Chiral Polyisocyanates from an Azomonomer with a Very High Chiral Induction

Ralf Mruk and Rudolf Zentel*

Institute of Organic Chemistry, University of Mainz, Duesbergweg 10-14, 55099 Mainz, Germany

Received March 21, 2001; Revised Manuscript Received October 9, 2001

ABSTRACT: The synthesis of new chiral polyisocyanates is described. For this purpose a new chiral azobenzene containing monomer with the chiral center in α-position to the isocyanate group was synthesized. The anionic copolymerization was carried out in THF as solvent with potassium cyanide that was complexed by 18-crown-6 as initiator. This allowed a better control of the reaction and thereby the synthesis of polyisocyanates with a fairly low polydispersity. The copolymers show an extremely high transfer of chirality from the chiral side groups to the helical backbone in dilute solution. Copolymers with only 1.6 mol % of chiral side groups show nearly the full optical rotation and exist predominantly in the P-helical conformation. It was found that the isomerization of the azobenzene groups hardly has any influence on the conformation of the helix. Lyotropic liquid crystalline phases were formed from the polymers and 1,2-dichlorobenzene. It could be shown that even polymers with a very low content of chiral side groups (1.6 mol %) form cholesteric phases with a selective reflection in the visible range. The pitch of the cholesteric phase and thereby the wavelength of the selective reflection bands could be reversibly altered by the isomerization of the azobenzene groups.

Introduction

Helical polymers[1] (e.g., DNA, polypeptides) are frequently found in nature. They have attracted attention due to their chiral structure and the resulting chiro-optical properties.[2−4] The helical structure of natural helical polymers is stabilized by hydrogen bonds and can be altered by temperature or pH changes.

In addition to these well-known natural helical polymers, several classes of synthetic helical polymers have been prepared.[5−9] One class of these synthetic helical polymers are poly(alkyl isocyanates) that can be prepared by cyanide initiated anionic polymerization of alkyl isocyanates in DMF at low temperatures.[10,11] It was shown that poly(alkyl isocyanates) possess a helical conformation due to steric reasons which exists in solution as well as in the crystalline state. The exclusive use of achiral isocyanate monomers leads to a racemic mixture of M- and P-helical sequences in the polymer. The ratio between M- and P-helices can be shifted by the use of chiral comonomers. Due to the high cooperativity within the polymer chains only small amounts of chiral side groups in copolymers are necessary to favor one twist sense of the helices. The ability of the chiral side groups to force the achiral groups into a certain conformation and to determine the twist sense of the helix is called the "sergeants-and-soldiers" effect.[12−14] The extent of this effect depends on the chiral induction of the monomer.

The conformation of the helices in a "sergeants-and-soldiers" copolymer can be additionally influenced by the isomerization of chiral side chains. The use of photoisomerizable side groups (e.g., azobenzene groups) may allow a photoinduced switching of the helix between two conformations.[15−17] The influence of the photoisomerization of azobenzene containing side groups on the conformation of the helix has been shown for several polymers by CD spectroscopy. In addition to the chiral induction of the monomer, the distance between the isomerizable group and the main chain is an important factor in this influence.

Polyisocyanates with chiral side groups form lyotropic cholesteric phases[18,19] at higher concentrations (about 40 wt %). It was found that even small amounts of chiral groups possess a large influence on the formation of the cholesteric phase.[20] The characterization of these cholesteric phases requires polymers with a narrow molecular weight distribution to minimize the occurrence of defects in the orientation. In addition to a low polydispersity, a fairly low molecular weight is favorable as a low viscosity improves the formation and orientation of the cholesteric phase.

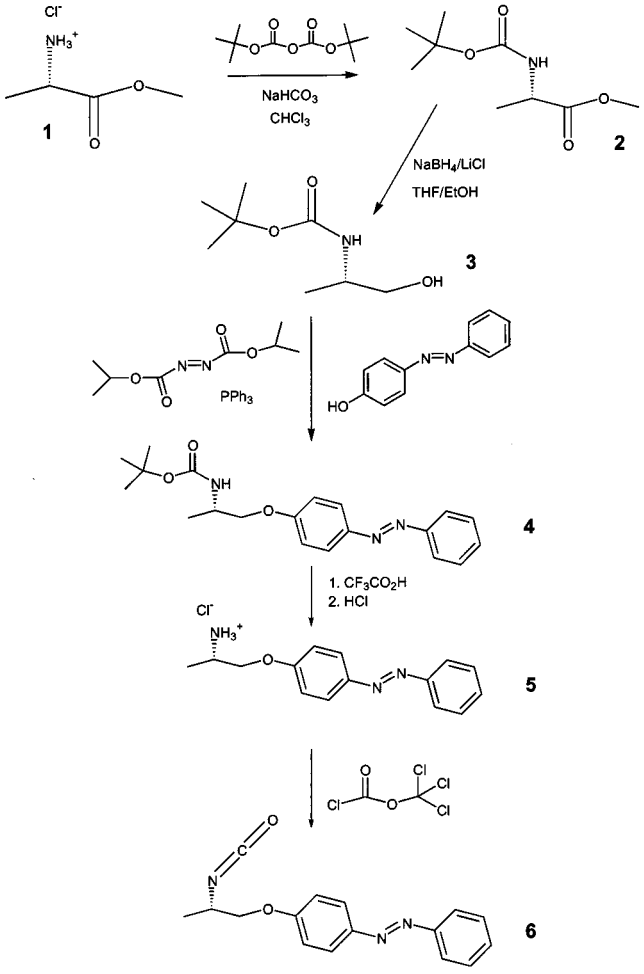
Here we report the synthesis of a new chiral azomonomer with an extremely high chiral induction and its polymerization to chiral copolymers, which follow the "sergeants-and-soldiers" principle. Due to a modification of the polymerization conditions the polydispersity could be kept fairly low. Finally, lyotropic cholesteric phases were prepared, the pitch of which can be switched by photoisomerization.

Results and Discussion

Synthesis of a New Chiral Monomer. The chiral center of the chiral side groups that were previously incorporated in photochromic polyisocyanates had a distance of at least two σ-bonds from the main chain.[17] By lowering this distance to one σ-bond, the chiral induction of the side groups should increase dramatically. This is confirmed by the work of Green et al. who reported very high values of specific rotation for poly-(2-deuteriohexyl isocyanate) whose chirality only consisted in an isotope effect.[21] However, the synthesis of polyisocyanates with a chiral center with a higher chiral induction in α-position to the main chain implies that the incorporation of a secondary isocyanate would be necessary. It is known that secondary isocyanates do not homopolymerize but the copolymerization of cyclohexyl isocyanate with butyl isocyanate has been reported in the literature.[22] According to this report, it should be possible to synthesize photochromic polyisocyanates with chiral centers in α-position to the main chain.

10.1021/ma010491n CCC: $22.00
Published on Web 11/30/2001

Scheme 1. Synthesis of Monomer 6

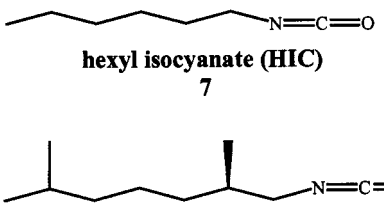


The new isocyanate monomer **6** was prepared in a five-step synthesis (Scheme 1) starting with alanine methyl ester hydrochloride **1**. After the BOC-protection of the amino group[23] the resulting ester was reduced by sodium boranate/lithium chloride[24] to give the BOC−protected amino alcohol **3**. In the next step the alcohol **3** was coupled with 4-hydroxyazobenzene in a Mitsunobu reaction.[25] For the cleavage of the BOC protection group the resulting ether **4** was treated with trifluoroacetic acid and afterward with hydrochloric acid to give the hydrochloride **5**. In the last step the hydrochloride **5** was transformed into the isocyanate **6** by reaction with trichloromethyl chloroformate[26,27] in dioxane.

The syntheses of the comonomers hexyl isocyanate (HIC, **7**) and (*R*)-2,6-dimethylheptyl isocyanate (DMHIC, **8**) were carried out as described in the literature.[17,21,28] All used monomers are listed in Scheme 2.

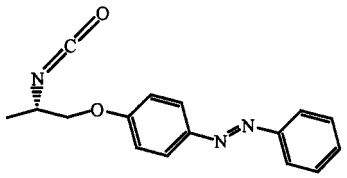
Synthesis of the Polymers. The conventional anionic polymerization of isocyanates is carried out in DMF with sodium cyanide as initiator at temperatures lower than −40 °C.[10,11] This method leads to polymers with high polydispersity and high molecular weights. As the formation of cholesteric phases from the resulting polymers should be examined a fairly low polydispersity and a fairly low molecular weight is required. An alternative polymerization method that leads to polyisocyanates with low polydispersities and low molecular weights is the coordination polymerization with titanium catalysts.[18,29] As these titanium catalysts are deactivated in the presence of azobenzene groups,[30] this method is completely unsuitable for the synthesis of photochromic polyisocyanates. Therefore an alternative method for the synthesis of azobenzene group containing polyisocyanates with a low polydispersity must be found.

Scheme 2. Used Monomers



hexyl isocyanate (HIC)
7

(R)-(+)-2,6-dimethylheptyl isocyanate (DMHIC)
8



4-((2,S)-isocyanatopropoxy)azobenzene
6

One reason for the poor controllability of the classical anionic polymerization is the fact that the polymer is insoluble in the solvent so that it readily precipitates after formation. The use of a better solvent (e.g., toluene or THF) should improve the controllability of the reaction. Another problem is the solubility of the initiator. As alkali cyanides are insoluble in most organic solvents the initiator has to be modified as well. Following this idea, Okamoto et al. polymerized HIC and DMHIC in toluene with a solution of sodium cyanide in DMF as initiator.[31] Our approach to this problem is the solubilization of cyanide in organic solvents by the use of crown ethers. Crown ethers form stable cryptates with alkali-metal ions and are able to solubilize alkali-metal salts in organic solvents.

The polymerization reactions were carried out in THF with a solution of 18-crown-6 and potassium cyanide in THF as initiator at a temperature of −60 °C. In contrast to the classical polymerization the precipitation of the polymer did not occur until 5 min after the injection of the initiator. The chiral monomer **6** was copolymerized with HIC and DMHIC to form co- and terpolymers. The structure of the resulting polymers is shown in Scheme 3.

Characterization of the Polymers. The amount of the azo-containing monomer **6** in the resulting polymer was determined by UV spectroscopy, whereas the ratio between DMHIC and HIC was determined by NMR spectroscopy. The ratio of the monomers in the reaction batch and in the polymer is listed in Table 1.

It can be seen that in most cases the fraction of azo monomer incorporated into the polymer was larger than in the reaction batch. This does not match the expectations because of the steric demand of this monomer. One possible explanation for this is that monomer **6** preferably coordinates to the potassium counterion.

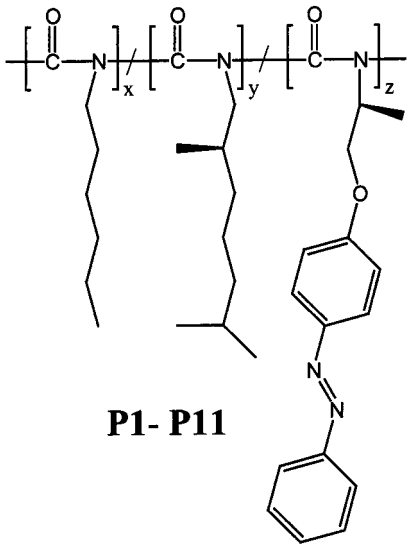
The polydispersities and the molecular weights of the polymers were determined by GPC with light scattering detection. The results of the GPC analysis are shown in Table 2.

Table 1. Characterization of Polymers P1−P11 (Scheme 3)[a]

	χ(HIC)		χ(DMHIC)		χ(monomer **6**)			specific rotation
polym	*m*	*p*	*m*	*p*	*m*	*p*	*M* (g/mol)	$[\alpha]_D^{20}$(0.1 deg·cm²·g⁻¹)
P1	0.995	0.995			0.005	0.005	128.0	+234
P2	0.990	0.984			0.010	0.016	129.7	+416
P3	0.984	0.988			0.016	0.012	129.0	+416
P4	0.983	0.970			0.017	0.030	131.9	+442
P5	0.974	0.970			0.026	0.030	131.7	+448
P6	0.971	0.965			0.029	0.035	132.6	+442
P7	0.962	0.953			0.038	0.047	134.5	+476
P8	0.854	0.928	0.146	0.072			130.2	−348
P9	0.860	0.927	0.126	0.055	0.013	0.017	132.2	+204
P10	0.870	0.921	0.110	0.050	0.020	0.029	133.8	+344
P11	0.869	0.905	0.103	0.046	0.029	0.049	136.6	+448

[a] χ(HIC): mole fraction of HIC; χ(DMHIC): mole fraction of DMHIC χ(monomer **6**): mole fraction of monomer **6** (Scheme 2). Key: *m* = monomer ratio in the reaction batch; *p* = ratio of comonomers in the polymer; *M* = average molecular weight of repeating units.

Scheme 3. Structure of Polymers



It can be seen that the polydispersity of all polymers is lower than 2 and the molecular weights of all polymers are fairly low when a high ratio of initiator is used. These results show that the new polymerization method leads to much narrower molecular weight distributions and lower molecular weights than the conventional precipitation polymerization.[18] The coordination polymerization leads to even lower polydispersities than the new method,[18,29] but it is not applicable to the synthesis of azobenzene containing polyisocyanates. Therefore the modified anionic polymerization represents the best way for the synthesis of low polydispersity azobenzene containing polyisocyanates known so far.

The influence of the chiral side chains on the twist sense of the helices was examined by measuring the specific rotations of the polymers in dilute solution (Table 1 and Figure 1). It can be observed that even polymer **P3** with a molar fraction of chiral side groups of only 1.2 mol % shows a specific rotation of over 400°. At higher fractions of chiral side groups, the specific rotation hardly increases with the concentration of the chiral groups but approaches a final value. The comparison of the azo-containing polymers with copolymers of HIC and DMHIC (Figure 2 and Scheme 4) shows that the final values of the specific rotation are quite similar. The difference between these polymers is the concentration of chiral monomers that is necessary to receive specific rotations that are close to the final value. In the case of the new azo-containing polymers 1.2 mol %

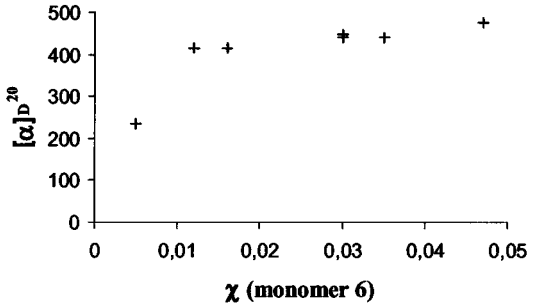


Figure 1. Specific rotation of the copolymers as function of the fraction of chiral side chains.

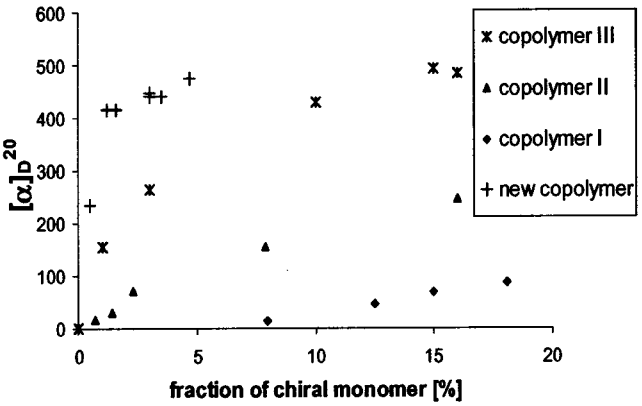


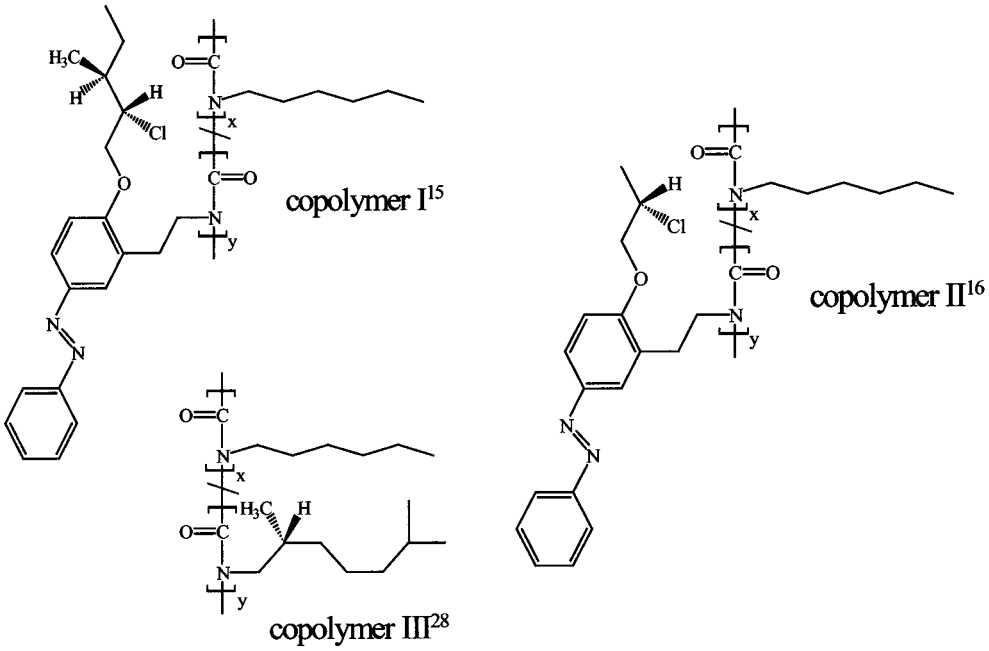
Figure 2. Specific rotation of several copolymers in dependence of the fraction of chiral side chains.

Table 2. Results of GPC Analysis

polymer	M_w (g/mol)	M_n (g/mol)	M_w/M_n
P1	112 600	64 300	1.75
P2	133 400	68 900	1.94
P3	197 300	107 500	1.84
P4	140 000	80 100	1.75
P5	243 000	156 800	1.55
P6	288 500	173 100	1.67
P7	268 100	170 500	1.57
P8	235 500	172 800	1.36
P9	238 200	148 000	1.61
P10	282 300	161 000	1.75
P11	230 900	134 600	1.72

of chiral monomer is a value sufficient to reach a value of specific rotation that is higher than 80% of the final value. In contrast to that, about 10 mol % of DMHIC must be incorporated in a copolymer with HIC to reach similar values of specific rotation.[28] Other chiral azo monomer containing polymers (Scheme 4) with a distance between the chiral center and the main chain that is larger than six σ-bonds do not reach comparably high

Scheme 4. Structure of Formerly Synthesized Polyisocyanate Copolymers



values of specific rotation even when the fraction of chiral monomers is as high as 20 mol %[12,15,16] (Figure 2).

The high values of specific rotation in the polymers are caused by a transfer of chirality from the chiral monomers to the main chain according to the "sergeants-and-soldiers" experiment. The occurrence of the plateau of specific rotation above a certain concentration of chiral monomers can be explained by the fact that almost all helices exist in one helix twist sense above this point. Therefore a further increase of the concentration of chiral monomers hardly has any further influence on the conformation of the helices. Only 1.2 mol % of monomer **6** is sufficient to reach the plateau of specific rotation. By that monomer **6** by far shows the strongest transfer of chirality according to the "sergeants-and-soldiers" experiment that is known so far.

The influence of the photoisomerization of the azobenzene side groups on the properties of the polymers was examinated by UV, ORD, and CD spectroscopy.

The photochemical trans → cis isomerization of the azobenzene group can be easily observed by UV spectroscopy.[32] The UV spectra of polymer **P7** before and after irradiation at a wavelength of 365 nm are shown in Figure 3. The most obvious sign of the isomerization is the shift of the $\pi-\pi^*$ transition to shorter wavelengths and the loss of intensity of this transition. As

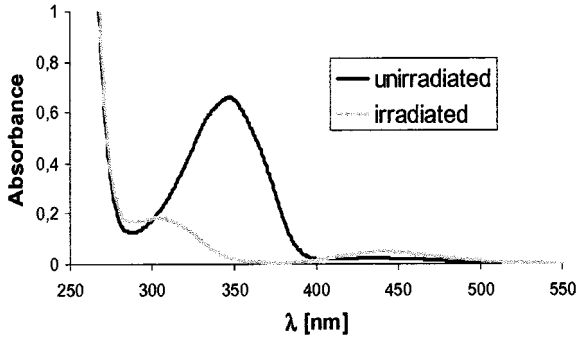


Figure 3. UV spectra before and after irradiation.

less than 10% of the initial absorbance at the maximum of the $\pi-\pi^*$ transition of the trans form is left after irradiation, it can be concluded that at least 90% of the azobenzene groups have been isomerized into the cis form.

The influence of the photochemical isomerization on the chirality of the system was examinated by ORD spectroscopy. The ORD spectra of several polymers in solution were measured before and after irradiation (Figure 4).

The optical rotation of the polymers increases during isomerization. The difference between the specific rotation of the cis and the trans form increases with shorter wavelengths. However, in comparison to other systems,[15,16] the influence of the photoisomerization on the specific rotation is rather small. Due to the extremely high chiral induction that is caused by the presence of the chiral group in α-position to the main chain, the helix is strongly forced into one conformation. This conformation is so stable that it is hardly influenced by the photoisomerization of the side chains.

The influence of the photoisomerization on the conformation of the main chain can also be observed by CD spectroscopy. With this method a direct observation in the absorption band of the main chain chromophore at about 250 nm is possible. CD spectra of all monomer **6** containing polymers were measured in this area. As the appearance of all CD spectra is quite similar with exception of the absolute values of the molar ellipticity only the spectrum of polymer **P7** is shown in Figure 5.

CD spectra in the range of the main chain absorption show that all polymers possess very high molar ellipticities. This result confirms the results of the ORD spectroscopy and is another proof for the transfer of chirality according to the "sergeants-and-soldiers" experiment. As the maximal ellipticities of all polymers show positive values it can be concluded that in all cases the majority of helices exists in P-conformation. The dependence of the maximal molar ellipticity on the mole fraction of the chiral polymer in the bipolymers **P1**–**P7** is shown in Figure 6. Again it can be observed that the increase of the maximal molar ellipticity levels off

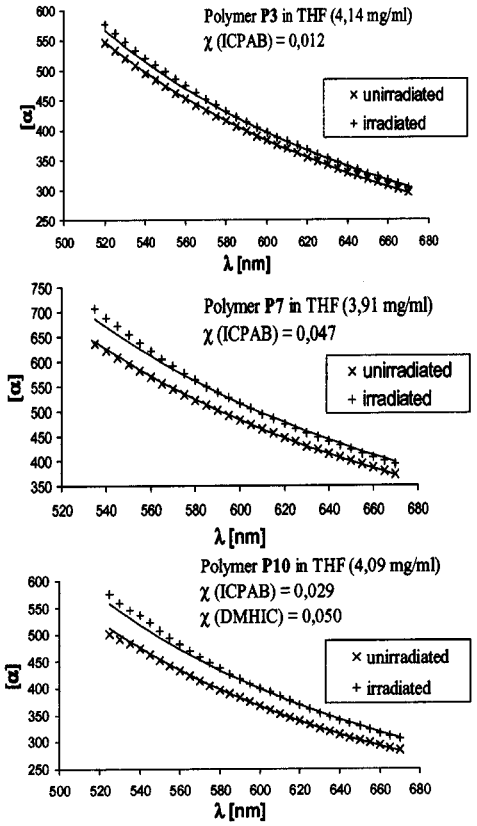


Figure 4. ORD spectra of several polymers before and after irradiation.

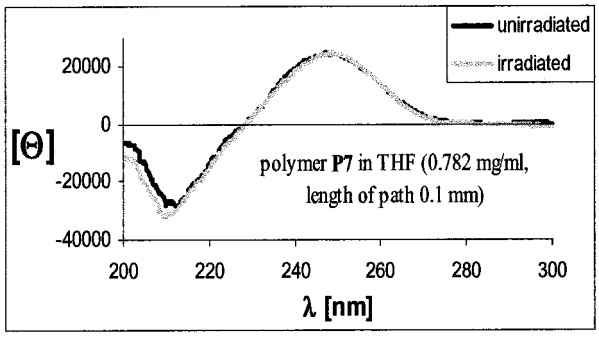


Figure 5. CD spectra of polymer **P7**.

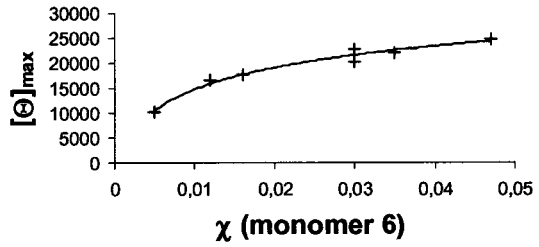


Figure 6. Dependence of molar ellipticity on the mole fraction of monomer **6**.

with increasing amount of monomer **6**. According to that almost all helices in polymer **P7** with a fraction of 4.7 mol % of chiral side groups are in P-conformation. Therefore a further increase of the fraction of chiral side groups would hardly influence the equilibrium between the helix twist senses.

Another result of the CD spectroscopy is the fact that the photoisomerization of the side groups almost has no influence on the conformation of the helix. This result

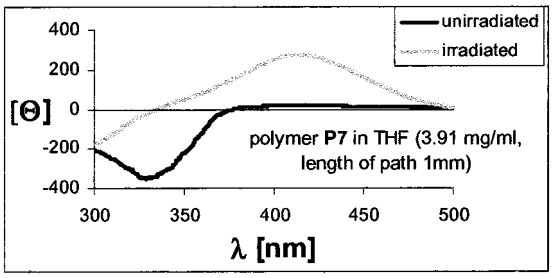


Figure 7. CD spectra of **P7** between 300 and 500 nm.

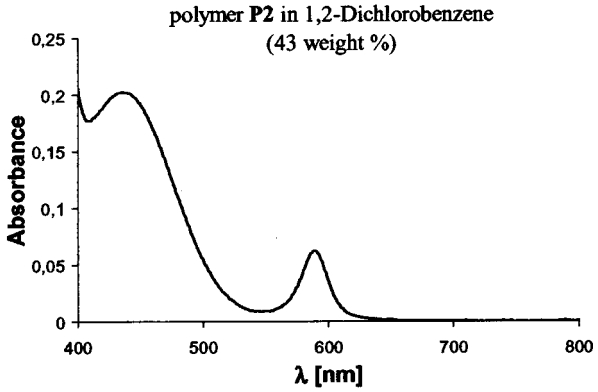


Figure 8. UV spectrum of LC phase 400−800 nm.

is compatible with the results of the ORD spectroscopy and confirms the high stability of the helix conformation. Therefore, the CD spectra are another proof for the fact that the helix twist sense cannot be significantly altered by photochemical isomerization.

In addition to the CD spectra in the range of the main chain absorption the CD spectra of polymer **P7** was measured in the area of the side chain absorption before and after irradiation (Figure 7). It can be observed that—in contrast to the range of the main chain absorption—the CD spectra of the side chain region of the cis and the trans isomer significantly differ from each other. As the side chain chromophore changes during the isomerization, this observation corresponds to the expectations. The molar ellipticity in the range of the side chain absorption is much lower than the ellipticity in the area of the main chain absorption. This can be explained by the fact that the main chain chromophore is chiral itself whereas the side chain chromophore only is positioned in a chiral environment.

Lyotropic Chlosteric Phases. To examine the formation of lyotropic liquid crystalline phases several polymers were mixed with varying amounts of 1,2-dichlorobenzene. It was found that mixtures with polymer concentrations of more than 40 wt % form liquid crystalline phases. Some of these phases reflect light in the visible range. For further examination, films of polymer **P2** were prepared from the lyotropic phase and examinated by UV spectroscopy (Figure 8).

The UV spectrum in Figure 8 shows that, in addition to the n → π^* absorption band of the azobenzene chromophore at 450 nm, a selective reflection band at 590 nm is found. This can be explained by the formation of a cholesteric phase. The wavelength of the selective reflection band λ relates to the helical pitch p of the cholesteric liquid crystalline phase by $\lambda = np$ (n being the refractive index, about 1.5 in our system).

The influence of the photoisomerization on the position and the intensity of this band can be examined by

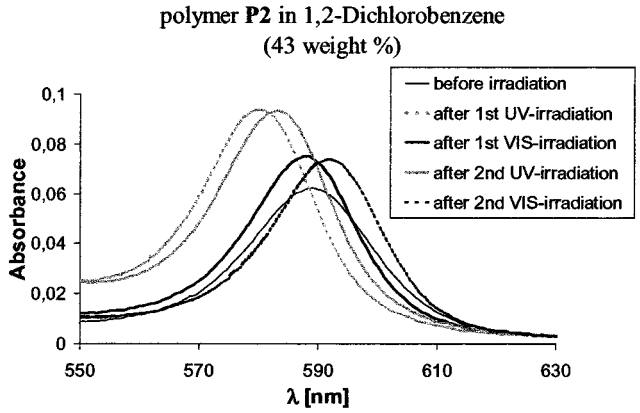


Figure 9. UV spectra of LC phase during the isomerization.

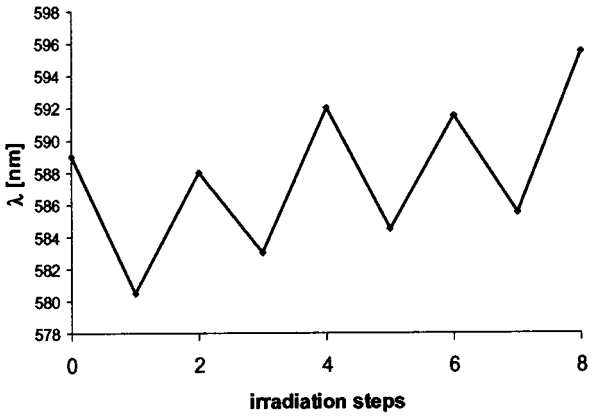


Figure 10. Shift of the selective reflection-band during irradiation.

irradiation of the film at a wavelength of 365 nm to carry out the isomerization from the trans to the cis isomer and with visible light to reisomerize the azobenzene groups. The process of isomerization and reisomerization was carried out four times. After each irradiation, the film was allowed to reorientate for 20 min. The resulting UV spectra are shown in Figure 9. For reasons of lucidity, only the spectra of the first two irradiation cycles are shown.

The UV spectra show that the photoisomerization causes a shift of the selective reflection band to shorter wavelengths. In addition to that an increase of intensity after the irradiation can be observed. The shift of the helical pitch and the increase of intensity can be reversed by reisomerization. The absorption bands possess the same intensity after the first and the second reisomerization and a similar position of the maximum. The difference between the spectrum before the first irradiation and the spectra after the reisomerization processes can be explained by the fact that in the case of the first spectrum almost all azobenzene chromophors exist as trans isomers whereas the reisomerization only leads to the photochemical equilibrium where a significant part of the chromophors still possess cis configuration. The shift of the maximum of the selective reflection bands during all irradiation processes is shown in Figure 10.

The reversibility of the shift of the maximum can also be observed in Figure 9. In addition to the shift caused by irradiation it is obvious that an additional shift takes place that leads to a slight increase of the wavelength of the maximum for the cis and the trans case. This shift is probably due to the change of concentration that is caused by the slow evaporation of the solvent. This change of concentration leads to a change of the dimension of helical pitch and by that to a shift of the selective reflection band.

The dependence of the position of the selective reflection band on the conformation of the azo group implies that the side groups must have an influence on the height of the helical pitch in the cholesteric phase. However, as the fraction of the chiral azo monomer in the examined polymer is as low as 1.6 mol %, it can be concluded that the pitch of the cholesteric phase is mostly caused by the helix itself and only minor changes are caused by the side groups.

Conclusion

A new photoisomerizable chiral isocyanate monomer branched in α-position was synthesized. Despite of its steric hindrance this monomer could be used successfully for the formation of bipolymers and terpolymers with HIC and DMHIC. Thereby a photoisomerizable monomer with an isocyanate group attached to a secondary carbon atom was incorporated into a polyisocyanate copolymer for the first time.

The polymerization was performed in THF and initiated by a solution of potassium cyanide complexed with 18-crown-6. Due to this variation of the conditions of the anionic polymerization relatively narrow molecular weight distributions and rather low molecular weights could be obtained. The polydispersity of the resulting polymers is low enough to allow the formation of lyotropic liquid crystalline phases without a priori fractionation. As azobenzene groups containing polyisocyanates are not polymerizable by coordination polymerization with titanium catalysts the modified anionic polymerization seems to be the best way to prepare azo-containing polyisocyanates with a narrow molecular weight distribution that is known so far.

The new polymers show extremely high specific rotations at a very low content of chiral side groups. Therefore the polymers act as an excellent example for the transfer of chirality between the side groups and the helix according to the "sergeants-and-soldiers" experiment. The extremely high chiral induction of the azo monomer (the highest known so far) leads to an enormous stability of the preferred helical conformation. Therefore the photoisomerization of the side chains does hardly influence the conformation of the helix. A photochemically induced switching of the helix conformation is not possible for this reason.

It could be shown that these polymers are able to form cholesteric lyotropic liquid crystalline phases with selective reflection in the visible range even when the molar fraction of chiral side groups is as small as 1.6 mol %. This result supports the thesis that the pitch of the cholesteric phase is mostly a result of the chirality of the helix and not of the chirality of the side groups. Otherwise it would be hard to explain, how a helical pitch as short as 500 nm could result from 1 mol % of chiral side groups. The position and the intensity of this band can be reversibly switched by isomerization of the azobenzene chromophore.

Experimental Part

Materials. Commercial chemicals were used without further purification. Solvents were dried according to literature processes.

Instrumentation. Gel permeation chromatography (GPC) at room temperature was used to determine molecular weights and molecular weight distributions, M_w/M_n of polymer samples with a Jasco PU-980 pump, standard column pore sizes 10^3 and 10^4 Å, Jasco RI-930 detector, Jasco UV-975 detector, and Viscothek T60A dual detector. For the determination of the molecular weight, the results of the light scattering detection were used. IR spectroscopy was done on a Nicolet Protege 460 IR spectrometer with a Specac Golden Gate single reflection ATR-unit. NMR spectra were measured on a Bruker 400 MHz NMR spectrometer. Mass spectroscopy was done on a Varian MAT 311 A mass spectrometer. UV/vis spectroscopy was performed on a Shimadzu UV-2102 PC. ORD spectroscopy and determination of the specific rotations were done on a Perkin-Elmer 241 MC polarimeter. CD spectroscopy was performed on a Jasco J-600 spectropolarimeter. For irradiation of the polymer solutions before the measurement of the UV spectra an Amco UV lamp with an integrated filter centered at 365 nm was used. The irradiations before the measurement of the ORD and CD spectra of polymer solutions and before the measurement of the UV spectra of the liquid crystalline films were performed with a Schott Sun-box. Melting points of air stable compounds were obtained by measurement with an Electrothermal IA 9100. The melting point of isocyanate **6** was obtained with a Perkin-Elmer DSC 7.

Synthesis of the monomer 4-((2,*S*)-isocyanatopropoxy)-azobenzene. *N*-*tert*-Butyloxycarbonyl-L-alanine Methyl Ester. A 11.63 g (83.4 mmol) sample of L-alanine methyl ester hydrochloride was suspended in 160 mL of chloroform. A solution of 6.98 g (82.8 mmol) of sodium hydrogen carbonate in 120 mL of water, 16.6 g of sodium chloride and a solution of 18.36 g (84.0 mmol) of di-*tert*-butyl carbonate in 80 mL of chloroform were added to the mixture. The mixture was refluxed for 3 h. After cooling, the phases were separated and the aqueous phase was extracted twice with 40 mL of chloroform. The organic phases were unified and dried over magnesium sulfate. After that the solvent was evaporated in a vacuum. For purification, the crude product was distilled in a vacuum. Thus, 16.33 g (80.4 mmol/97%) of a colorless liquid with a boiling point of 66 °C at 0.015 mbar were obtained. ^{1}H NMR ($CDCl_3$), δ [ppm]: 5.13 (bs, 1H, NH), 4.23 (m, 1H, CH), 3.67 (s, 3H, OCH_3), 1.37 (s, 9H, $C(CH_3)_3$), 1.31 (d, 3H, CH_3, ^3J = 6.4 Hz). ^{13}C NMR ($CDCl_3$), δ [ppm]: 173.6 (1C, R−C(O)−OR), 155.0 (1C, RHN−C(O)−OR), 84.9 (1C, O−CMe_3), 52.0 (1C, R−CH(NHR)−R), 49.0 (1C, OCH_3), 28.1 (3C, $C(CH_3)_3$), 18.3 (1C, CH_3). IR (film), $\tilde{\nu}$ [cm^{-1}]: 3370, 2980, 1715, 1455.

***N*-*tert*-Butyloxycarbonyl-L-alaninol.** A 10.6 g (52.2 mmol) sample of *N*-*tert*-butyloxycarbonyl-L-alanine methyl ester was dissolved in 85 mL of THF p.a. The flask was flooded with nitrogen. After that 4.4 g (104 mmol) of anhydrous lithium chloride, 4.1 g (108 mmol) of sodium boranate, and 150 mL of anhydrous ethanol were added. The mixture was stirred under nitrogen at room temperature. After about 15 min, the reaction temperature increased under vehement foaming. The stirring was continued for about 16 h. After that the solution was acidified with 10% aqueous citric acid until a pH of 4 was reached. The solvent was evaporated until about 50 mL of liquid was left. Now 50 mL of water was added. The mixture was extracted with 100 mL of dichloromethane four times. The unified organic phases were dried over magnesium sulfate and the solvent was evaporated in a vacuum. The obtained colorless oil was cooled to 4 °C and slowly began to form a crystalline solid. The crude product was recrystallized from a mixture of diethyl ether and hexane to yield 8.31 g (47.4 mmol/91%) of a colorless solid with a melting point of 53−55 °C. ^{1}H NMR ($CDCl_3$), δ [ppm]: 4.78 (bs, 1H, NH), 3.73 (m, 1H, CH), 3.60 (dd, 1H, CH_2, ^2J = 10.7 Hz, ^3J = 4.1 Hz), 3.48 (dd, 1H, CH_2, ^2J = 10.7 Hz, ^3J = 6.1 Hz), 1.43 (s, 9H, $C(CH_3)_3$), 1.13 (d, 3H, CH_3, ^3J = 6.6 Hz). ^{13}C NMR ($CDCl_3$), δ [ppm]: 156.3 (1C, RHN−C(O)−OR), 79.6 (1C, O−CMe_3), 67.0 (1C, R−CH_2OH), 48.6 (1C, R−CH(NHR)−R), 28.3 (3C, $C(CH_3)_3$), 17.3 (1C, CH_3). IR (ATR), $\tilde{\nu}$[cm^{-1}]: 3455, 3350, 2985, 1675, 1530, 1160, 1060, 1025.

4-((2,*S*)−(*tert*-Butyloxycarbonylamino)propoxy)azobenzene. A 7.01 g (40 mmol) sample of *N*-*tert*-butyloxycarbonyl-L-alaninol, 7.93 g (40 mmol) of 4-hydroxyazobenzene, and 10.5 g (40 mmol) of triphenylphosphane were dissolved in 100 mL of anhydrous diethyl ether under nitrogen atmosphere. The solution was cooled to 0 °C. Then a solution of 8.5 mL (8.9 g/40 mmol) of diisopropyl azodicarboxylate (90% purity) in 30 mL of anhydrous diethyl ether was added dropwise over 45 min. After that the mixture was stirred for further 2 h at 0 °C and for 20 h at room temperature. The precipitated triphenylphosphane oxide was separated by filtration. A 50 mL aliquot of diethyl ether was added to the filtrate. After that the organic phase was washed with 40 mL of 2 N aqueous sodium hydroxide three times and with 40 mL of water once and dried over magnesium sulfate. The solvent was evaporated in a vacuum. The crude product was purified by flash chromatography with a 4:1 mixture of petrol ether and ethyl acetate as eluent. 7.70 g (21.7 mmol/54%) of an orange-colored solid with a melting point of 123−124 °C was obtained. ^{1}H NMR ($CDCl_3$), δ [ppm]: 7.89−7.95 (m, 4H, arom), 7.43−7.53 (m, 3H, arom), 7.01−7.04 (m, 2 H, arom), 4.79 (bs, 1H, NH), 4.13 (m, 1H, CH), 4.03 (d, 2H, R−CH_2−OR), 1.48 (s, 9H, CCH_3), 1.33 (d, 3H, CH_3, ^3J = 7.1 Hz). ^{13}C NMR ($CDCl_3$), δ [ppm]: 161.2 (1C, arom), 155.2 (1C, RHN−C(O)−OR), 152.7 (1C, arom), 147.2 (1C, arom), 130.4 (1C, arom), 129.0 (2C, arom), 124.8 (2C, arom), 122.6 (2C, arom), 114.8 (2C, arom), 79.6 (1C, O−CMe_3), 71.3 (1C, R−CH_2−OR), 45.9 (1C, R−CH-(NHR)−R), 28.4 (3C, $C(CH_3)_3$), 17.8 (1C, CH_3). IR (ATR), $\tilde{\nu}$ [cm^{-1}]: 3375, 2985, 2940, 1680, 1600, 1510, 1450, 1235, 1165, 1065, 1025, 840. Mass, *m*/*z* (intensity): 44 (52%, CO_2), 57 (100%, CMe_3^+), 77 (75%, $C_6H_5^+$), 102 (C(O)OCMe_3^+ + H), 121 (50%, HO−C_6H_5−N_2^+), 198 (59%, HO−C_6H_4−N=N−$C_6H_5^+$), 282 (10%, M^+ − HOCMe_3), 355 (16%, M^+).

4-((2,*S*)-Aminopropoxy)azobenzene Hydrochloride. A 4.0 g (11.3 mmol) sample of 4-((2,*S*)-(*tert*-butyloxycarbonyl-amino)propoxy)azobenzene was dissolved in 70 mL of dichloromethane. Then 8 mL of trifluoroacetic acid was added under stirring. Thereby the former orange yellow color of the solution turned into deep red. The reaction flask was closed with a bubble counter. The formation of a gas could be observed at the beginning of the reaction. The solution was stirred for 4^1/$_2$ h. After that it was poured on 200 mL of 2 N hydrochloric acid. The hydrochloride precipitated as an orange yellow solid. After cooling to 4 °C the solid was filtered and recrystallized from a 1:1 mixture of ethanol and ethyl acetate. 2.01 g (6.9 mmol/61%) of a yellow solid that decomposes over 190 °C was obtained. ^{1}H NMR (DMSO-d_6), δ [ppm]: 8.42 (bs, 3H, RNH_3^+), 7.80−7.89 (m, 4H, arom), 7.46−7.56 (m, 3H, arom), 7.14−7.18 (m, 2H, arom), 4.11−4.25 (m, 2H, R−CH_2−OR), 3.58 (m, 1H, CH), 1.31 (d, 3H, CH_3, ^3J = 7.1 Hz). ^{13}C NMR (DMSO-d_6), δ [ppm]: 160.6 (1C, arom), 152.0 (1C, arom), 146.5 (1C, arom), 130.9 (1C, arom), 129.4 (2C, arom), 124.5 (2C, arom), 122.2 (2C, arom), 115.4 (2C, arom), 69.0 (1C, R−CH_2−OR), 46.0 (1C, R−CH(NH_3^+)−R), 15.0 (1C, CH_3). IR (ATR), $\tilde{\nu}$ [cm^{-1}]: 2860, 1600, 1500, 1240, 1145, 1040, 840. Mass, *m*/*z* (intensity): 36 (66%, $H^{35}Cl$), 38 (17%, $H^{37}Cl$), 44 (100%, H_2N−CH^+−CH_3), 58 (89%, $CH_3CH(NH_2)CH_2^+$), 77 (67%, $C_6H_5^+$), 121 (23%, HO−C_6H_4−N_2^+), 198 (15%, HO−C_6H_4−N=N−$C_6H_5^+$), 212 (10%, C_6H_5−N=N−C_6H_4−O−CH_2^+ + H), 255 (21%, M^+ − HCl).

4-((2,*S*)-Isocyanatopropoxy)azobenzene. An 800 mg (2.7 mmol) sample of 4-((2,*S*)-aminopropoxy)azobenzene hydrochloride was suspended in 30 mL of anhydrous dioxane under nitrogen. Then, 1.8 mL (3.0 g/15.2 mmol) of trichloromethyl chloroformate was added. The mixture was heated to 70 °C. After about 1 h, the former suspension had transformed into a clear solution. The mixture was stirred for another 16 h at 50 °C. After that the volatile components were evaporated in a vacuum. The crude product was fractionated in a Kugelrohr (Büchi GKR 51). Then 590 mg (2.1 mmol/78%) of an orange red solid with a melting point of 71−72 °C (DSC) was obtained. Specific rotation: $[\alpha]^D_{20}$ = +19.2 [0.1·deg·cm^2·g^{-1}]. ^{1}H NMR ($CDCl_3$), δ [ppm]: 7.90−7.97 (m, 4H, arom), 7.44−7.55 (m, 3H, arom), 7.03−7.07 (m 2H, arom), 3.96−4.08 (m, 3H, R−CH_2−OR + R−CH(NCO)−R), 1.41 (d, 3H, CH_3, ^3J = 6.1 Hz). ^{13}C NMR ($CDCl_3$), δ [ppm]: 160.5 (1C, arom), 152.7 (1C, arom), 147.5 (1C, arom), 130.5 (1C, arom), 129.0 (2C, arom), 125.1 (1C, R−N=C=O), 124.8 (2C, arom), 122.6 (2C, arom), 114.9

(2C, arom), 71.9 (1C, R−CH_2−OR), 50.4 (1C, CH), 19.3 (1C, CH_3). IR (film), $\tilde{\nu}$ [cm^{-1}]: 2940, 2235, 1600, 1500, 1235, 1145, 1040, 845, 765, 685. Mass, *m*/*z* (intensity): 41 (71%, CH_2═CH−CH_2^+), 56 (86%, H_2C═N^+═C═O), 77 (79%, $C_6H_5^+$), 84 (58%, Me_2C═N^+═C═O), 176 (100%, M^+−C_6H_5−N_2), 204 (32%, M^+−C_6H_5), 281 (96%, M^+)

Polymerization. HIC and DMHIC were distilled a few days before use. Monomer **6** was used not later than 3 days after purification. A varying amount of the solid monomer **6** was placed in a 10 mL flask. After that the flask was closed with a septum, evacuated, and filled with dry nitrogen. The liquid monomers (about 800 mg of HIC and in some cases 100−150 mg of DMHIC) and 4 mL of anhydrous THF were added through syringes. After the solid monomer was dissolved completely, the mixture was cooled to −60 °C. The solution was stirred at −60 °C for 15 min. After that 2.0 mL of the initiating solution was added. About 5 min after the injection of the initiator, the formation of a gel could be observed. Then, 45 min after the injection of the initiator, the polymerization was stopped by injection of 2 mL cold methanol. The mixture was poured into 80 mL of methanol. The liquid was separated by filtration. The polymer was solved in 30−50 mL of THF and precipitated after the addition of 100−150 mL of methanol. For the initiating solution, 65.1 mg (1 mmol) of potassium cyanide and 264.3 mg (1 mmol) of 18-crown-6 were put into a Schlenk flask. The flask was closed with a septum, evacuated, and filled with dry nitrogen. After that, 20 mL of anhydrous THF was added through a syringe. The mixture was shaken several times and allowed to stand for several hours. As the potassium cyanide did not dissolve completely, only the solution was used as initiator while the undissolved solid was placed at the bottom of the flask.

Formation of Lyotropic Phases. For the formation of lyotropic phases, 30−40 mg of the polymer and the corresponding amount of 1,2-dichlorobenzene (40−80 mg) were allowed to stand in an Eppendorf micro test tube for 24 h. Afterward, the mixture was cropped out on a microscope slide. A cover slide was put on the film and was fixed with tape. The film was allowed to orientate for 90 min, after that the UV measurements were performed.

Acknowledgment. Financial support by the DFG is gratefully acknowledged.We also thank Prof. Wulff's group in Düsseldorf for the access to the CD spectrometer.

References and Notes

(1) Lehninger, A. L. *Prinzipien der Biochemie*; Walter de Gruyter: Berlin, 1987; p 168 ff.
(2) Vogl, O.; Jaycox, G. D. *Polymer* **1987**, *28*, 2179−2182.
(3) Pu, L. *Acta Polym.* **1997**, *48*, 116−141.
(4) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349−372.
(5) Nolte, R. J. M. *Chem. Soc. Rev.* **1994**, *23*, 11.
(6) Green, M. M.; Gross, R. A.; Schilling, F. C.; Zero, K.; Crosby, Ch., III. *Macromolecules* **1988**, *21*, 1839.
(7) Kollmar, Ch.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 8230.
(8) Okamoto, Y.; Honda, S.; Okamoto, I.; Yuki, H. *J. Am. Chem. Soc.* **1981**, *103*, 6971.
(9) Nolte, R. J. M.: van Beijnen, A. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1974**, *96*, 5932.
(10) Shashoua V. E.; Sweeny, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960**, *82*, 866−873.
(11) Bur, A. J.; Fetters, L. J. *Chem. Rev.* **1976**, *76*, 727−746.
(12) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Willson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6452−6454.
(13) Green, M. M.; Park, J.-W.; Sato, T.; Teramoto, A.; Lifson, F.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem.* **1999**, *111*, 3328−3345.
(14) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Lifson, S. *Science* **1995**, *268*, 1860.
(15) Maxein, G.; Zentel, R. *Macromolecules* **1995**, *28*, 8438−8440.
(16) Müller, M.; Zentel, R. *Macromolecules* **1996**, *29*, 1609−1617.
(17) Mayer, S.; Zentel, R. *Macromol. Chem. Phys.* **1998**, *199*, 1675−1682.
(18) Maxein, G.; Mayer, S.; Zentel, R. *Macromolecules* **1999**, *32*, 5747−5754.
(19) Sato, T.; Sato, Y.; Umemura, Y.; Teramoto, A.; Nagamura, Y.; Wagner, J.; Weng, D.; Okamoto, Y.; Hatada, K.; Green, M. M. *Macromolecules* **1993**, *26*, 4551−4559.
(20) Green, M. M.; Zanella, S.; Gu, H.; Sato, T.; Gottarelli, G.; Jha, S. K.; Spada, G. P.; Schoevaars, A. M.; Feringa, B.; Teramoto, A. *J. Am. Chem. Soc.* **1998**, *120*, 9810−9817.
(21) Green, M. M.; Andreola, C.; Munoz, B.; Reidy, M. P. *J. Am. Chem. Soc.* **1988**, *110*, 4063−4065.
(22) Aharoni, S. M. *Macromolecules* **1979**, *12*, 94−103.
(23) Tarbell, D. S.; Yamamoto, Y.; Pope, B. M. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 730−732.
(24) Hamada, Y.; Shibata, M.; Sugiura, T.; Kato, S.; Takayuki, S. *J. Org. Chem.* **1987**, *52*, 1252−1255.
(25) Mitsunobu, O. *Synthesis* **1981**, *1*, 1−28.
(26) Kurita, K.; Matsumura, T.; Iwakura, Y. *J. Org. Chem.* **1976**, *41*, 2070−2071.
(27) Aranda, G.; Riant, O. *Synth. Comm.* **1990**, *20* (5), 733−750.
(28) Müller, M.; Zentel, R. *Makromol. Chem.* **1993**, *194*, 101−116.
(29) Patten, T. E.; Novak, B. M. *Macromolecules* **1993**, *26*, 436−439.
(30) Maxein, G. Personal communication.
(31) Okamoto, Y.; Nagamura, Y.; Hatada, K.; Khatri, C.; Green, M. M. *Macromolecules* **1992**, *25*, 5536−5538.
(32) Zimmerman, G.; Chow, L.-Y.; Paik, U.-J. *J. Am. Chem. Soc.* **1958**, *80*, 3528−3531.

MA010491N