Interplay of Chiral Side Chains and Helical Main Chains in Polyisocyanates

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ABSTRACT: Here we describe the synthesis of seven new copolymer series prepared by copolymerization of hexyl isocyanate with seven new chiral azo chromophores with an isocyano functionality. The resulting copolyisocyanates (Nylon 1) possess a helical polymer conformation. In the cases in which the chiral group and polymer chain are linked to the same phenyl ring (copolymer series **VI**−**IX**) a transfer of chirality to the polymer chain is possible. I.e. one helical twist sense is preferred in this case. By variation of the chiral center, polymers with preferable right- or left-handed helical conformation are accessible. The photochemical isomerization of the azo chromophore (trans → cis) is possible in high yields (>90%). This leads, depending on the nature of the chiral center, either to an increase of the chiral interaction (further increase of the amount of already preferred helix conformation) or to a decrease of the chiral interaction (more racemic situation). Based on these results, a picture for the interplay of chiral side chains and helical polymer chain is developed. Measurements of circular dichroism (CD) spectra in the range of the azo-chromophore absorption prove the dominant role of the helical polymer chain. They show, in addition, that the chromophores can form a chiral superstructure mediated by the polymer chain. Some of these polymers show strong changes of their optical rotation during photoisomerization. This can be caused either by a shift of the equilibrium between right- and left-handed helical segments or by Cotton effects of the azo chromophores.

Introduction

Poly(alkyl isocyanates) (Nylon 1) possess a helical main chain conformation in the crystalline state (X-ray analysis of poly(butyl isocyanate) indicates a 3/8 helix).[1,2] In solution, the secondary structure is similar.[2−4] Functionalized polyisocyanates, for example poly(3-(benzoyloxy)-*n*-propyl isocyanate)[5] and poly(3-[(benzoyloxy)carbonyl]-*n*-propyl isocyanate),[5] are also known to possess a helical conformation in solution. As long as the side chains are achiral, the main chains exist as racemic mixtures of right- and left-handed helices. If the side chains possess chiral centers of one configuration, then right- and left-handed helical segments of the polymer chain become diastereomers and are no longer thermodynamically equivalent. Due to the high cooperativity of the helical conformation (a helix reversal is likely to occur only after several 100 monomer units[6]) small energy differences per monomer between a right- and a left-handed conformation are amplified. It is thus possible to shift the dynamic equilibrium between right-handed (P helices[2]) and left-handed (M helices) by chiral isotope effects[8,9] or by small amounts of chiral comonomers in copolymers.[10] These polymers exist predominantly in one helical conformation and show high optical activities. [The assignment of P and M is based according to refs 6 and 7 on the sign of the Cotton effect for the long wavelength absorption of the amide chromophore in the main chain (UV maximum at 250 nm), which is positive for right-handed helices and vice versa. It should not be mixed with the mathematical twist sense of a right-handed helix, which is negative.]

Here we present polyisocyanates which are functionalized with chiral azo chromophores as side chains. Although the asymmetric carbon atom is far away from the main chain in these polymers (6−15 σ-bonds) a strong preference for one helical conformation (twist sense) of the polymer chain is often achieved.

It was the aim of this work to vary the chirooptical properties (optical rotation and circular dichroism) of these polymers by the reversible photoisomerization of the azo-dye unit. Such materials are interesting for optical data storage. Principally, this is possible in two ways using the photochemically induced variation of the interaction of chiral side groups and the helical main chain. In one case this may lead to a shift of the equilibrium between P and M helices. Alternatively, also changes of the Cotton effects of the azo chromophores can lead to strong changes in the optical rotation.

In two short papers[11,12] we were able to demonstrate such an effect for one system. Here we want to present detailed investigations on seven copolymer systems to establish structure property relations and to study the transfer of chirality from the azo chromophores to the polymer backbone and vice versa.

Results and Discussion

Synthesis. Starting from the observation that a chiral center seven σ-bonds away from the polymer backbone can induce an excess of one helical twist sense,[11] we decided to vary the position and the nature of the chiral center systematically in order to establish structure−property relations. For this purpose seven new chiral azo chromophores, which are functionalized with isocyanate groups, were synthesized (monomers **3**−**9**, see Chart 1).

These monomers were copolymerized with hexyl isocyanate (**1**) to prepare the copolymer series **III**−**IX** (see Chart 2). For comparison the achiral azo chromophore **10** was synthesized and terpolymerized with hexyl isocyanate (**1**) and (*R*)-2,6-dimethylheptyl isocyanate (**2**) to produce the terpolymer series **X**.

During polymerization it turned out that the molecular weight generally decreases with increasing amount of azo monomers. A homopolymerization of the azo monomers was not possible with sodium cyanide, presumably due to steric hindrance. The first attempts to

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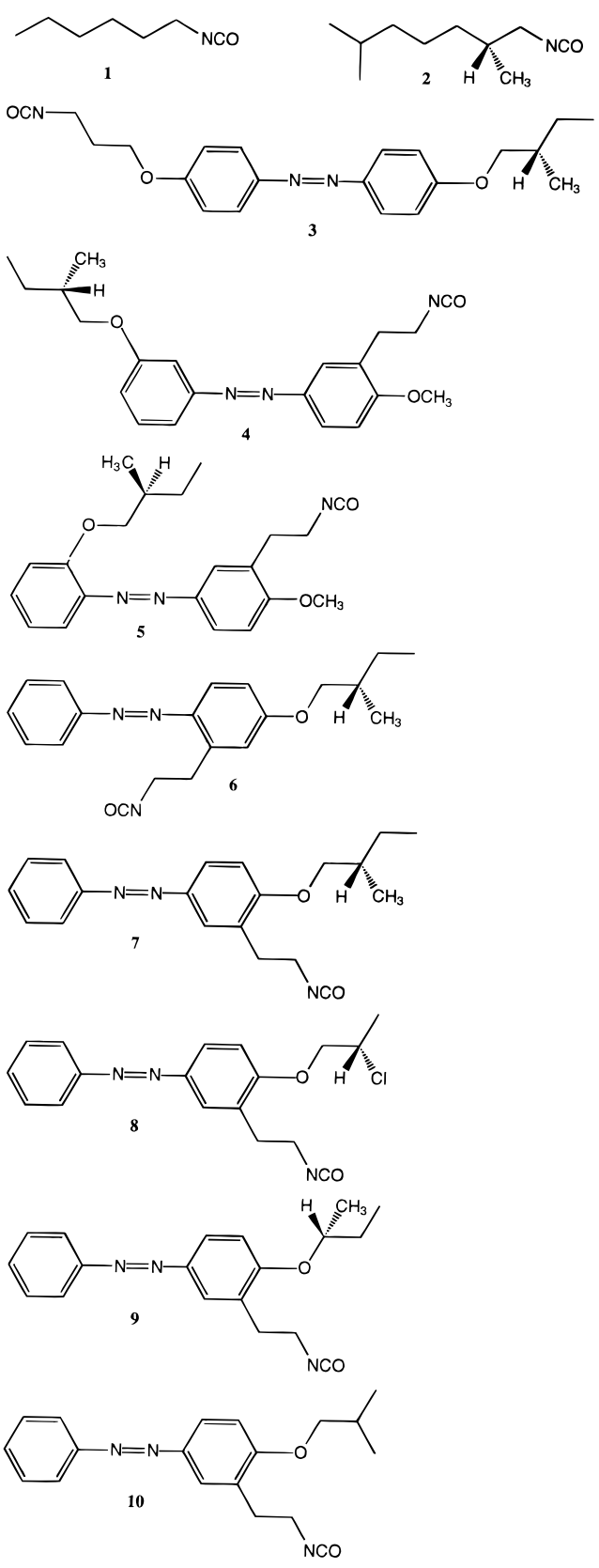
Chart 1



use $TiCl_3(OCH_2CF_3)$[13] were not successful, even in the case of copolymers that could be polymerized without problems by using sodium cyanide.

The composition of the copolymers was determined, for at least one member of each series, by ^1H NMR spectroscopy, after degradation of the polymer to trimers. With this composition the extinction coefficient of the polymer-linked azo chromophore (trans $\pi \rightarrow \pi^*$ transition) was determined for each series. This was used to determine the composition of the remaining copolymers of the series. The results are compiled in Tables 1−5. Usually, the composition of the copolymers is very close to the composition of the monomer mixture. This points to a nearly ideal copolymerization. In agreement with the NMR results of ref 10 and the mass spectrometry results in ref 14, the chirality of the comonomer has no influence on the incorporation into the helical polymer.

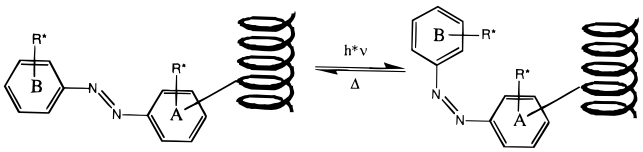


Figure 1. Schematic representation of the isomerization of the chiral azo-dye side chains.

Variation of the Position of the Chiral Center. In the copolymer series **III**−**VII** (Table 1 and Figure 1) the same chiral group (2-(*S*)-methylbut-1-oxy) was used, but it was linked to the azo chromophore in very different positions (see Figure 1). This was done to find the optimal geometry, in which the interaction with the polymer chain is still strong enough to favor one twist sense, but at the same time strongly dependent on the conformation of the azo chromophore (trans or cis). Especially the geometry realized in copolymers **IV** and **V** seemed promising for this purpose. This did, however, not hold true. All copolymers (series **III**−**V**), in which the chiral groups were linked to the phenyl ring B (Figure 1), did not show the chirooptical properties typical for chiral isocyanates. This means no high optical rotation and no CD bands in the region of the main chain absorptions (amide chromophore below 280 nm).

This was found both for the cis and trans conformation (Table 1). Obviously, the distance between the chiral center and the polymer backbone is too large to allow an efficient transfer of chirality.

A transfer of chirality is only observed in the copolymer series **VI** and **VII**, in which the chiral group is linked to phenyl ring A (Figure 1) meta or ortho to the linkage to the polymer chain. For these copolymers the optical rotation is much higher than that of monomers **6** and **7** (see Tables 1 and 2) and CD bands are observed in the region of the amide chromophore (main chain). While these effects are still small for copolymers **VI** (Table 1), they are very large for the copolymer series **VII** (ortho substitution, Table 2). This shows that it is essential to link the chiral group and polymer backbone to the azo chromophore in close proximity.

Variation of the Chiral Center. In the series of copolymers **VII**−**IX** (Tables 2−4) different chiral groups were linked at the same position (ortho to the polymer chain) to the azo chromophore. This was done to investigate the influence of the chiral center's nature on the chiral induction. Copolymers **VIII** and **IX** differ from copolymer **VII** concerning the fact that strongly polar atoms (chlorine or oxygen) are linked to the asymmetric carbon atom.

CD spectra of these three series show the properties typical for chiral polyisocyanates (Figure 2) in the absorption range of the amide chromophore (<300 nm). This proves the preference for one helical twist sense according to the "sergeants and soldiers principle".[10] Using the sign of the CD spectra (Figure 2), it is possible

Chart 2

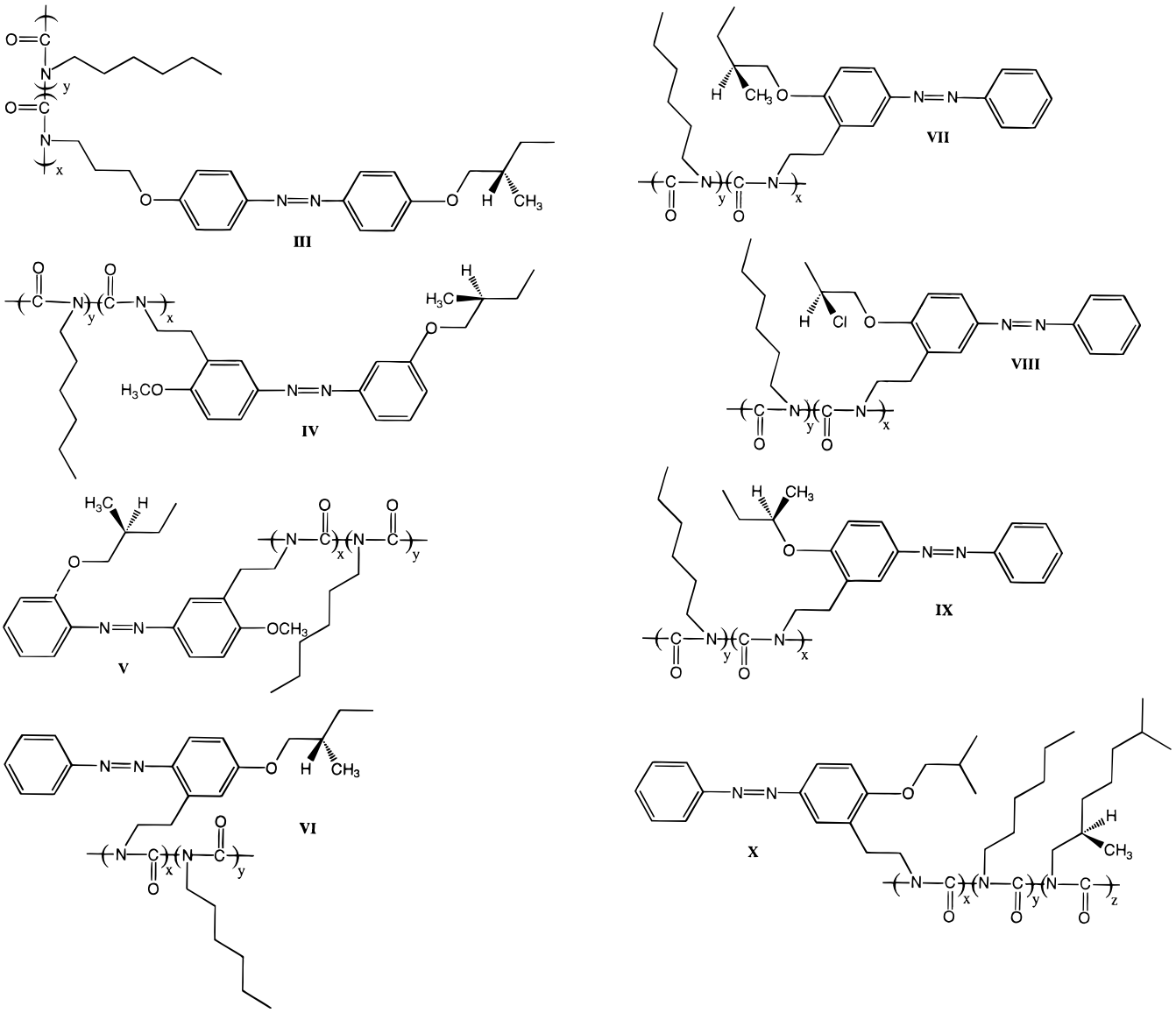


Table 1. Characterization and Properties of Copolymers of Series III−VII

polymer	x_{mon}[a]/mol %	$x_{^1H\ NMR}$[b]/mol %	x_{UV}[c]/mol %	yield/%	M[d]/1000	$[\alpha]^{20}_D$[e,f]/deg dm^{-1} g^{-1} cm^3	$[\alpha]^{20}_D$[e,g]/deg dm^{-1} g^{-1} cm^3
III 3	11	9	9	20	>300	+2	
III 5	38		36	43	40	+5	+10
IV 4	20	17	17	56	>1000	+3	−17
IV 5	36		34	52	800	+9	−19
V 4	23	19	19	63	250	<+1	−8
VI 1	3		3	68	300	+10	+5
VII 3	2		2	69	>300	+29	+43
VII 6	10	10	10	70	>300	+94	+130

[a] Dye concentrations before the polymerizations. [b] Dye concentrations determined from the ^{1}H NMR spectra of trimers. [c] Dye concentrations determined from the UV spectra of the polymers. [d] Peak maxima: GPC, Hewlett-Packard 1048B with UV detector (λ = 254 nm); THF as solvent; columns, Waters Ultrastyragel 10^3 Å (30 cm) and PL-Gel 10^4 Å (30 cm); calibrated against polystyrene. [e] Measured in THF at concentrations of 2 mg/mL; cell length, 10 cm. [f] Before irradiation. [g] After irradiation.

to determine the preferred twist sense of the polymer chains in comparison to poly((*R*)-2,6-dimethylheptyl isocyanate) (the homopolymer from monomer **2** (Chart 1) has a left-handed helix. The twist sense of this reference has been assigned by a force field evaluation[6] and by investigations of lyotropic cholesteric states[9,15]). It turns out that the copolymer series **VIII** and **IX** exist preferably in the left-handed helical (M) conformation, whereas the copolymer series **VII** prefers the right-handed (P) conformation. For all these copolymer series the molar ellipticities at the n → π^* transition of the main chain are comparable, if comparable amounts of chiral chromophores are used.

Photochemical Isomerization and Its Influence on the Main Chain Conformation. The photochemical isomerization (trans → cis) of the azo side chains was performed with a mercury low-pressure lamp by exposing a solution of the polymers to the emitted light (maximal intensity at 365 nm) for 60 min. Since the absorption spectra of the cis and trans forms overlap only slightly, the isomerization can be easily followed by UV spectroscopy (see Figure 3). After irradiation the

Table 2. Characterization and Properties of the Copolymers of Series VII

polymer **VII**	x_{mon}[a]/ mol %	$x_{^1HNMR}$[b]/ mol %	x_{UV}[c]/ mol %	yield/ %	M[d]/ 1000	$[\alpha]^{20}_D$[e,f]/deg dm^{-1} g^{-1} cm^3	$[\alpha]^{20}_D$[e,g]/deg dm^{-1} g^{-1} cm^3	$[\Theta]$[f,h]/0.1 deg cm^2 mol^{-1}	$[\Theta]$[f,h]/0.1 deg cm^2 mol^{-1}	$[\alpha]$[g,h]/0.1 deg cm^2 mol^{-1}	λ[g,i]/nm
1	0.6		0.4	69	>300	+10	+13	500	251	400	253
2	1.4		1.4	64	>300	+23	+26	800	250	1100	252
3	2.3		2.2	69	>300	+29	+43	1400	252	1700	251
4	5.4		5.3	64	>300	+72	+95	3100	255	4600	255
5	7.6		7.6	40	>300	+81	+112	4000	253	4800	252
6	10	10	10	70	>300	+94	+130	4500	255	6700	256
7	15	15	17	55	240	+110	+144	6300	256	8600	255
8	26	23	27	65	140	+139	+164	7200	257	9700	255
9	33	33	33	69	130	+153	+168	9000	255	12000	256
10	42		42	65	77	+129	+128	7700	258	11000	259
11	55		53	80	66	+114	+96	8600	260	12900	255

[a–g] Cf. Table 1. [h] Maximum molar (all monomeric units) ellipticities correlated to the n ↔ π^* transition of the main chains; measured in THF at concentrations of 0.5 mg/mL; cell length, 1 mm. [i] Wavelength of the CD maxima correlated to the n → π^* transition of the main chains.

Table 3. Characterization and Properties of the Copolymers of Series VIII

polymer **VIII**	x_{mon}[a]/ mol %	$x_{^1HNMR}$[b]/ mol %	x_{UV}[c]/ mol %	yield/ %	M[d]/ 1000	$[\alpha]^{20}_D$[e,f]/deg dm^{-1} g^{-1} cm^3	$[\alpha]^{20}_D$[e,g]/deg dm^{-1} g^{-1} cm^3	$[\Theta]$[f,h]/0.1 deg cm^2 mol^{-1}	λ[f,i]/nm	$[\alpha]$[g,h]/0.1 deg cm^2 mol^{-1}	λ[g,i]/nm
1	1.0		0.7	66		−16	−18	−900	254	−1100	253
2	2.4		2.3	74	300	−70	−83	−3600	256	−4000	255
3	5.0		1.4	45	30	−30					
4	8.4		7.9	75	130	−154	−160	−8200	256	−8200	255
5	17	15	16	72	70	−216	−209	−12100	256	−11700	256
6	26	24	24	67	180	−208	−194	−13400	258	−11600	256

[a–c] Cf. Table 1. [d] Peak maxima: GPC, Waters liquid chromatography system with UV detector (λ = 254 nm); $CHCl_3$ as solvent; columns, PL-Gel 10^3 Å and PL-Gel 10^4 Å; calibrated against polystyrene. [e–g] Cf. Table 1. [h,i] Cf. Table 2.

Table 4. Characterization and Properties of the Copolymers of Series IX

polymer **IX**	x_{mon}[a]/ mol %	$x_{^1HNMR}$[b]/ mol %	x_{UV}[c]/ mol %	yield/ %	M[d]/ 1000	$[\alpha]^{20}_D$[e,f]/deg dm^{-1} g^{-1} cm^3	$[\alpha]^{20}_D$[e,g]/deg dm^{-1} g^{-1} cm^3	$[\Theta]$[f,h]/0.1 deg cm^2 mol^{-1}	λ[f,i]/nm	$[\Theta]$[g,h]/0.1 deg cm^2 mol^{-1}	λ[g,i]/nm
1	2.6		1.8	46	>1000	−20	−19	−780	255	−780	256
2	4.6		4.6	70	>1000	−48	−47	−2000	254	−1900	256
3	11	10	10	68	700	−98	−85	−4200	256	−4100	255
4	20	17	18	35	200	−129	−85	−6000	258	−5000	256
5	50	47	47	69	80	−189	+9	−12300	260	−8500	257

[a–c] Cf. Table 1. [d] Cf. Table 3. [e–g] Cf. Table 1. [h,i] Cf. Table 2.

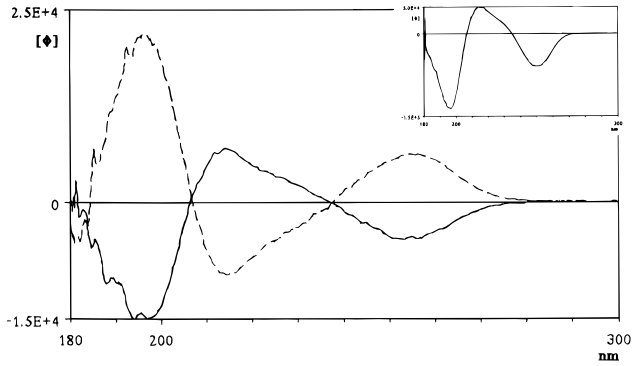


Figure 2. CD spectra of poly (*R*)-2,6-dimethylheptyl isocyanate (right corner, left-handed helix), copolymer **VII 6** (− −, right-handed helix) and copolymer **IX 2** (—, left-handed helix). The spectra were measured with hexane as solvent and concentrations of 0.5 mg/mL.

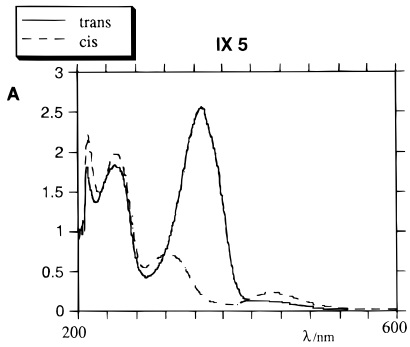


Figure 3. UV spectra of copolymer **IX 5**. The spectra were measured with THF as solvent and a concentration of 0.47 mg/mL.

absorption at the maximum of the $\pi \rightarrow \pi^*$ transition of the trans component is decreased to less than 10% in all cases. Since the cis component shows also some absorption at this wavelength, this means that less than 10% of the trans component remains in the photochemical equilibrium. The kinetics of the thermal back-reaction (cis → trans) was measured for polymers **VII 6** and **IX 4** in detail. The half-life times were in the range of 1 day. Therefore the properties of these cis components can be measured easily after irradiation (time required about 1 h) without changing the ratio of cis- to trans-azo chromophores significantly.

CD spectra taken before and after irradiation allow it to detect changes in equilibrium between right- and left-handed helical segments caused by the photochemical isomerization. Figure 4 presents an example (copolymer **VII 6**, Table 2), for which the molar ellipticity, and thus the preference for a right-handed conformation, is increased by the trans → cis isomerization. The maxima and the zero points of the bands associated with the amide chromophore in the main chain remain unchanged during isomerization (this is of course not found for the Cotton effects of the azo-chromophore discussed later). Figure 5a and Table 2 show that this is a general property. For the copolymers of series **VII** the photochemical trans → cis isomerization, indepen-

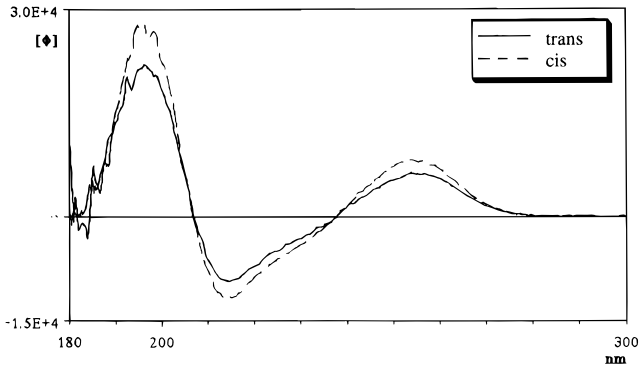


Figure 4. CD spectra of copolymer **VII 6**. The spectra were measured with hexane as solvent and concentrations of 0.5 mg/mL.

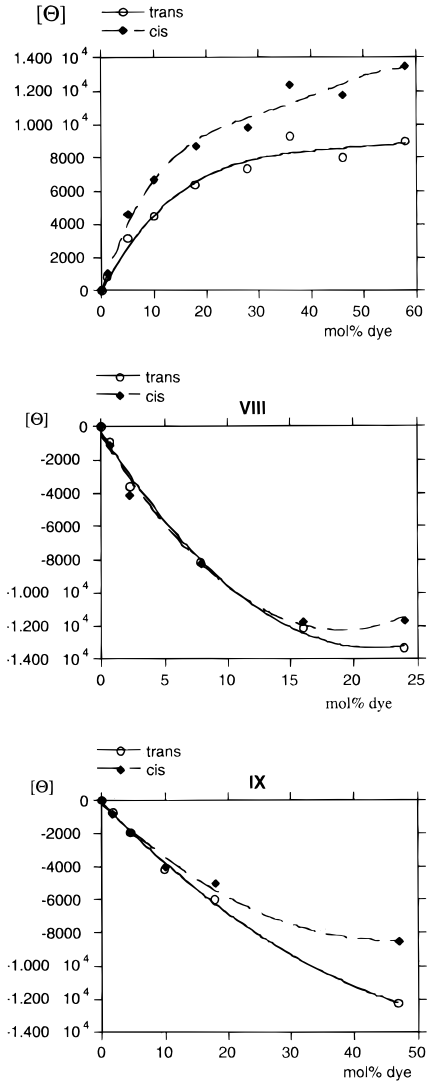


Figure 5. Dependence of the molar ellipticities (n → π^* transition of the main chain at about 250 nm) on the concentrations of chiral dye side chains of copolymer series **VII** (a), **VIII** (b), and **IX** (c).

dent of the amount of chiral azo chromophores, leads to an increase of the amount of right-handed (P) helices.

For the copolymer series **VIII** (Table 3 and Figure 5b) the effect of the photochemical isomerization depends on the amount of azo chromophore in the polymer. For small amounts of azo chromophore the percentage of left-handed helices is increased upon irradiation (trans → cis); for high amounts of azo chromophores it is

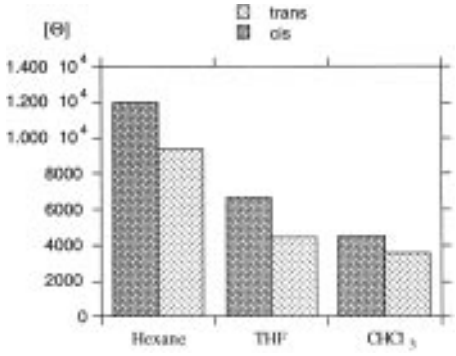


Figure 6. Molar ellipticities (n → π^* transition of the main chain at about 250 nm) of copolymer **VII 6** in different solvents at similar concentrations (about 0.5 mg/mL).

decreased. For intermediate concentrations of azo chromophores, no effect of the isomerization is observed.

For the copolymer series **IX** (Table 4 and Figure 5c) photochemical isomerization does influence the equilibrium between right- and left-handed helical segments only for high dye concentrations. In this case a decrease of the amount of left-handed helices is observed. For smaller amounts of azo chromophores, the photochemical isomerization does not influence the chiral induction between chiral side chains and helical polymer chains.

An explanation of these rather differing results would require a detailed understanding of the interaction of the chiral center in the side chains with the helical polymer chain. Little is, however, known about this, because the side chains are conformationally highly flexible. Thus, the vicinity of the chiral center can exist in different conformations. It is, presumably, most of the time solvated and interacts with the helical polymer chain only every now and then. The magnitude of this interaction, and presumably even their sign, will be different for the different conformations of the side chains. The preference for one twist sense of the polymer main chain results finally from an excess of side chains being in a favorable conformation. The energy gain per repeat unit may, however, still be small and the effect only detectable due to the strong amplification by the polymer main chain (remember that a chiral isotope effect[8] is enough for a chiral induction). The situation is therefore completely different from polypeptides, in which there is a strong preference for one conformation. Theoretically, it is, however, very difficult to predict small differences between larger opposing effects. It is, therefore, not yet possible to predict the twist sense, or even the magnitude of the interaction, from the structure of these chiral side groups.

The fact that the interaction between chiral side chains and the helical polymer main chain depends on a delicate balance of different effects shows up clearly in the solvent dependence (Figure 6). The great differences in the molar ellipticities measured for the trans and cis forms in different solvents show that the equilibrium between right- and left-handed helices is strongly solvent dependent. The high molar ellipticities in hexane, which show that the equilibrium is strongly shifted to one side, can be explained by the poor solvating power of hexane for the azo side chains. In fact, polymers with more than ca. 20 mol % of azo side chains are insoluble in hexane. Since the chiral side chains are poorly solvated, they will interact more strongly with the polymer chain.

The next effect to be explained is the dependence of the molar ellipticities (Figure 5) and thus of the equi-

librium of right- and left-handed helices on the concentration of the chiral azo chromophores.

As to be expected from the "sergeants and soldiers principle",[10] they increase and saturate finally. The limiting value of a molar ellipticity of −50 000 deg 0.1 cm^2 mol^{-1}, measured for poly((*R*)-2,6-dimethylheptyl isocyanate) is, however, not reached by any of the copolymer series **VII**−**IX**. This value would correspond to a polymer chain, which is only right- or left-handed. It seems, thus, that the interaction between chiral side chains and the helical main chain is reduced, as the concentration of side chains is increased. Possible reasons for this might be (i) simple space requirements (as the concentration of bulky side chains is increased, they might find the space required to interact with the main chain already occupied by a neighbor. They might then adopt a conformation in which the chiral center stretches away from the main chain), (ii) the formation of superstructures of the chromophores, which might interact with the main chain in a different way, and (iii) in an extreme case the high concentration of bulky side groups possibly disturbing the helical conformation of the backbone. This should lead to a decrease of the cooperativity. It should be mentioned that this should lead to a change of the CD spectra in the range of the exciton-couplet of the amide chromophores (180−235 nm). Within the experimental limitations this has so far not been observed. The wavelength region of interest is, however, only partially accessible, because polymers with high concentrations of azo chromophores are not soluble in pure hydrocarbons.

Chiral Environment of the Azo Side Chains. One method to learn more about the orientation of the side chains with respect to the helical main chain and possible interactions among the side chains are CD measurements in the absorption range of the azo chromophore (300−400 nm, $\pi \rightarrow \pi^*$ transition, 400−550 nm, n $\rightarrow \pi^*$ transitions). In a first step we tried to determine the origin of these CD signals, which are small compared to the CD signals of the polymer backbone (<300 nm). They might either result from the chiral center directly attached to the chromophore or from an interaction with the helical polymer chain. A first hint that the interaction of the azo chromophores with the helical polymer chain is most important comes from a comparison of copolymer **VII 10** with its trimer (see Figure 7). While CD signals are clearly detectable for the helical polymer, only noise can be detected for the trimer that lacks the helical conformation. The direct interaction between chiral carbon atom and azo chromophore should, however, be similar in both systems.

In order to determine the most important chiral element for the CD signals more accurately, the terpolymer **X** was used for comparison (see Table 5). In terpolymer **X** only the interaction of the achiral azo chromophore with the helical polymer chain is likely (see Figure 8). The chiral side chains (monomer **2**) are present only to 5 mol %. Figure 8 shows a comparison of the CD spectra of copolymer **VII 10** (Table 2) and terpolymer **X 6** (Table 5). Both spectra are, except for the opposite sign, identical. This is as to be expected, if the chiral main chain conformation is the origin of the CD spectra of the azo chromophores.

Since polymer **VII 10** has a preferably right-handed helix and polymer **X 6** a preferably left-handed helix, opposite signs of the CD signals are to be expected in this case.

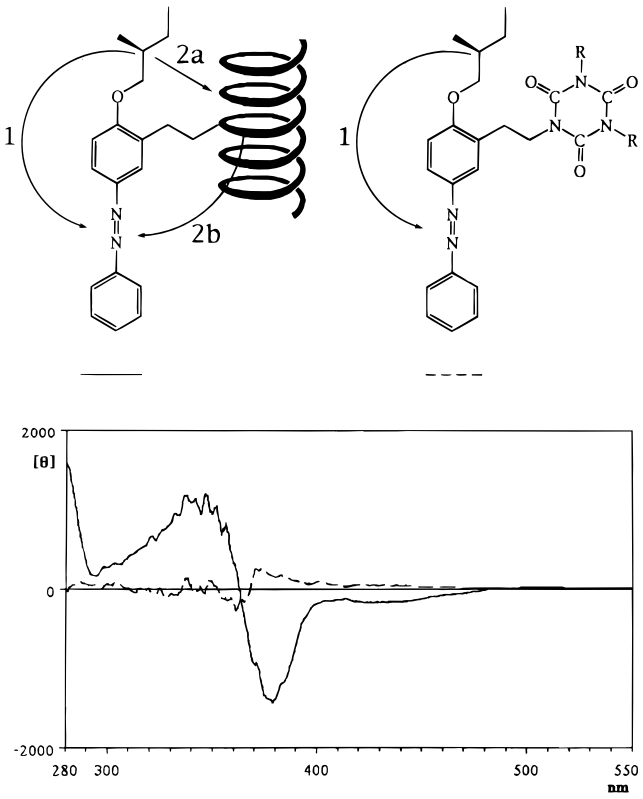
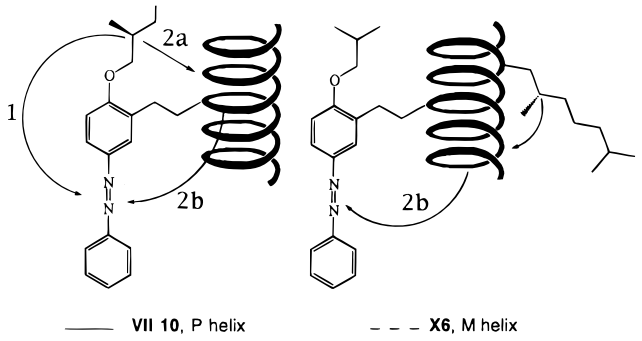


Figure 7. CD spectra of copolymer **VII 10** (42 mol % chiral dye side chains, trans form) before and after the decomposition to trimers. The spectra were measured in the absorption range of the dye side chains with THF as solvent at concentrations of 0.5 mg/mL.

Another observation in Figure 8 is very important. The band corresponding to the $\pi \rightarrow \pi^*$ transitions of the trans-azo chromophore (see Figure 3, 360 nm) is split into two bands with opposite sign. They cross the wavelength axis (zero transition) at the wavelength of maximal absorption in the UV spectrum. They have therefore to be considered as exciton couplets, which prove a superstructure. Therefore at least two, or more, chromophores have to interact electronically in a chiral superstructure imposed by the polymer chain.

According to these results the interplay of helical polymer chain and chiral side chains is rather complex. The chiral centers in the side chain are the only permanent source of chiral information; so they determine the preference for right- or left-handed helices of the main chain. Once this preference is established, the helical main chain takes over and dominates the electronic properties of the side chain chromophores. More than this, it orients the chromophores into chiral superstructures. This can explain the concentration dependence of the chiral induction. For small amounts of chiral side chains, each side chain interacts individually with the polymer chain. At higher dye concentrations, when the chances for nearest neighbor interactions are great, a chiral superstructure of the chiral side chains is formed, as evident from the appearance of CD couplets. These superstructures will have a different conformation than individual chromophores and will interact differently with the polymer chain.

If this is true, the CD spectra should change for polymers with small amounts of azo chromophores, for which most of the chromophores are isolated. Unfortunately, this could not yet be measured due to intensity problems. At first the signals for isolated chromophores



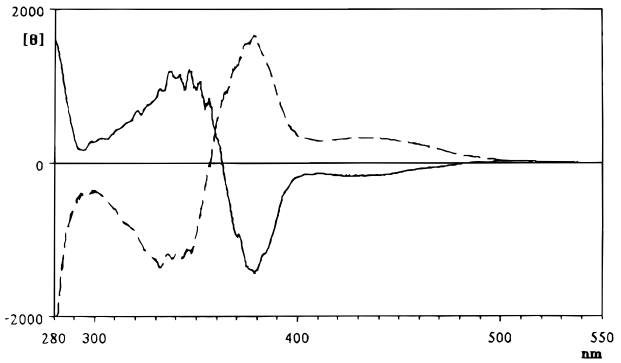
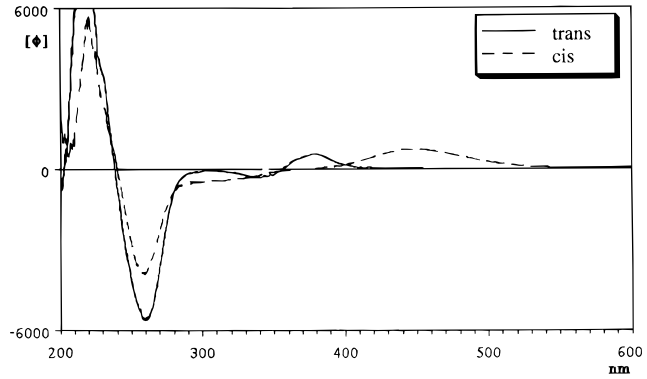


Figure 8. CD spectra of copolymer **VII 10** (42 mol % chiral dye side chains, trans form) and terpolymer **X6** (42 mol % achiral dye side chains, trans form, and 5 mol % chiral alkyl side chains). The spectra were measured in the absorption range of the dye side chains with THF as solvent at concentrations of 0.5 mg/mL.

are likely to be much less intense than the CD couplets. Secondly, they are present only in small concentrations for the polymers of interest. Thirdly, CD measurements in the range from 300 to 400 nm are only possible in low concentrations, due to the strong linear absorption of the azo chromophores. Therefore the CD signals disappear, for polymers with a low concentration of azo chromophores, just under the experimental noise.

Our investigations give a clue to the interplay of side chains and helical polymer backbones. In addition the polyisocyanates we synthesized are also interesting from the point of view of materials science: Materials, which change their optical rotations upon irradiation, are promising candidates for optical data storage applications.

Switching of the Optical Rotation by Photoisomerization. Characterization of the polymer series **VII**−**X** (Tables 2−5) has shown that it is possible to switch the optical rotation by light. This can be done using different principles. For copolymers of series **VII** and dye concentrations of less than 66 weight % (42 mol %) one concept is realized. For these polymers the ORD spectra above 500 nm are comparable to those of the non-dye-containing chiral polyisocyanates.



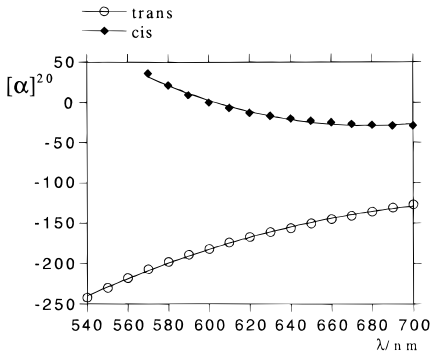


Figure 9. CD spectra (a, c = 0.5 mg/mL in THF) and ORD spectra (b, c = 2.0 mg/mL in THF) of copolymer **IX 5**.

The photoisomerization (trans → cis) increases the percentage of right-handed (P) helical segments. This leads to an increase of the optical rotation[11] (see Table 2).

If the concentration of chromophores is increased further in the copolymer series **VII**, Cotton effects of the side chain chromophores become important. They act in this case opposite to the increase of the percentage of right-handed helical segments. This leads to a decrease of the change of optical rotation during photoisomerization.

A second concept, which gives rise to strong changes in the optical rotation during photoisomerization, is realized in the polymer series **IX** and **X**. In this case the optical effects are mainly based on changes of the Cotton effects of the side chain chromophores. This is shown in Figure 9 for copolymer **IX 5**. Photochemical trans → cis isomerization leads in this case to a decrease of the excess of left-handed helical segments (i.e. a more racemic situation). In addition the Cotton effects in the range of the azo chromophore absorption change strongly (see Figure 9a). Both effects act in the same direction. This leads to a decrease of the specific rotation $[\alpha]^{20}_D$ from −189 to +9 deg dm^{-1} g^{-}1cm^3 (see Figure 9b).

A similar effect, but this time exclusively based on changes of the Cotton effects of the azobenzene chromophores, is found for terpolymer **X D** (see Figure 10).

Table 5. Characterization and Properties of the Terpolymers of Series X

polymer **X**	**1**/ mol %	**2**/ mol %	x_{mon}[a]/ mol %	$x_{^1HNMR}$[b]/ mol %	x_{UV}[c]/ mol %	yield/ %	M[d]/ 1000	$[\alpha]^{20}_D$[e,f]/deg dm^{-1} g^{-1} cm^3	$[\alpha]^{20}_D$[e,g]/deg dm^{-1} g^{-1} cm^3	$[\Theta]$[f,h]/0.1 deg cm^2 mol^{-1}	λ[f,i]/nm	$[\Theta]$[g,h]/0.1 deg cm^2 mol^{-1}	λ[g,i]/nm
0	95	5	0			65	1000	−350		17 400	255		
1	91	5	4		4	70	410	−323	−340	19 000	255	19 300	255
2	89	5	6		7	75	1500	−301	−323	18 100	255	18 500	255
3	87	5	8		8	68	1000	−281	−307	14 200	255	14 400	255
4	84	5	11	11	11	66	990	−288	−318	16 900	256	17 600	255
5	70	5	25		26	61	110	−227	−252	13 700	256	15 700	256
6	51	5	44	42	42	54	600	−159	−157	10 600	258	14 600	256
D	0	79	21		21	77	120	−435	−765	36 600	250	39 600	250

[a−c] Cf. Table 1. [d] Cf. Table 3. [e−g] Cf. Table 1. [h,i] Cf. Table 2.

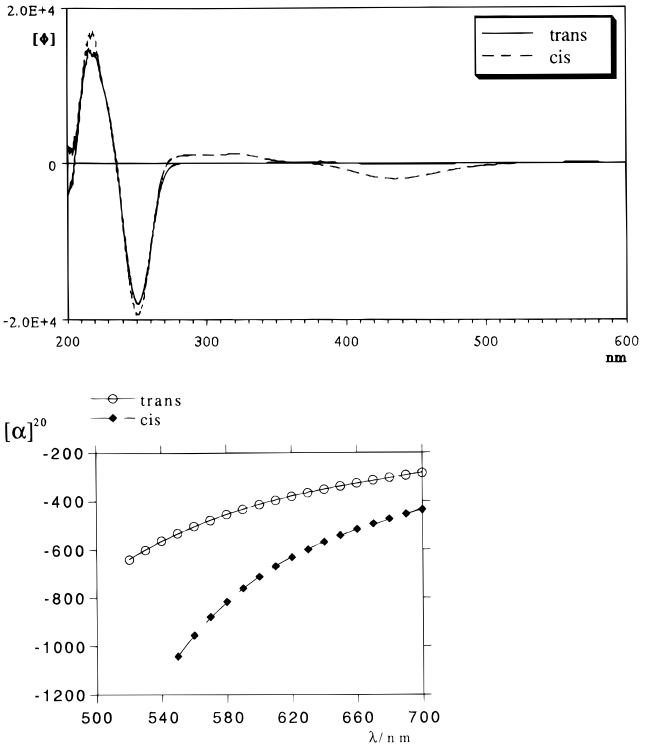


Figure 10. CD spectra (a, $c = 0.5$ mg/mL in THF) and ORD spectra (b, $c = 2.0$ mg/mL in THF) of copolymer **X D**.

Figure 10a shows the CD spectra before and after isomerization. Only small changes are observed at wavelengths smaller than 300 nm.

In this case, in which the vicinity of the chiral center is unchanged upon photoisomerization (the chiral center stems from monomer **2**, Chart 1), the equilibrium between right- and left-handed helices is unaffected. However, the Cotton effects of the azo chromophores change strongly upon isomerization. As a consequence (see Figure 10b) the specific rotation $[\alpha]^{20}_D$ is increased from −435 to −765 deg dm^{-1} g^{-1} cm^3.

Experimental Part

The hexyl isocyanate (**1**) we used was commercially available from Kodak. (*R*)-(+)-2,6-Dimethylheptyl isocyanate (**2**) was synthesized as described in refs 8 and 16. The synthesis of the monomers **3**−**6** are presented in ref 17.

3-(1-Hydroxy-4-(phenylazo)-2-phenyl)propionic Acid. 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.[18] 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. ^{1}H NMR (acetone-d_6): δ 2.6−2.8 (triplet, −CH$_2$−COO−, 2H), 2.8−3.1 (triplet, Ar−CH$_2$−, 2H), 6.9−7.1 (doublet, Ar−H, 1H), 7.3−8.0 (multiplet, Ar−H, 7H).

3-(1-Hydroxy-4-(phenylazo)-2-phenyl)propionic Acid Ethyl Ester. 3-(1-Hydroxy-4-(phenylazo)-2-phenyl)propionic acid (30.0 g, 111 mmol), 75 mL of ethanol, 250 mL of chloroform, and 3 mL of concentrated sulfuric acid were heated under reflux for 8.5 h by the procedure of an azeotropic esterification. The solution was extracted two times with water (250 mL), two times with a saturated solution of $NaHCO_3$ (250 mL), and again three times with water (250 mL). After evaporating the solvent, the product remained as a red oil, which crystallized slowly. Yield: 33.1 g (100%). Mp: 92−98 °C. ^{1}H NMR ($CDCl_3$): δ 1.1−1.4 (triplet, methyl, 3H), 2.6−2.8 (triplet, −CH$_2$−COO−, 2H), 2.8−3.1 (triplet, Ar−CH$_2$−, 2H), 6.8−7.0 (doublet, Ar−H, 1H), 7.3−7.6 (multiplet, Ar−H, 3H), 7.6−8.0 (multiplet, Ar−H, 4H).

3-(1-((*S*)-2-Methylbutoxy)-4-(phenylazo)-2-phenyl)propionic Acid. 3-(1-Hydroxy-4-(phenylazo)-2-phenyl)propionic acid ethyl ester (29.4 g, 99 mmol), 4.25 g (103 mmol) of (*S*)-2-methyl-1-butyl tosylate,[19] 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.[20] The precipitate was filtered off and extracted with acetone. After evaporation of the solvent the ester remained in the form of 28.1 g of red crystals. When the crude compound 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. 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: 18.5 g (75%). Mp: 88−94 °C. $[\alpha]_D^{20} = 9.8$ deg dm^{-1} g^{-1} cm^3 (20 mg/mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.8−1.2 (multiplet, methyl, 6H), 1.2−1.6 (multiplet, −CH$_2$−, 2H), 1.6−2.1 (multiplet, methine, 1H), 2.9−3.2 (triplet, −CH$_2$−COO−, 2H), 3.4−3.7 (triplet, Ar−CH$_2$−, 2H), 3.7−4.0 (quartet, O−CH$_2$−, 2H), 6.8−7.0 (doublet, Ar−H, 1H), 7.2−7.6 (multiplet, Ar−H, 3H), 7.6−8.0 (multiplet, Ar−H, 4H).

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 3-(1-((*S*)-2-methylbutoxy)-4-(phenylazo)-2-phenyl)propionic acid 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-phenyl)-ethyl Isocyanate (7). Trimethylsilyl azide[21] (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). ^{1}H 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 (triplet, Ar−CH$_2$−, 2H), 3.4−3.7 (triplet, −CH$_2$−NCO, 2H), 3.7−4.0 (quartet, O−CH$_2$−, 2H), 6.8−7.0 (doublet, Ar−H, 1H), 7.2−7.6 (multiplet, Ar−H, 3H), 7.6−7.8 (multiplet, Ar−H, 4H).

2-(1-[((*S*)-2-Chloropropyl)oxy]-4-(phenylazo)-2-phenyl)ethyl Isocyanate (8). Monomer **8** was synthesized in the same way as monomer **7**. Instead of (*S*)-2-methyl-1-butyl tosylate, (*S*)-2-chloro-1-propyl tosylate was used for the Claisen etherification. (*S*)-2-Chloro-1-propanol for the synthetization of the tosylate analogous to that in ref 19 was prepared from L-alanin.[22,23] IR (neat): 2260 cm^{-1} (vs, NCO). ^{1}H NMR ($CDCl_3$): δ 1.6−1.7 (doublet, methyl, 3H), 2.95−3.1 (triplet, Ar−CH$_2$−, 2H), 3.55−3.7 (triplet, −CH$_2$−NCO, 2H), 4.1−4.2 (doublet, O−CH$_2$−, 2H), 4.25−4.45 (multiplet, methine, 1H), 6.85−7.0 (doublet, Ar−H, 1H), 7.4−7.6 (multiplet, Ar−H, 3H), 7.75−7.95 (multiplet, Ar−H, 4H).

3-(1-((*R*)-2-Butyloxy)-4-(phenylazo)-2-phenyl)propionic Acid. 3-(1-((*S*)-2-Methylbutoxy)-4-(phenylazo)-2-phenyl)-propionic acid (6.0 g, 20 mmol), 7.9 g (30 mmol) of triphenylphosphine, 1.8 g (24 mmol) of (*S*)-2-butanol, and 60 mL of dry ether were stirred in a freezing mixture of NaCl/ice. After the slow (25 min) addition of 4.8 mL of diethyl azodicarboxylate the mixture was stirred 1 h under cooling and 6 h at room temperature.[24] The precipitate was filtered off and extracted with ether. The solvent was evaporated, and the remaining oil was extracted with boiling ligroin (bp: 80 −100 °C). After the ligroin was evaporated, the crude compound was purified by flash chromatography and Kugelrohr distillation (ca. 220 °C at 0.05 mbar).

When the crude compound was heated in a solution of 3 g of sodium hydroxide in 30 mL of water and 30 mL of ethanol under reflux for 1 h, the ester was saponified. The product was precipitated by neutralization with hydrochloric acid and separated by vacuum filtration. It was a deep red oil, which did not crystallize. Yield: 4.9 g (70%). $[\alpha]_D^{20} = -34$ deg dm^{-1} g^{-1} cm^3 (20 mg/mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.9−1.1 (triplet, methyl, 3H), 1.25−1.5 (doublet, methyl, 3H), 1.6−1.9 (multiplet, $-CH_2-$, 2H), 2.65−2.8 (triplet, $-CH_2-COO-$, 2H), 2.95−3.15 (triplet, $Ar-CH_2-$, 2H), 4.35−4.55 (multiplet, methine, 1H), 6.85−7.0 (doublet, Ar−H, 1H), 7.35−7.6 (multiplet, Ar−H, 3H), 7.7−8.0 (multiplet, Ar−H, 4H).

3-(1-((*R*)-2-Butyloxy)-4-(phenylazo)-2-phenyl)ethyl Isocyanate (9). Monomer **9** was prepared from 3-(1-((*R*)-2-butyloxy)-4-(phenylazo)-2-phenyl)propionic acid in the same way as monomer **7** was synthesized from 3-(1-((*S*)-2-methylbutoxy)-4-(phenylazo)-2-phenyl)propionic acid. $[\alpha]_D^{20} = -23$ deg dm^{-1} g^{-1} cm^3 (20 mg/mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.9−1.1 (multiplet, methyl, 3H), 1.25−1.45 (multiplet, methyl, 3H), 1.6−1.9 (multiplet, $-CH_2-$, 2H), 2.8−3.1 (two triplets, $Ar-CH_2-$, 2H), 3.35−3.65 (two triplets, $-CH_2-NCO$, 2H), 4.3−4.55 (multiplet, methine, 1H), 6.85−7.0 (triplet, Ar−H, 1H), 7.35−7.55 (multiplet, Ar−H, 3H), 7.7−7.95 (multiplet, Ar−H, 4H).

2-(1-[(2-Methylpropyl)oxy]-4-(phenylazo)-2-phenyl)-ethyl Isocyanate (10). Monomer **10** was synthesized in the same way as monomer **7**. Instead of (*S*)-2-methyl-1-butyl tosylate, 2-methyl-1-propyl tosylate was used for the Claisen etherification. ^{1}H NMR ($CDCl_3$): δ 1.0−1.2 (doublet, methyl, 6H), 2.0−2.3 (multiplet, methine, 1H), 2.95−3.15 (triplet, $Ar-CH_2-$, 2H), 3.5−3.65 (triplet, $-CH_2-NCO$, 2H), 3.75−3.95 (doublet, $-O-CH_2-$, 2H), 6.9−7.0 (doublet, Ar−H, 1H), 7.35−7.6 (multiplet, Ar−H, 3H), 7.7−7.8 (multiplet, Ar−H, 4H).

Synthesis and Characterization of the Polymers. From monomers **3**−**9** and hexyl isocyanate, commerically available from Kodak, a series of copolymers (**III**−**IX**) were prepared. The terpolymer series **X** was synthesized from the monomers **1**, **2**, and **10**. The properties of these copolymers are listed in Tables 1−5. The polymerizations were carried out in DMF at about −60 °C using a sodium cyanide initiator.[25] The dye concentrations of the copolymers were analyzed by UV and ^{1}H NMR spectroscopy. For the first method the absorbances of the $\pi \rightarrow \pi^*$ transitions (trans form) was used. The extinction coefficients of these transitions were determined from the UV spectra of the copolymers, which had been analyzed by ^{1}H NMR spectroscopy.

To obtain well-resolved ^{1}H NMR spectra, the polymers had to be decomposed to trimers, as described in refs 10 and 16. Both methods gave the same results and show the dye concentrations in the monomer mixture and in the resulting copolymers to be identical.

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