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Structure−Property Relations in Cholesteric Networks from Chiral Polyisocyanates

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ABSTRACT: In this work we prepared lyotropic cholesteric phases from new polyisocyanate terpolymers in styrene and were able to "freeze" this supramolecular structure—and thereby the associated optical properties—in a cross-linked polymer blend by photopolymerization. We synthesized the new chiral polyisocyanates (nylon 1) by living polymerization techniques, using a new titanium catalyst of Bruce Novak. In this way it is possible to incorporate methacrylate groups, which are necessary to prevent a demixing during the photo-cross-linking process, and to control the molecular weight, which is necessary to obtain lyotropic phases of low viscosity. Terpolymers with more than 8 mol % of chiral side groups give rise to lyotropic phases with selective reflection in the visible range. Unexpectedly, we observed a minimum in the plot of wavelength of reflection versus polymer concentration. The selective reflection shifts to larger wavelengths (red shift) with increasing temperature. Photo-cross-linking at different temperatures allows a permanent "freezing" of different colors without loss of the optical quality. In this way flexible polymer films with opalescent colors and an angular dependent color are accessible.

Introduction

The cholesteric phase (chiral nematic phase) of liquid crystals has outstanding optical properties: It selectively reflects (Bragg reflection) visible light and exhibits brilliant colors if the pitch of the cholesteric helix coincides with the wavelength of visible light within the material ($\lambda = np$).[1] Due to the angular dependence of the reflection conditions (angle between incident light and the cholesteric helix), different colors are seen depending on the observation angle. This creates shiny "rainbow-like" colors. Furthermore, the reflected light is right- or left-handed circularly polarized, depending on the handedness of the cholesteric superstructure (helix) in the system. A right-handed cholesteric helix, for example, reflects only the right-handed circularly polarized part of the incident light of wavelength $\lambda_0 = np$; the rest of the spectrum ($\lambda \neq \lambda_0$) together with the left-handed circularly polarized light of wavelength λ_0 is transmitted.

Recently, highly cross-linked cholesteric pigments have aroused a great deal of interest as dye pigments for cars or as "copy safe" colors for documents or money.[2] These cholesteric pigments have been prepared so far from cholesteric monomers or oligomers by a photo-cross-linking process.[3−5] Helical biopolymers offer the same potential, and thermotropic and lyotropic phases that exhibit selective reflection are known for polypeptides[6] and cellulose derivatives.[7] With this polymeric approach, we recently discovered a system of lyotropic selective reflecting mesophases based on aryl urethanes of cellulose in commercially available mono- or bifunctional derivatives of acrylic and methacrylic acids. To obtain solid films and to preserve the selective reflection, the solvents were polymerized photochemically, thus yielding a semiinterpenetrating network of cellulose urethanes and polyacrylates.[8]

As a continuation of our work with helical polymers, we tried to use chiral polyisocyanates to create cholesteric networks. Polyisocyanates (PICs) are an unusual class of macromolecules, because they are one of the few types of synthetic polymers that adopt a stable helical conformation in solution as well as in the solid state.[9] In several studies, remarkably large optical activities, associated with the polymer backbone chromophore, have been observed for homo- and copolymers prepared from optically active isocyanates.[10,11] This is due to the extremely high cooperativity along the rigid polymer backbone, in which, following the so-called "sergeants and soldiers principle",[12] P and M helices become diastereomers. These unique chiral properties even became photochemically switchable if chiral azo dyes are incorporated in the side chain.[13−15]

The property of polyisocyanates to form lyotropic liquid crystalline (LC) structures is well-known.[16] Appropriate solvents to achieve a lyotropic LC phase are, for example, chloroform, toluene, tetrachloroethane, and styrene. Typically these LC structures are nematic. If instead of an achiral a chiral side group is attached to the stiff polyisocyanate backbone (by homo- or copolymerization of chiral isocyanate monomers), the LC superstructure is no longer nematic but cholesteric.[17] Styrene, as a solvent for lyotropic phases, offers the general possibility to freeze the cholesteric structure after polymerization in a polymer blend. This approach suffers, however, from the immiscibility of polyisocyanates and polystyrene, which are typical representatives of rigid-rod and flexible-coil polymers. If the polymerization is done rapidly, however, a macro phase separation can be suppressed. The cholesteric phase is, however, sensitive to concentration fluctuations in the 100 nm range. Therefore, the optical properties of the cholesteric phase deteriorated because of partial demixing during our attempts to lock in the cholesteric phase by polymerization.[18] This problem can be overcome by incorporation of acrylate side groups into the chiral polyisocyanate, which can be done with new titanium catalysts reported by Novak et al.[18−20] A first example of "opalescent cholesteric networks" obtained by this method was described previously.[18] Here we present lyotropic mixtures of functionalized polyisocyanates

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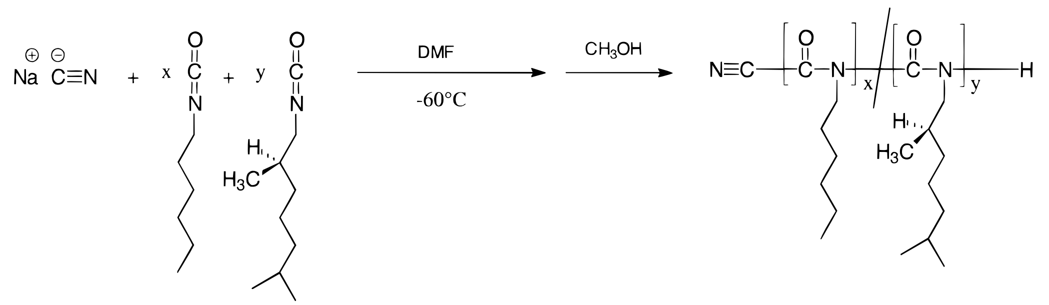
Scheme 1



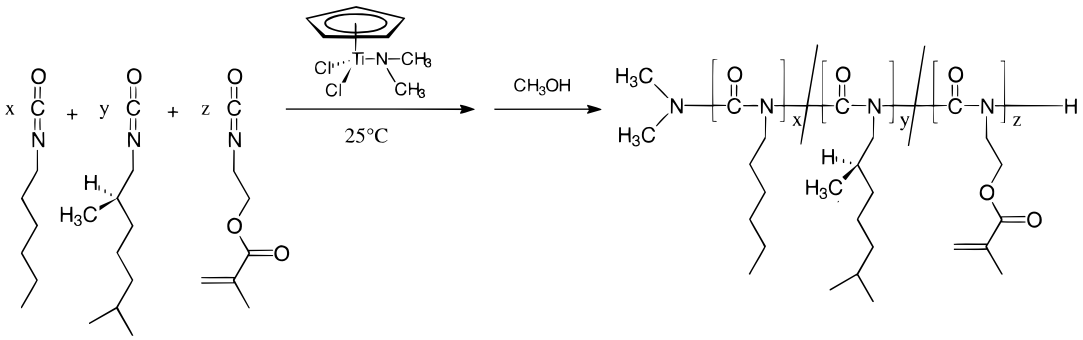
C1-C3

Table 1. Characterization of the Copolymers C1−C3 (see Scheme 1), Prepared by Polymerization with Sodium Cyanide

polymer	DP[a]	*y* [%][b]	$[\alpha]_D^{20}$	yield [%]	M_w[c]	M_p[c]	PDI[c]
C1	1030	4.8 (5)	−337	81	105 800	131 000	2.39
C2	1350	7.2 (7)	−437	79	129 400	172 000	2.48
C3	960	9.1 (10)	−451	57	98 000	122 400	2.30

[a] Degree of polymerization of the copolymers calculated based on M_p assuming a molecular weight of the monomers of 127.19 g mol^{-1} (HIC). [b] Mole percent of the chiral comonomer DMHIC which is incorporated into the copolymer (determined by NMR spectroscopy); in brackets: mole percent in the monomer mixture. [c] Determined by GPC in chloroform calibrated against poly(hexyl isocyanate) standards.

Scheme 2



T1-T21

Table 2. Characterization of the Terpolymers T1−T7 (see Scheme 2), Obtained by Living Polymerization with Titanium Catalysts. In This Series the Amount of Chiral DMHIC Was Varied, While Keeping the Degree of Polymerization Approximately Constant

polymer	DP[a]	*y* [%][b]	*z* [%][b]	$[\alpha]_D^{20}$	yield [%]	M_w[c]	M_p[c]	PDI[c]
T1	348	0.9 (1)	9.3 (10)	−19.6	87	39 630	44 240	1.26
T2	341	2.6 (2.5)	9.4 (10)	−60.5	85	37 060	43 340	1.31
T3	352	4.5 (5)	8.9 (10)	−111.5	88	40 640	44 780	1.24
T4	331	6.1 (7.5)	10.1 (10)	−155.9	83	36 190	42 120	1.31
T5	338	7.7 (10)	9.7 (10)	−190.6	85	38 780	42 700	1.21
T6	268	8.9 (10)	9.7 (10)	−258.6	80	32 250	34 120	1.14
T7	314	11.9 (15)	9.6 (10)	−311.6	79	36 030	39 900	1.21

[a] Degree of polymerization of the terpolymers calculated based on M_p assuming a molecular weight of the monomers of 127.19 g mol^{-1} (HIC). [b] Mole percent in the terpolymers determined by NMR spectroscopy; in brackets: mole percent in the monomer mixture. [c] Determined by GPC in chloroform calibrated against poly(hexyl isocyanate) standards.

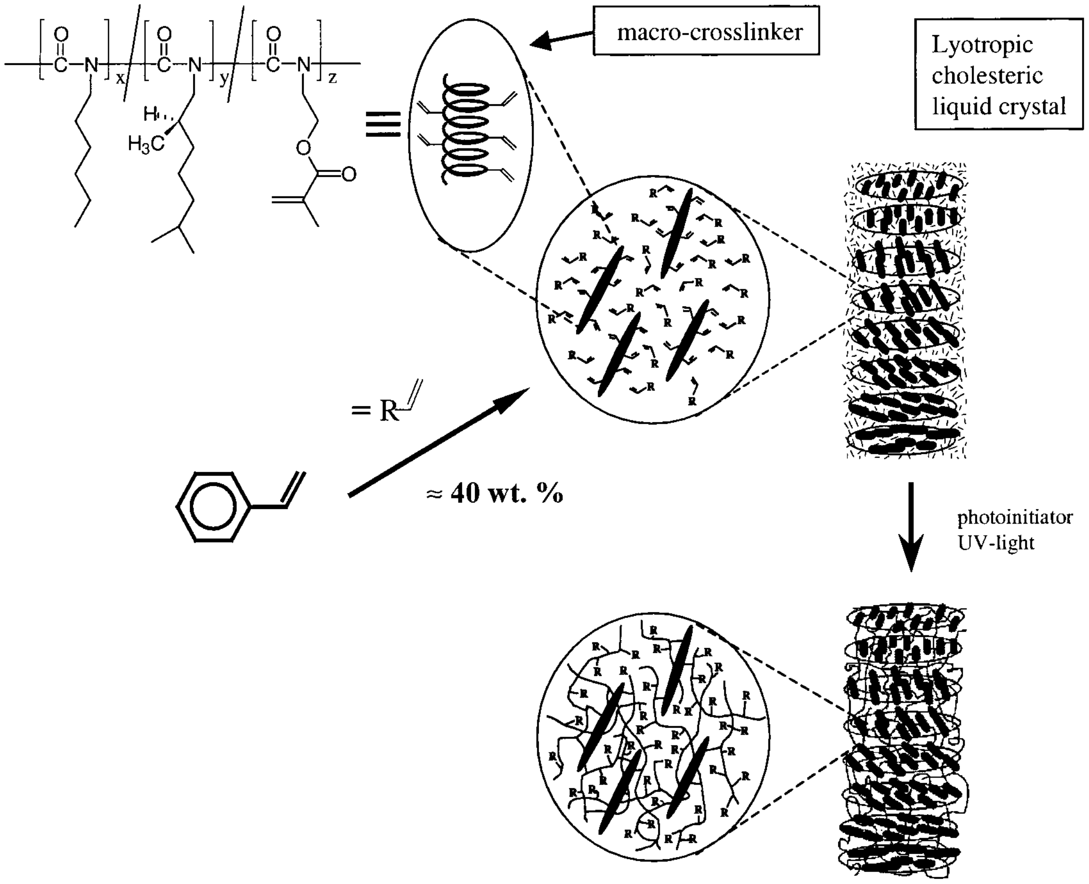
with focus on the relation: polymer structure−cholesteric phase properties.

Results and Discussion

Synthesis and Properties in Dilute Solution. For the investigations described here, we synthesized the copolymers **C1**−**C3** (Scheme 1, Table 1) and the terpolymers **T1**−**T21** (Schemes 2 and 3, Tables 2 and 3). The copolymers **C1**−**C3** were prepared from hexylisocyanate (HIC) and (*R*)-2,6-dimethylheptyl isocyanate (DMHIC) according to the classical route.[21] Due to their synthesis, they have high molecular weights and a large polydispersity (PDI) (see Table 1). The copolymers **C1**−**C3** contain between 5 and 10 mol % of chiral comonomer, which corresponds to the percentage present in the monomer mixture. They cannot be incorporated into the polystyrene network, because they are lacking the methacrylate side groups. According to the "sergeant and soldiers principle", they show already high optical rotation but are not yet in the range of saturation (see Figure 1 in ref 22).

The terpolymers **T1**−**T21** are prepared by living polymerization techniques[18−20] (see Schemes 2 and 3 and Experimental Part). Table 2 summarizes work to vary the amount of chiral comonomers, while keeping the molecular weight constant. The polydispersity is small. The molecular weight is lower compared to that

Scheme 3



of copolymers **C1** to **C3**, and it can be adjusted. This is an important prerequisite for the preparation of lyotropic phases of low viscosity. The comonomers are incorporated differently. The nonbranched 2-isocyanatoethyl methacrylate is incorporated according to its concentration in the reaction batch. The branched chiral DMHIC is, however, incorporated into the polymer chain in reduced amounts. Mixtures with higher concentrations of DMHIC polymerize slower than mixtures without DMHIC. In this context it is noteworthy that DMHIC cannot be homopolymerized with the titanium catalyst used here.

In agreement with the molecular weight dependence of the optical rotation—to be discussed later—the optical rotations of the terpolymers **T1** to **T7** (Table 2) are lower than those of the copolymers **C1**−**C3**. Figure 1 shows a linear dependence of the optical rotation on the amount of chiral comonomers up to 12 mol %. Such a relation can only be expected far from saturation. High molar mass systems (see Table 1 and ref 22) are—on the contrary—already close to saturation at 12 mol % of chiral comonomer.

This result made us look closer at the influence of the molecular weight on the optical rotation in dilute solution. Table 3 summarizes work to keep the concentration of the chiral DMHIC constant at 10 or 15 mol %, while varying the molecular weight. It demonstrates the advantage of the living polymerization technique. Low molecular weights can be predetermined very well. If high molecular weights are aspired, problems arise because of very long reaction times (several weeks) and a gelling of the sample at higher conversion. This limits the conversion, and the molecular weights are lower than expected. In addition, the same conclusion as from Table 2 can be drawn. The resulting dependence of the optical rotation on the molecular weight is illustrated in Figure 2.

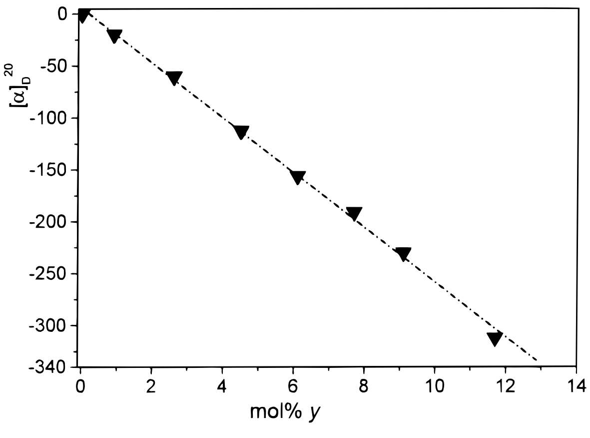


Figure 1. Dependence of the optical rotation $[\alpha]_D^{20}$ on the mole percent of chiral comonomer in polymers **T1**−**T7** (see Table 2 and Scheme 1).

It shows that the optical rotation increases with the molecular weight and then levels off at a degree of polymerization of about 300. This is in accordance with the theoretical understanding of the chiral amplification in these systems[12] and has been tested by detailed studies of the molecular weight dependence of the optical activity.[23] It can be understood if the number of chiral comonomers between two helix reversals determines the probability of right- or left-handed sequences. If the molecular weight is higher than the average distance between two helix reversals, no molecular

Table 3. Characterization of the Terpolymers T8−T21 (See Scheme 2), Obtained by Living Polymerization with Titanium Catalysts. In This Series the Amount of Chiral DMHIC Was Kept Constant at Two Different Levels, While the Molecular Weight Was Varied

polymer	DP[a]	y [%][b]	z [%][b]	$[\alpha]_D^{20}$	yield [%]	M_w[c]	M_p[c]	PDI[c]
T8	59 (50)	7.7 (10)	9.6 (10)	−40.2	85	7 490	7 450	1.10
T9	94 (100)	7.5 (10)	9.9 (10)	−73.4	94	11 450	11 990	1.10
T10	223 (200)	7.7 (10)	8.9 (10)	−153.3	93	26 530	29 670	1.15
T11	243 (300)	7.9 (10)	10.1 (10)	−168.5	81	28 520	30 930	1.16
T12	314 (400)	7.6 (10)	9.7 (10)	−182.5	79	37 740	39 900	1.21
T13	388 (500)	7.4 (10)	9.2 (10)	−191.2	78	45 220	49 390	1.27
T14	455 (600)	7.8 (10)	9.5 (10)	−209.6	76	53 120	57 870	1.26
T15	94 (100)	8.7 (15)	8.8 (10)	−158.6	40	12 160	11 980	1.08
T16	149 (200)	9.9 (15)	9.6 (10)	−219.9	60	18 210	18 890	1.14
T17	251 (300)	11.6 (15)	8.0 (10)	−318.6	70	30 060	31 880	1.19
T18	314 (400)	11.7 (15)	9.6 (10)	−311.6	79	36 030	39 900	1.21
T19	352 (500)	11.8 (15)	9.5 (10)	−339.8	71	42 230	44 780	1.25
T20	387 (600)	11.0 (15)	9.4 (10)	−339.8	73	46 420	49 250	1.29
T21	403 (700)	10.9 (15)	9.2 (10)	−336.1	72	47 710	51 300	1.32

[a] Degree of polymerization of the terpolymers calculated based on M_p assuming a molecular weight of the monomers of 127.19 g mol^{-1} (HIC); in brackets: theoretical degree of polymerization based on the monomer/initiator ratio. [b] Mole percent in the terpolymers determined by NMR spectroscopy; in brackets: mole percent in the monomer mixture. [c] Determined by GPC in chloroform calibrated against poly(hexyl isocyanate) standards.

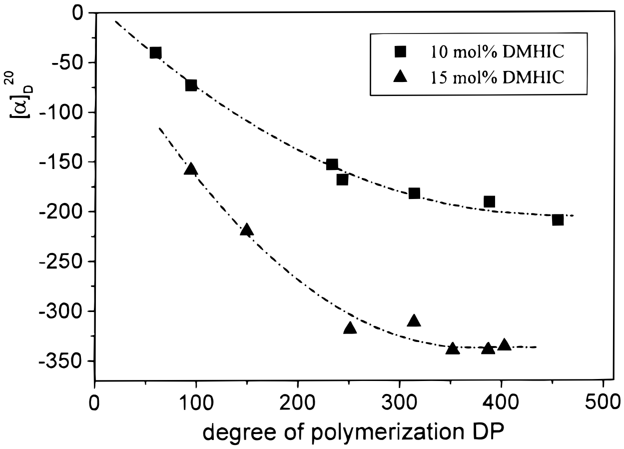


Figure 2. Dependence of the optical rotation $[\alpha]_D^{20}$ on the molecular weight for polymers **T8**−**T21** (see Table 3).

weight dependence is to be expected. If the molecular weight is lower, then the number of chiral comonomers per helical sequence increases with the molecular weight.

Lyotropic Cholesteric Phases. The concept for the preparation of lyotropic cholesteric phases and the freezing of this structure by polymerization is presented in Scheme 3. The formation of a lyotropic phase requires a dense packing of the stiff polyisocyanate polymers (sufficient solubility) and a high axial ratio. Thus, the limiting concentration must depend on the molecular weight. This is indeed found. **C2** forms a single cholesteric phase starting at 20 wt %; for **T18** 28 wt % is necessary. The cholesteric phases formed at low concentrations possess, however, a large pitch and do not reflect light in the visible range. For **C2**, e.g., 38 wt % is necessary to observe a green reflection.

When a cholesteric structure is formed, two helices are present at the same time, but at different length scales (see Scheme 3). There is, on one hand, the helix of the polyisocyanate chains, which has a fixed pitch of about 0.5 nm.[9] The optical rotation $[\alpha]_D^{20}$—determined from dilute solution—gives a measure for the preference of one twist sense in these molecular helices. In addition, there is the supramolecular cholesteric helix with a pitch of several 100 to several 1000 nm. The question is now, how does the preference for one helical twist sense —on a molecular level—transform into the twist of the supramolecular helix? A second aspect is whether the interaction of the chiral carbon atoms in the polymer side chains influences the twist of the supramolecular helix. These questions have been studied in model systems in the polyisocyanates.[17b]

We found the following: selective reflection in the visible, which requires a relatively short cholesteric pitch, is only found for the polymers **C1**−**C3**, **T6**, **T7**, and **T15**−**T21**. The other polymers form cholesteric phases as well, but the pitch of these phases is—even for highly concentrated solutions—still in the micrometer region. This result allows us to address the question raised before. From Tables 2 and 3 it is evident that all terpolymers with selective reflection in the visible contain more than 8 mol % of chiral side chains. For the optical rotation the correlation is not equally perfect. Basically, a high optical rotation in dilute solution results in a short pitch in the cholesteric phase. But the molecular weight is here of crucial importance. **T15** (DP = 94) with $[\alpha]_D^{20} = -159$ shows selective reflection in the visible, while **T14** (DP = 455) with $[\alpha]_D^{20} = -210$ does not. The copolymers **C1**−**C3** with very high molecular weight (DP around 1000) all exhibit selective reflection in the visible, though **C1** and **C2** have less than 8 mol % chiral side chains. The relative importance to the cholesteric pitch of helical characteristics of the polymer backbone compared to the asymmetric side chains is difficult to judge although in model studies the helical characteristics predominate.[17b]

Temperature and Concentration Dependence of Selective Reflection. On the basis of the investigations described before, we examined the temperature and concentration dependence of lyotropic solutions from **C1**, **T6**, and **T19**−**T21** in more detail. For this purpose the virtual absorption of the cholesteric phase (due to reflection of 50% of the light) was measured in a UV−vis spectrometer. Figure 3 shows typical results for the temperature dependence. For **T20**—a terpolymer that forms a low-viscosity phase—it can be seen (Figure 3a) that (i) the pitch increases with increasing temperature (red shift) (this increase is approximately linear with temperature), (ii) about 50% of the light is reflected, as to be expected for a well-oriented cholesteric monodomain (an absorption of 50% transforms into an extinction of about 0.3), and (iii) the half-width of the

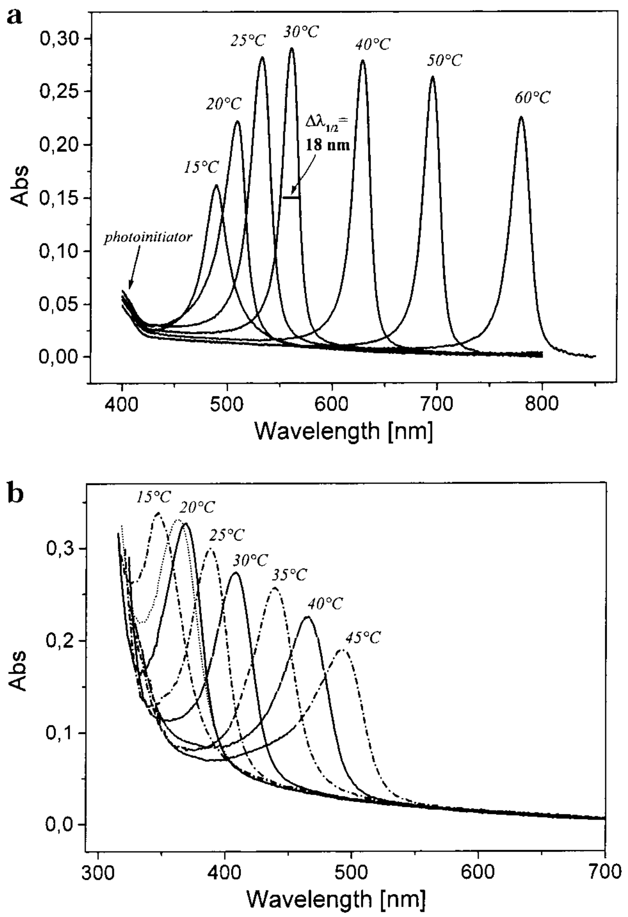


Figure 3. Temperature dependence of the selective reflection of lyotropic cholesteric phases: (a) 60 wt % of **T20** in styrene; (b) 50 wt % of **C1** in styrene.

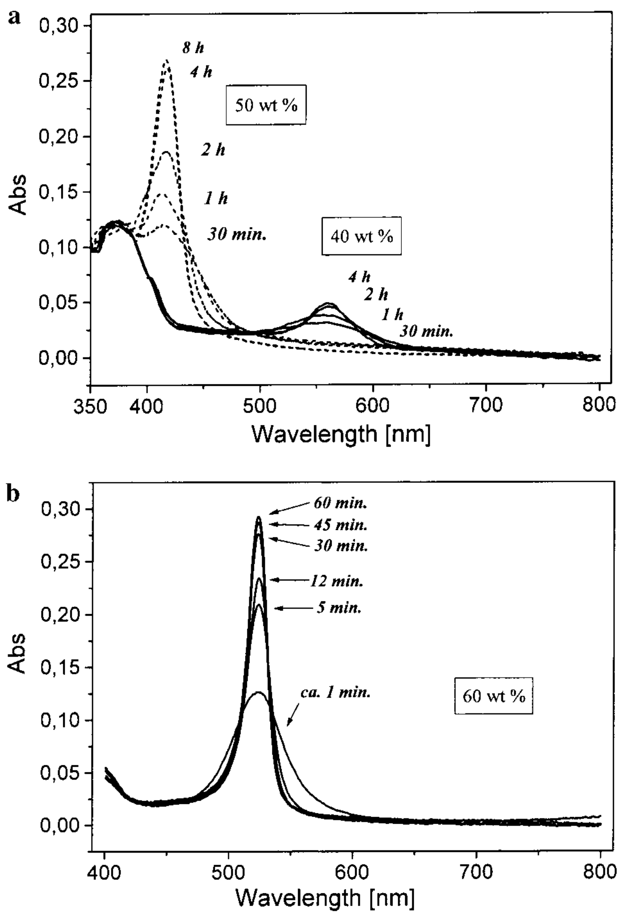


Figure 4. Time dependence of the evolution of the selective reflection at 25 °C for (a) 50 or 40 wt % of **C1** in styrene and (b) 60 wt % of **T20** in styrene.

selective reflection is very small (18 nm), which again proves the quality of the orientation and the homogeneity of the cholesteric phase.

This is due to the low viscosity of the terpolymers prepared by living polymerization techniques and their low polydispersity. **C1** prepared by—nonliving—anionic polymerization with sodium cyanide gives, on the contrary, broad reflection bands (see Figure 3b).

To separate kinetic effects from static differences of the cholesteric phases, we looked more closely at the time dependence of the formation of a cholesteric monodomain. We found that it depends on the molecular weight (see Figure 4). For the high molecular weight polymer **C1**, about 5 h is necessary to orient a 50 wt % lyotropic phase. The phase with only 40 wt % of polymer orients more quickly, but the final intensity is smaller. For the terpolymer **T20** with lower molecular weight, 45 min is already enough to orient a 60 wt % solution. Since the measurements presented in Figure 3 were taken after 45 min (terpolymer **T20**) or 4 h (copolymer **C1**), they present therefore equilibrium values. This is at least true for the measurements performed above 25 °C (the temperature of the kinetic measurements of Figure 4). Broad reflection bands at low temperature (see especially Figure 3a) may be due to an incomplete orientation.

First results regarding the concentration dependence of the selective reflection are presented in Figure 5 for polymer **T21**. As to be expected, and seen in model studies,[17] the pitch shortens with increasing concentration due to an increasing interaction of the more densely packed chiral polymer chains.

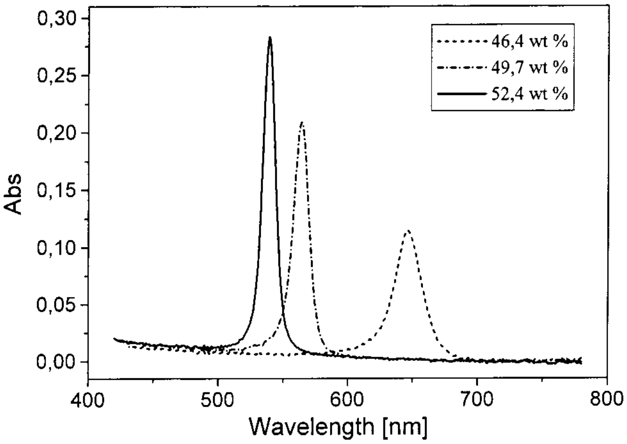


Figure 5. Variation of the selective reflection with the concentration of the lyotropic cholesteric phase for polymer **T21** at 25 °C.

More extensive measurements covering a wider concentration region show, however, a more complex behavior (see Figure 6). All systems have the strongest interactions and therefore the shortest pitch at concentrations between 55 and 60 wt % of polymer. Both lower and higher concentrations lead to an increase (red shift) of the pitch. The polymers can be separated into three groups, depending on their position in Figure 6. **C1** has the shortest pitch. For this polymer with a high molecular weight, the increase of the pitch cannot be followed

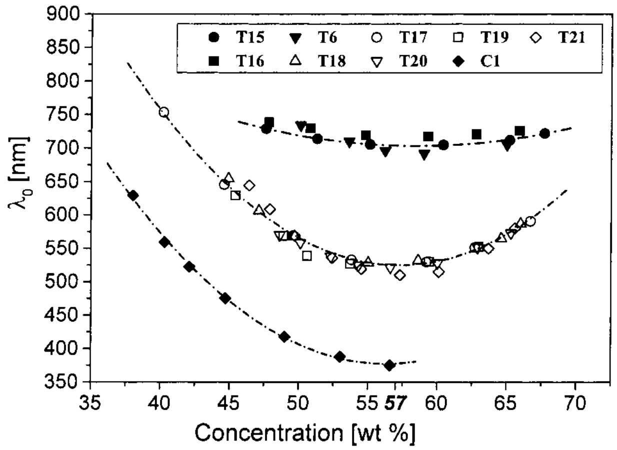


Figure 6. Collection of the concentration dependence of selective reflection for polymers **C1**, **T6**, and **T15**−**T21** at 25 °C.

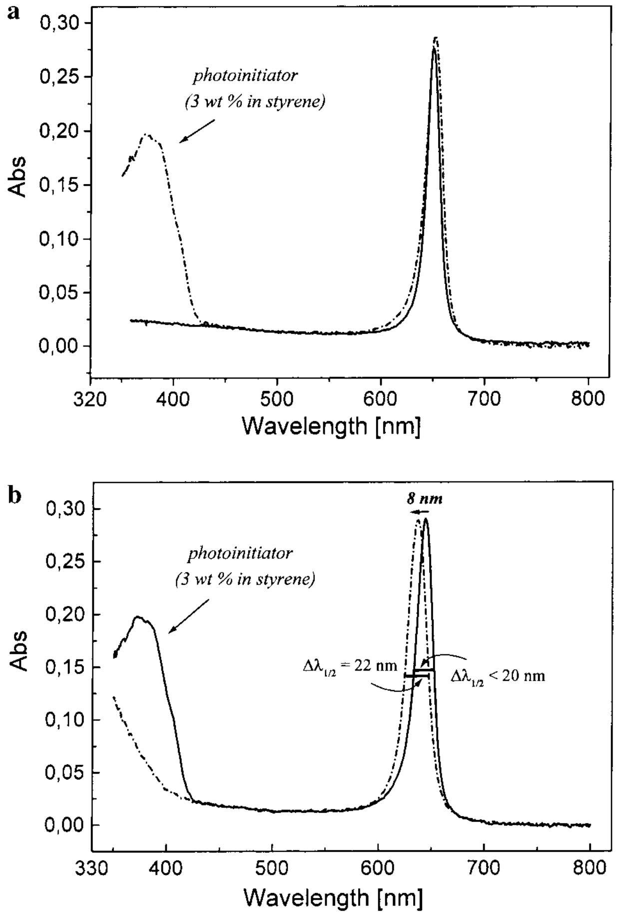


Figure 7. Influence of (a) the presence of photoinitiator and (b) cross-linking on the selective reflection of 60 wt % of **T6** in styrene at 25 °C.

experimentally at high concentrations, because these phases are too viscous. The second group contains the polymers **T17**−**T21**. The third group contains the polymers **T6**, **T15**, and **T16**. Except for **T6**, this grouping follows the molecular weight, being highest for **C1** and lowest for **T15**.

Effect of Cross-Linking. Cross-linking transforms a polymer solution with a viscosity similar to honey into a flexible polymer film. Its influence on the selective reflection is demonstrated in Figures 7 and 8. The first step in this process is the addition of the photo-cross-linker to the lyotropic phase. Figure 7a shows that 3% of photo-cross-linker has nearly no effect on the selective reflection. The subsequent photo-cross-linking (Figure 7b) leads to a small blue shift of 8 nm of the selective reflection. This is probably due to the volume shrinkage during polymerization. The half-width of selective reflection increases slightly during polymerization from less than 20 to 22 nm. This value is, however, still very low. The optical quality of the cholesteric film, obtained by cross-linking, is thus very good.

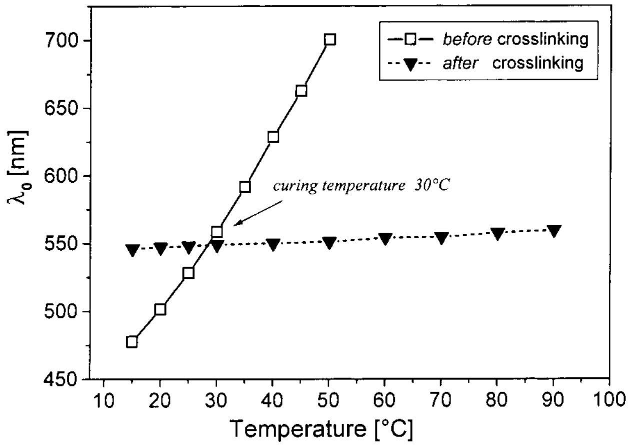


Figure 8. Temperature dependence of selective reflection before and after cross-linking for a system with 60 wt % of **T19** in styrene.

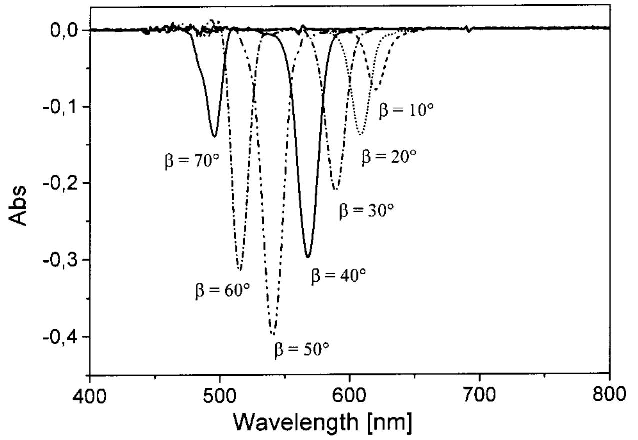


Figure 9. Angular dependence of selective reflection for a film prepared from 65 wt % of **T6** in styrene, cross-linked at 20 °C.

After cross-linking the pitch of the cholesteric helix—and thus the selective reflection—no longer depends on temperature (see Figure 8). For an un-cross-linked sample of **T19**, a variation of temperature from 15 to 50 °C shifted selective reflection from 470 to 700 nm. After cross-linking the pitch of the cholesteric helix is frozen and can no longer readjust to the temperature variation. The tiny temperature dependence still remaining for the cross-linked sample is probably due to the thermal expansion of the whole sample. Photo-cross-linking the sample at various temperatures allows "freezing" of different colors (see Figure 10).

Angular Dependence of Selective Reflection. The special interest in cholesteric colors is related to the angular dependence of selective reflection. This property gives rise to opalescent colors. To quantify this effect, we measured the wavelength of the reflected light as a function of the angle between light source and detector. The results are displayed in Figure 9. The

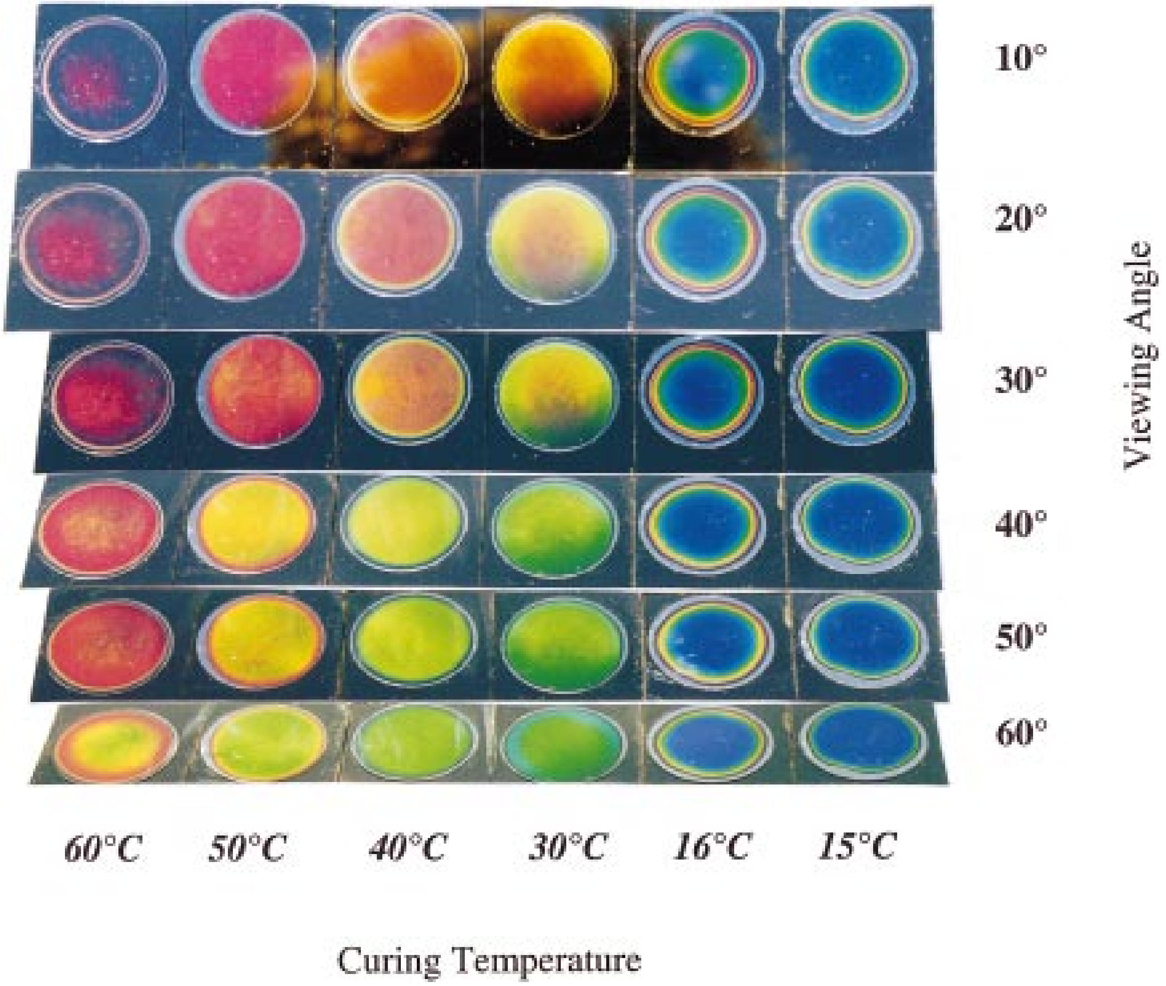


Figure 10. Optical impression of the angular dependence of films from 65 wt % of **T6**. The films were cross-linked between 15 and 60 °C.

intensity of reflection measured at different angles cannot be compared, because the measuring geometry changes. Nevertheless Figure 9 shows that the half-width remains narrow, and the maximum of selective reflection shifts by more than 100 nm by varying the angle. The associated optical impression is presented in Figure 10.

Experimental Part

General Procedures. Air- and moisture-sensitive compounds were handled under inert atmosphere using standard Schlenk techniques. All steps involving titanium compounds were carried out in a drybox. All monomers were stirred over calcium hydride for 24 h and vacuum-distilled before use. ^{1}H NMR spectra were determined at 400 MHz, using a Bruker AC 400 FT-NMR spectrometer. Polarimetry was performed using a Perkin-Elmer 241 MC polarimeter. UV spectra were determined using a Shimadzu 2102 UV/vis spectrometer.

Monomers. Hexyl isocyanate was prepared from heptanoyl chloride.[16]

(*R*)-(+)−2,6-Dimethylheptylisocyanate was prepared from commercially available (*R*)-(+)-Pulegone by HCl addition, followed by hydrogenation.[24] The resulting (*R*)-(+)-dihydrocitronellic acid was then treated with oxalyl chloride to obtain the acid chloride; subsequent Curtius rearrangement with azidotrimethylsilane yielded the isocyanate.[25]

2-(Isocyanatoethyl) methacrylate was purchased from Polyscience.

Anionic Nonliving Polymerization. Only freshly distilled monomers were used. The polymerizations were carried out in DMF at about −60 °C under nitrogen atmosphere using sodium cyanide as initiator.[21] The raw product was dissolved in THF and reprecipitated from methanol and then dried at 30 °C under vacuum.

Cyclopentadienyl(dimethylamino)titanium Dichloride ($CpTiCl_2N(CH_3)_2$). In a synporportion reaction titanocene dichloride (Cp_2TiCl_2) and titanium tetrachloride ($TiCl_4$) were converted into 2 equiv of cyclopentadienyltitanium trichloride ($CpTiCl_3$), which was then reacted with *N*-trimethylsilyl-*N*,*N*-dimethylamine ($(CH_3)_3SiN(CH_3)_2$) at room temperature to yield the desired product.[19]

Ti(IV)-Catalyzed Living Polymerization. A volumetric solution of the catalyst (typically 0.2 mol/L in chloroform or toluene) was prepared.

(a) Solution: A measured amount of this solution, depending on the monomer-to-initiator ratio, was added by syringe to the degassed monomer mixture in a 4 mL screw cap vial with a magnetic stir bar.

(b) Bulk (DP $\leq$ 100): A measured amount of catalyst was weighed into the vial, and about 200 μL of toluene was added. After some minutes the monomers were added by syringe. The catalyst rapidly dissolved in the monomers.

The vial was closed and stirred at room temperature in the drybox for 3−10 days, depending on the planned molecular weight.

All workup steps involving polymers with methacrylate side groups were performed in the dark or under yellow light.

After the polymerization was complete, the solid orange mass was dissolved in 15 mL of a degassed mixture of methylene chloride and methanol (4:1). This solution was poured into 350 mL of cold methanol, and a white solid precipitated. The polymer was isolated by filtration and reprecipitated from methylene chloride/methanol. The volatile materials were removed under vacuum.

Polymer Characterization. Gel permeation chromatography (GPC) was performed using a Waters 510 HPLC pump equipped with a Waters model 440 absorbance detector (λ = 254 nm); the solvent was chloroform. The molecular weights given in the tables are the weight-average molecular weight M_w and the molecular weight at the peak of the GPC curve M_p. Molecular weights were determined relative to polyisocyanate standards, six samples of polyhexyl isocyanate synthesized with the living polymerization procedure described above. Their absolute molecular weights were determined by tandem GPC light scattering (in the group of B. M. Novak, University of Massachusetts, Amherst).

Data of the standards are available as Supporting Information.

The polymer compositions were analyzed by ^{1}H NMR spectroscopy. To obtain well-resolved spectra, the polymers were decomposed to trimers.[12] This was done directly in the NMR tube. About 30 mg of polymer, 1.5 mL of DMF-d_6, and 3 mg of sodium cyanide were reacted at 70−80 °C for 10 h. After sedimentation of the undissolved residue, the spectrum was taken. The following signals were used for the evaluation: ^{1}H NMR (400 MHz, DMF-d_6), δ (ppm) 3.85 (triplet, 2H, HIC), 3.7 (doublet, 2H, DMHIC), signals between 4.1 and 4.5 (4H, 2-(isocyanatoethyl) acrylate).

Preparation of the Cholesteric Films. A mixture of the isocyanate polymer in freshly distilled styrene and 3 wt % of the photoinitiator (LR8893X, BASF AG) was prepared in a screw cap vial. Small portions of the homogeneous liquid crystalline solution were sandwiched between pairs of microscope slides. Irradiation with a low-pressure mercury lamp for about 20 s caused the styrene to copolymerize with the methacrylate functionalities. The resulting stiff polymer films had a thickness of ~100 μm.

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Supporting Information Available: Table 4 containing data of the polyisocyanate standards. This material is available free of charge via the Internet at http://pubs.acs.org.

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