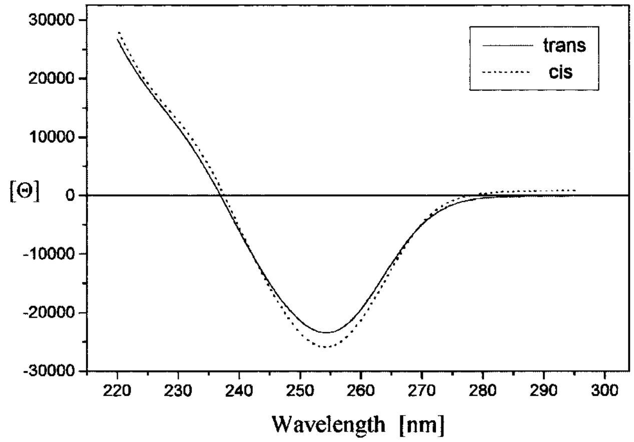

Figure 2. CD measurements for **P2** before and after irradiation. Molar ellipticities [Θ] (in 0.1 deg·cm^2·mol^{-1}) are based on the average molecular weight of the repeat unit.

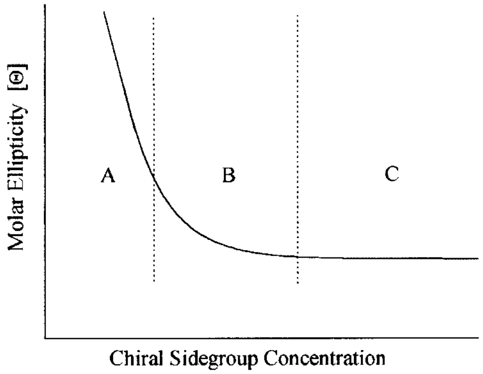

Figure 3. Dependence of the molar ellipticity [Θ] of a copolyisocyanate consisting of chiral and achiral side groups on the amount of chiral groups.

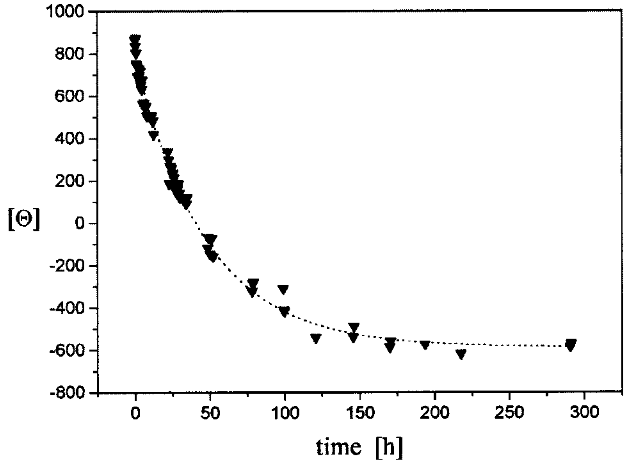

Figure 4. Thermal back-reaction of **P1**. Peak maximums of the molar ellipticity of the main chain absorption band (see Figure 1) plotted against time (0 h = end of irradiation).

region of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ absorption bands of the azo side groups due to interaction of the inherently achiral azo chromophore with its chiral surroundings.

Molar ellipticities of copolyisocyanates consisting of chiral and achiral side groups show a typical dependence on the amount of chiral groups (see Figure 3). At low chiral group concentration the ellipticity increases linearly (region A), at higher concentrations the ellipticity increases less (region B), and finally it reaches a saturation point (region C). Systems with small chiral induction show a linear dependence until higher concentrations and have lower ellipticities at the saturation point than systems with high chiral induction. The two polymer systems chosen represent different regions in Figure 3. **P1** has a small chiral induction due to a large distance between the chiral group and the helical main chain. The chiral group concentration (8 mol %) belongs to the linear part of the ellipticity–concentration curve (region A). **P2** has a chiral center close to the main chain leading to a very strong chiral induction.[10] The linear region of the ellipticity–concentration plot for this type of polymer is small; the system reaches its saturation value at low concentrations. The chiral group concentration (also 8 mol %) places it in region B but close to the saturation region.[10]

From both polymers diluted solutions (0.5 mg/mL THF) were prepared and irradiated until the photostationary state was reached. At first it turns out that immediately after a photoisomerization (about 5 min) a new ellipticity of the main chain absorption is reached. This value relaxes back to the original value during some days. This means that a new equilibrium between right- and left-handed helical sequences can be reached—under irradiation—in some minutes. During this process, multiple isomerizations do however occur, and they may facilitate the formation of helix reversals. We investigated therefore the thermal back-reaction (dark reaction) in more detail. CD and UV spectra were recorded at defined times (see Figures 4 and 5), and the solutions were stored in the dark at room temperature between measurements.

In earlier work[8,10] it had been determined that the azo groups relax back thermally in a first-order process with a half-time of about 1 day for **P1** and 2 days for **P2** (see Table 2). In a plot of the molar ellipticity Θ of the main chain absorption band—determined by CD spectroscopy—vs time (Figures 4 and 5) we see that the helix equilibrium relaxes back to the preirradiation state as well, in what seems to be a first-order process.

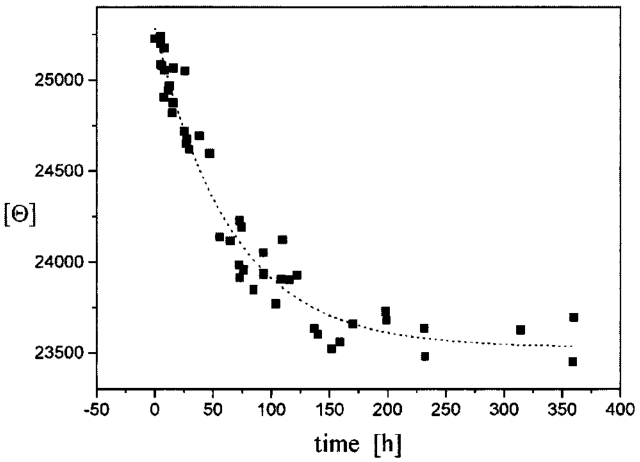

Figure 5. Thermal back-reaction of **P2**. Peak maximums of the molar ellipticity of the main chain absorption band (see Figure 2) plotted against time (0 h = end of irradiation).

Table 2. Results of the Back-Relaxation Process

polymer	half-time azo/h	half-time main chain/h
P1	25 ± 3	30 ± 2
P2	43 ± 6	43 ± 3

Under the assumption that this relaxation process shows an exponential dependence on time, its half-time $t_{1/2}$ was determined from the linearization of

$$\ln(\Theta_t - \Theta_\infty) = A - kt$$

$$t_{1/2} = (\ln 2)/k$$

(Θ_t = molar ellipticity at time t, Θ_∞ = molar ellipticity after complete re-isomerization, k = rate constant, and A = constant).

The half-time is of the same order of magnitude as that of the azo dye (Table 2). This means that the helix reversals are at room temperature on this time scale fast enough and the conformational equilibrium can follow the changes of azo isomer concentration. However, since there is a lot of scattering in the data points, deviations from first-order relaxation cannot be excluded.

For a refined investigation the molar ellipticity of the main chain absorption band (about 254 nm) is plotted vs the momentary mole fraction of trans azo dye, i.e., the fraction which has already re-isomerized to the thermodynamically more stable dye isomer. It can be calculated from the UV data, which were collected simultaneously to the CD measurements.

During re-isomerization the polyisocyanate contains two different chiral species with different chiral inductions, the trans isomer and the cis isomer. Green has stated a majority rule[13] saying that in a polyisocyanate with two competing chiral groups with opposite inductions the group with higher concentration determines the helical twist sense. If the relative chiral group concentrations are varied, the polymer exhibits the CD spectrum of the majority group except close to a 50:50 composition. In his investigation the two chiral groups have always been enantiomers and the polyisocyanate contained no achiral side groups, so it is unknown if the majority rule applies also to "sergeant and soldiers" polymers. Probably this depends on the total chiral group concentration in the polyisocyanate. It can be expected that in region A (Figure 3) the total chiral group concentration is too low, but a majority rule is more likely in region B and C, though it is probably less pronounced than in a polyisocyanate without achiral groups.

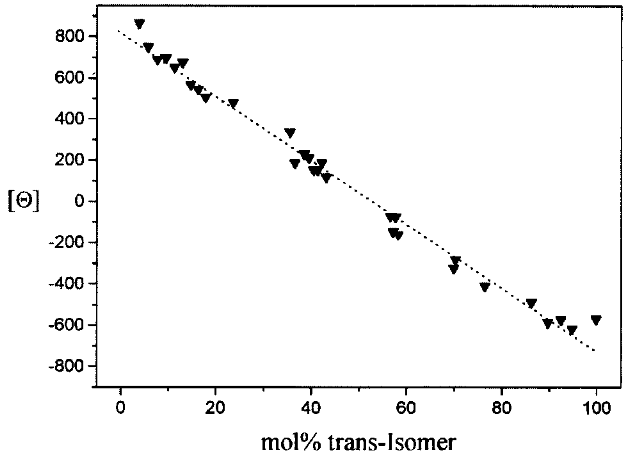

Figure 6. Molar ellipticity of the main chain absorption band of **P1** plotted against the momentary mole fraction of trans azo dye during the thermal back reaction.

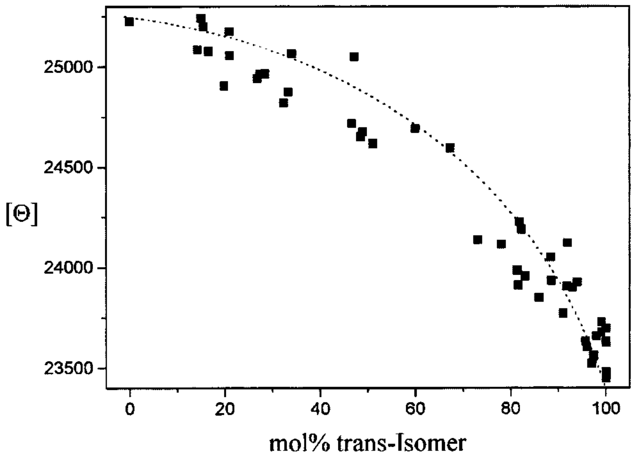

Figure 7. Molar ellipticity of the main chain absorption band of **P2** plotted against the momentary mole fraction of trans azo dye during the thermal back reaction.

The investigation shows a linear relation for **P1** (Figure 6). In this case the molar ellipticity results from a linear average of both types of chiral groups. This is expected for the region A polymer with small induction.

P2 shows a deviation from a linear relation in the plot ellipticity vs mole fraction of trans isomer (Figure 7). Here the two competing chiral species both prefer the M-helical twist sense, but for the cis-isomer the interaction is much larger. In this case the cis-isomer dictates the ellipticity till its concentration is strongly reduced. The deviation from a linear relation results from the nonlinear concentration dependence of the molar ellipticity on the chiral group concentration in region B and C.

The larger interaction between the cis-isomer and the polymer backbone in **P2** can also be seen from the strong Cotton effect at the n → π^* absorption band of the side groups. The molar ellipticity of the azo n → π^* absorption band (432 nm) has a linear correlation to the mole fraction of trans isomer during the thermal re-isomerization process (Figure 8), as is expected for a band which depends directly on azo isomer concentration and not on an excess of one helical sense. This is

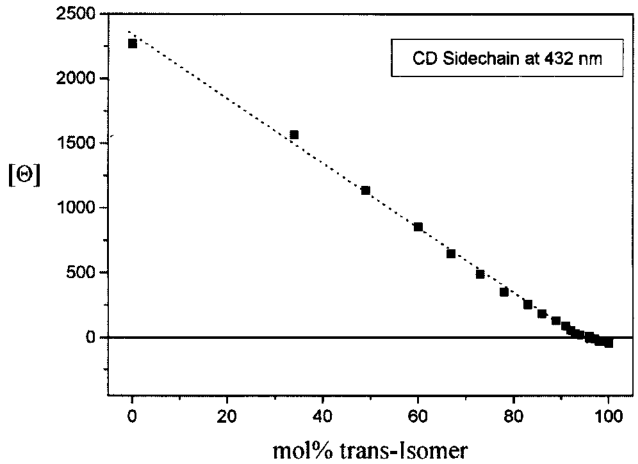

Figure 8. Changes in Cotton effects of the side groups of **P2** during back relaxation. Peak maximums of the molar ellipticity in the region of the n → π* side group absorption band (432 nm) plotted against the momentary mole fraction of trans azo dye.

another proof that the change in molar ellipticity in the amide chromophore region is connected to a change in the helix equilibrium rather than being a result of side chain Cotton effects.

The Cotton effects are a localized property of the side chain, but this microscopic change in the side chain conformation has through chiral induction and the amplification by the polymer chain a dramatic effect on the macroscopic chirooptical properties. This effect, which can be triggered photochemically, is fully reversible and repeatable which makes this material interesting for optical data storage.

Experimental Part

Molecular weights of the copolymers **P1** and **P2** were calculated from GPC measurements with polystyrene calibration (Table 1, M_w(PS)), for **P2** also with polyisocyanate standards (Table 1, M_w(PIC)). These polyisocyanate standards (4 samples of polyhexylisocyanate with different molecular weights and narrow polydispersity) were obtained by organotitanium(IV)-catalyzed polymerization, using a procedure developed by Novak et al.[14] Their molecular weights were determined by tandem GPC−light scattering and were used for linear calibration of the GPC elution volume. Comparison of the values show that molecular weights determined by polystyrene calibration are by a factor of 5 too large, due to the rodlike shape of the polyisocyanates, which cannot be compared to the polystyrene coils. Details are described elsewhere.[10]

For the investigation solutions of **P1** and **P2** with a concentration of 0.5 g/L in THF were prepared. They were irradiated with 365 nm light with a low-pressure mercury lamp (Osram HQV 125 W) with integrated filter. During irradiation the solutions were cooled with ice water. CD spectra were recorded with a computer-supported Jasco J500 A spectropolarimeter, UV spectra were obtained with a Schimadzu UV 2102 spectrometer.

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