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Synthesis and lyotropic liquid crystal properties of chiral helical polycarbodiimides

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Chiral helical polymers have been expected to exhibit optical activity with a significantly large optical rotation power. In this paper polymethylphenylethylcarbodiimides (Poly-PhEMCDI) with helical structure were synthesized by the insertion polymerization of a corresponding chiral monomeric carbodiimide initiated by a copper complex. The circular dichroism spectra and optical rotation power induced by the ordered rigid main chain helical structure of polycarbodiimides, in solution and as cast films, were studied. Polycarbodiimides have a rigid rod helical structure and form lyotropic liquid crystal (LLC) in organic solvents such as dichloromethane (DCM), chloroform and THF. The LLC phase was studied using polarizing optical microscopy and X-ray diffraction. A chiral nematic phase was formed in DCM and chloroform in the concentration range 20–36%. Spherulites were formed in more concentrated solution. The formation of a LLC phase in polycarbodiimides organic solutions makes it possible to align the polymer helical chain to form an ordered film for electro-optical applications.

1. Introduction

Chirality is a unique feature which plays an important role in nature. Optically active polymers, either natural or synthetic, have attracted much attention in connection with stereochemistry, conformation and the functions of polymer materials. Helical polymers with an extended chain have macromolecular chirality, which can endow these materials with improved chiro-optical and even additional properties, such as polymeric liquid crystallinity [1–4]. Helical polymers in the solid state may exhibit considerable optical activity because of the generation of a helical electron orbital in the helical structure formed by chiral monomer molecules. Until now very few observations on the optical rotatory power of polymer films have been reported [5, 6]. A uniformly drawn poly-L-lactic acid (PLLA) sample was found to have an optical rotatory power 100 times larger than that of α-quartz crystal [7, 8]. It has also been demonstrated that a circular plate of PLLA higher order crystal has very fast light modulation—the response change in the amplitude of transmitted light up to 10 MHz [9]. Thus helical polymers are promising candidates for electro-optical applications if suitable functional groups are introduced into polymer.

Chiro-optical properties are usually increased with the size of the chiral entity and can become very large due to the formation of chiral helical superstructures such as a chiral liquid crystal phase and a helical polymer structure. It has been reported that the optical rotation ($[\alpha]_D^{20}$) increased from 1 to 500 deg dm^{-1} g^{-1} in helical polymers on transforming a monomer into a polymeric entity [10]. Unichiral helical polymer superstructures and liquid crystalline phases, in this way, act as amplifying media to induce very large optical rotations [10]. Polymers with a relatively rigid backbone, planar or helicoidal, and relatively flexible side groups attached to their main chains, are potentially lyotropic liquid crystal-forming materials in organic solution and thermal liquid crystals in bulk. Extensive studies in this field have been conducted on natural biomacromolecules, such as DNA and polypeptides [11] with helical structures, and on many synthetic polymers [12], such as polyamides [13], polyisocyanates [14], polyisocyanides and cellulose derivatives [15].

Helical polymers, such as polyisocyanides and polyisocyanates, show different conformational and rheological properties due to differences in their corresponding

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helix conversion barrier, $\geqslant 27\,\mathrm{kcal\,mol^{-1}}$ [16] and 3–5 $\mathrm{kcal\,mol^{-1}}$ [17], respectively, and persistence lengths, 30Å and 600Å, respectively. In polycarbodiimides a helical conformation exists with a 6/1 helix (six repeat units form one turn) in the solid state and in solution. This may combine the persistence length of polyisocyanates (adopted 8/3 helical conformation: eight repeat units form three turns) and the high inversion barriers close to that of alkyl polyisocyanides (with bulky imine substituent that adopts 4/1 helices: four repeat units form one turn). Polycarbodiimides can be synthesized through the natural polymerization of carbodiimide monomers with Ti(VI), Cu(I) or Cu(II) complexes. The molecular masses of the resulting polymer can be controlled by adjusting the initiator to monomer ratios, due to the natural polymerization nature of the insertion polymerization [18–20].

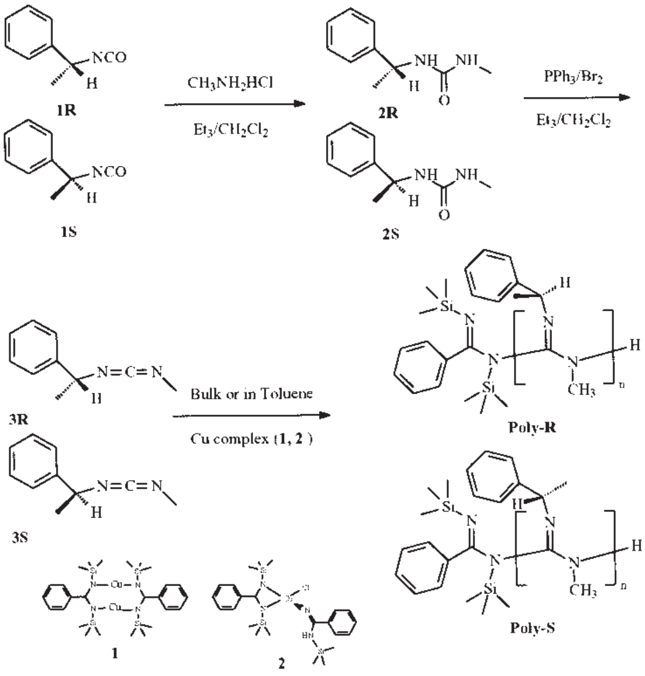
Concentrated organic solutions of polycarbodiimides can form LLC phases at room temperature. In this paper the synthesis of homochiral helical polycarbodiimides with different chiral side groups are described. Their chiro-optical properties and LLC-forming tendency in organic solvents are reported for the first time.

2. Experimental

2.1. *General*

All the chemicals were reagent grade and used without further purification. The title polycarbodiimides were synthesized by the procedures shown in the scheme. All the synthetic operations were carried out under dry inert gas (nitrogen or argon) unless otherwise noted. The compounds were stored under inert atmosphere after preparation.

Circular dichroism, and UV-Vis spectra measurement were performed on a Jasco J-820 Spectropolarimeter; Quartz or glass slides were cleaned thoroughly by plasma. ^{1}H NMR spectra were recorded on a JEOL 270 MHz spectrometer. Lyotropic liquid crystal textures were observed with a polarizing optical microscope (POM). X-ray diffraction (XRD) measurements were performed on a Rigaku R-AIXS X-ray diffractometer with CuK$_\beta$ radiation ($\lambda = 1.542$ Å, half-width = 0.005 Å) with beam size 0.5 mm Ø. LLC samples for XRD were sealed in thin wall quartz sample tubes using a fast solidified resin to prevent evaporation of the solvent, and prepared just before the measurement. Second harmonic generation (SHG) of the films was measured by the Maker-fringe method using a Q-switched Nd-YAG laser (New Wave Research Minilase III, 1064 nm, 8 ns, 3 mJ pulse).



Scheme. Preparation of the polycarbodiimides.

2.2. *Carbodiimide monomer*

The *R*-(+)-N-Methyl–*N*′-(α-phenylethyl)carbodiimide (**3R**: RPhEMCDI), *S*-(-)-*N*-methyl–*N*′-(α-phenylethyl)-carbodiimide (**3S**: SPhEMCDI) were synthesized from the corresponding ureas (**2R** and **2S**) which were readily prepared quantitatively, without separation, by stirring equimolar corresponding isocyanate compounds (**1R** and **1S**) with methylamine hydrochloride in dry dichloromethane at room temperature for 24 h, following literature procedures with little modification [21]. The carbodiimides **3R** and **3S** were purified by distillation under vacuum in the presence of CaH$_2$ in good yield as clear, colourless oils. The monomers were used for polymerization immediately after distillation. RPhEMCDI and SPhEMCDI, b.p. 65–67°C/0.05 mm Hg, yield 70%, d^{25}0.992. ^{1}H NMR (CDCl$_3$, δ, ppm) 1.55(3H, CH$_3$), 3.2(3H, CH$_3$), 4.6(1H, CH), 7.2–7.3 (5H, phenyl ring).

2.3. *Initiators*

Three initiators, the copper(I) amidinate complex (**1**), copper(II) amidinate complex (**2**) and CuCl$_2$ (**3**) were possible candidates for initiation of the polymerization of the carbodiimides. CuCl$_2$ (**3**) was prepared by dehydration of CuCl$_2\cdot$2H$_2$O with an excess of SOCl$_2$, and kept dry under a dry N$_2$ atmosphere before use. The copper complexes were prepared from CuCl or CuCl$_2$ and *N*, *N*, *N*′-tris(trimethylsilyl)benzamidine in dry acetonitrile, as a white powder (**1**) or dark green crystal (**2**), according to the literature method [22]. *N*, *N*, *N*′-tris(trimethylsilyl)benzamidine was itself prepared by the reaction of benzonitrile with LiN(SiMe$_3$)$_2$ and ClSiMe$_3$ [23]; it was obtained by distillation under vacuum (110°C/0.1 mm Hg) as an oil or solid in 70% yield. ^{1}H NMR (CDCl3, δ, ppm) 0.10–0.10 (CH$_3$), 7.2–7.4(phenyl ring).

2.4. *Polymerization*

Polymerization was performed under inert atmosphere in sealed bottles or flasks after mixing the initiator with monomer at a certain molar ratio typically 1:5 to 1:500. All the mixtures were vigorously stirred for a period of time, typically 24 to 96 h. The resulting solid or viscous solutions were thinned with toluene and precipitated by dropping into a large amount of vigorously stirred absolute methanol to recover the polymer as white spongy solid; yields 70–100%. ^{1}H NMR (CDCl$_3$, δ, ppm) 1.44(3H, CH$_3$), 3.09(3H, CH$_3$), 4.57(1H, CH), 7.19–7.28 (5H, phenyl ring).

3. Results and discussions

3.1. *Polymerization*

The polymerization of the carbodiimide monomers was performed under dry Ar or N$_2$ at room temperature in bulk with no solvent. The monomers can polymerize completely in 24hrs. In general, several hours after the addition of initiator solution (concentrated solutions of initiator in the corresponding carbodiimide monomer) the reaction mixture became viscous and then solidified, depending on the initiator to monomer ratio. All three initiators are good catalysts for the polymerization at room temperature, however their action can accelerate at higher temperature to yield less polymer with a narrower polydispersity. For initiator **1**, the solubility in monomer or its toluene solution is very low, thus making it difficult to control the reaction. All the samples used for further study in this paper were polymerized using **2** as initiator, and purified by at least three dissolve/precipate cycles from THF into methanol unless otherwise noted. Samples prepared by this method have molecular masses ranging from 3 000 Da up to 10^5 Da with a polydispersity index (M_w/M_n) in the range 1.20–1.5 measured using GPC with THF as eluant.

3.2. *Circular dichroism spectra and optical rotation dispersion spectra*

The UV and CD spectra for the monomers **3R** and **3S** and their corresponding polymer **Poly-R** and **Poly-S** are shown in figure 1. The UV absorption peaks of the phenyl ring appeared on the spectra in the region from 240–270 nm, overlapped with the n-π* transition of >N–C–N< for the monomers **3R** and **3S**. After polymerization the UV absorption peak of the phenyl ring as side chain for polymers **Poly-R** and **Poly-S** became a shoulder around 265 nm. The n-π* transition peak of >N–C–N< disappeared, and a new peak appeared at 235 nm attributed to the n-π* transition of –N–C<.

In the CD spectra of **3R** and **3S**, distinct peaks appeared between 240 and 270 nm, attributed to both the phenyl ring and >N–C–N<. Similar peaks for **Poly-R** and **Poly-S** appeared in CD spectra, possibly attributable to phenyl rings in the side chain. The peak at 235 nm was attributed to the negative couplet for **3R**, indicative of P helix and positive couplet, and M helix for **3S**.

The mean residual ellipticity (θ) of **Poly-R** and **Poly-S** was greatly enhanced, about 10-fold that of the

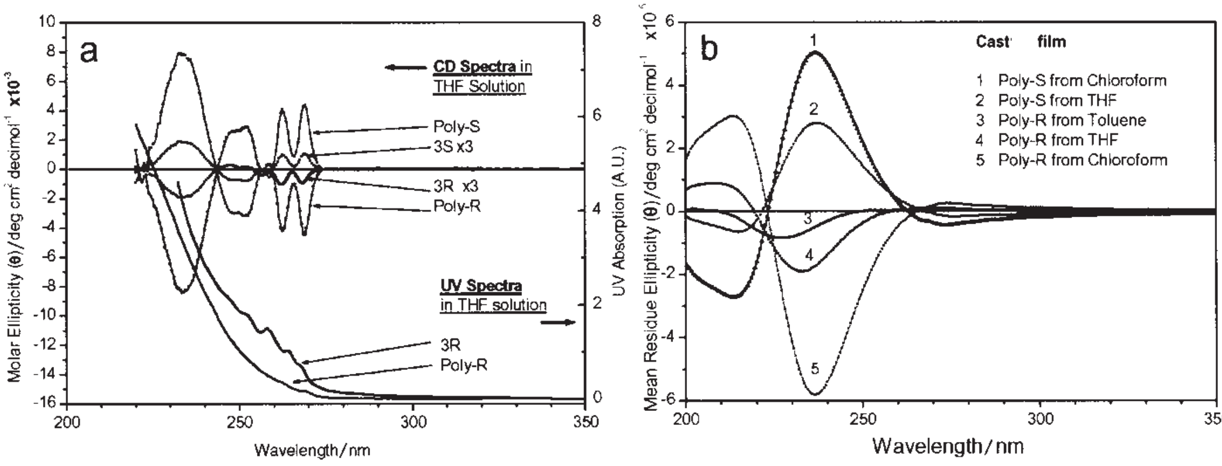


Figure 1. (a) CD spectra and UV-Vis spectra of **Poly-R** and **Poly-S** and their corresponding monomers **3R** and **3S** in solution. (b) Representative CD spectra of cast films of **Poly-R** and **Poly-S** from solutions of different solvents.

corresponding monomers **3R** and **3S**, with respect to the CD bands at 268 nm.

The CD bands of cast films of **Poly-R** and **Poly-S** are enhanced as shown in figure 1, in which bands at 237 nm are enhanced to about 50 to 200 times those of the corresponding polymers in solution; this is attributed to the ordered packing of helical main chain structures. The CD spectra of **Poly-R** and **Poly-S** cast films prepared from chloroform solution were enhanced the most, indicating that chloroform may be the best solvent for formation of an ordered film. One reasonable explanation for the largest enhancement is the alignment of the helical main chain caused by the formation of an LLC phase that was observed in concentrated solutions of polycarbodiimides. It is not always easy to prepare well ordered transparent cast films from **Poly-R** and **Poly-S** solutions because the polymers readily form small crystals due to their rigid-rod nature. Fast evaporation of the solvent from a fast spread of a very thin film is helpful in obtaining transparent films, which may yield good spectra.

From ORD results in solution shown in figure 2, it can be seen that **Poly-R** and **Poly-S** showed larger optical rotatory power than did the monomers **3R** and **3S**, especially at wavelengths shorter than 230 nm. Both the chiral groups in the side chain, and the main chain helical structure of **Poly-R** and **Poly-S** can induce rotatory power.

SHG measurement is a very useful tool in the study of the ordering of the polymer main chain because chirality is asymmetric. Various solvents, including THF, toluene, dichloromethane and chloroform were used to prepare cast films for SHG measurement. SHG signals could be detected for all the solvents except toluene; films prepared by casting from chloroform showed the strongest SHG signal, indicating the formation of ordered asymmetric structure in the films, which may be liquid crystalline glass. In bulk toluene solutions of **Poly-R** and **Poly-S**, no ordered textures were observed by POM and the solutions were always isotropic at any concentration; an isotropic glass was formed in cast films. The SHG measurement thus gave a positive indication that the best ordered structure was formed in chloroform solution. This result agrees well with the same enhanced order of mean residue ellipticity of films cast from solutions of different solvents. Extensive research on enhanced SHG and large optical rotatory power is in progress.

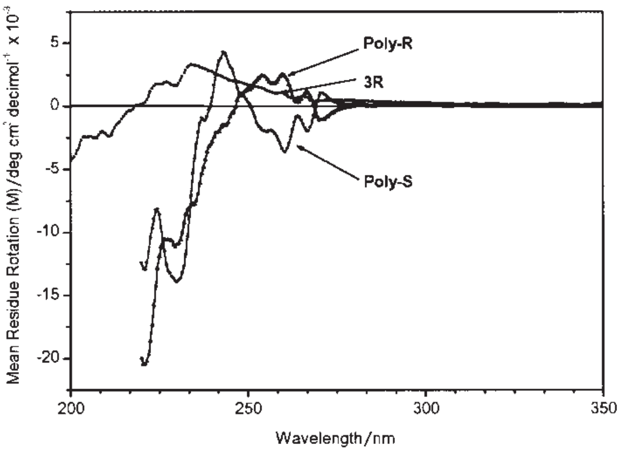


Figure 2. ORD spectra of **Poly-R** and **Poly-S** and corresponding monomers **3R** and **3S** in dilute THF solution.

3.3. *Lyotropic liquid crystal phase*

3.3.1. *Solubility of polycarbodiimides and the lyotropic liquid crystal phase*

Poly-R and **Poly-S** have similar phase behaviour and we will discuss only **Poly-R**, for the sake of clarity. **Poly-R** is soluble in toluene, THF, $CHCl_3$, CH_2Cl_2, CCl_4, $C_2H_3Cl_3$, $CHBr_3$ and 1,4-dioxane; it is insoluble in Et_2O, CH_3CN, EtOAc and DMF. In general, the concentrations of newly prepared **Poly-R** solutions are too low for the formation of the LLC phase so that the solutions are clear and viscous. On evaporation of the solvent and annealing for several hours under a N_2 flow, the solutions become concentrated and LLC phases are gradually formed. Solutions containing the LLC phase have the typical reflection colour of a cholesteric phase. If the solution was annealed for several days, a more ordered LLC phase was formed.

The solution of **Poly-R** in THF is isotropic and clear at low concentration. The concentration range of the LLC phase is narrower than that of the LLC phase in DCM and chloroform solutions. The solubility of **Poly-R** is lower in THF than in DCM and chloroform. At concentrations above 35 wt% and at room temperature, spherulites were observed by POM in the anisotropic supersaturated solution of the LLC phase.

Poly-R forms clear solutions when heated in dioxane but only forms gel after cooling to room temperature. In toluene, trichloroethane and tetrachloroethane **Poly-R** formed only clear solutions at almost all possible concentrations. Casting of these solutions resulted in uniform transparent films with no indication of spherulite formation.

3.3.2. *Lyotropic liquid crystal texture in DCM and chloroform*

Poly-R and **Poly-S** have the same mesomorphic behaviour. For simplicity and clarity, **Poly-R** only is discussed in this paper. In general, DCM and chloroform solutions are isotropic at concentrations below 20 wt% and become anisotropic above this critical

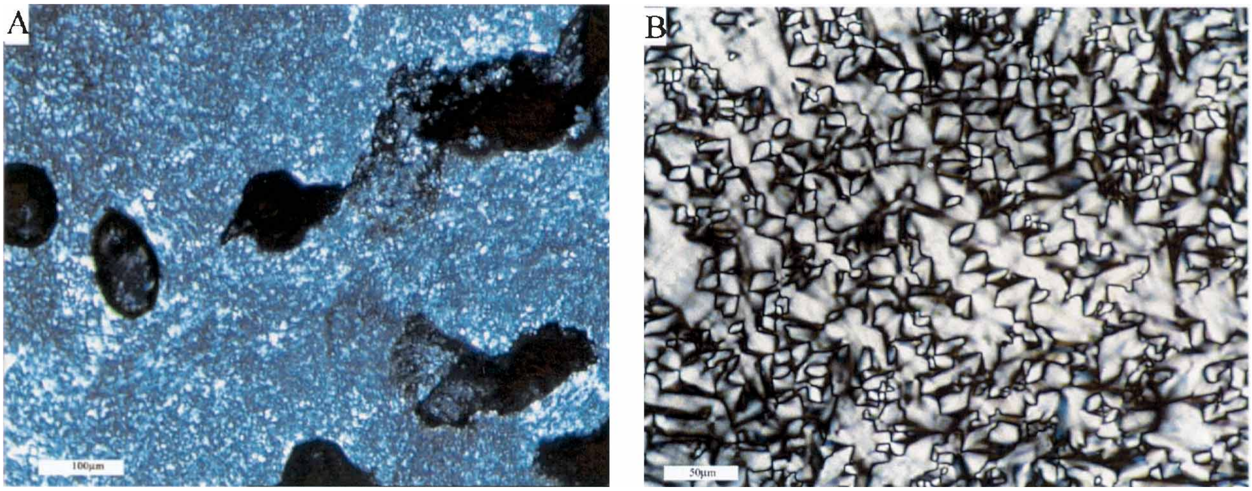


Figure 3. POM textures of the liquid crystal phase formed in concentrated **Poly-R** solutions. A: Precholesteric texture in DCM 20 wt % solutions; B: nematic texture appearing near the boundary of solution droplets.

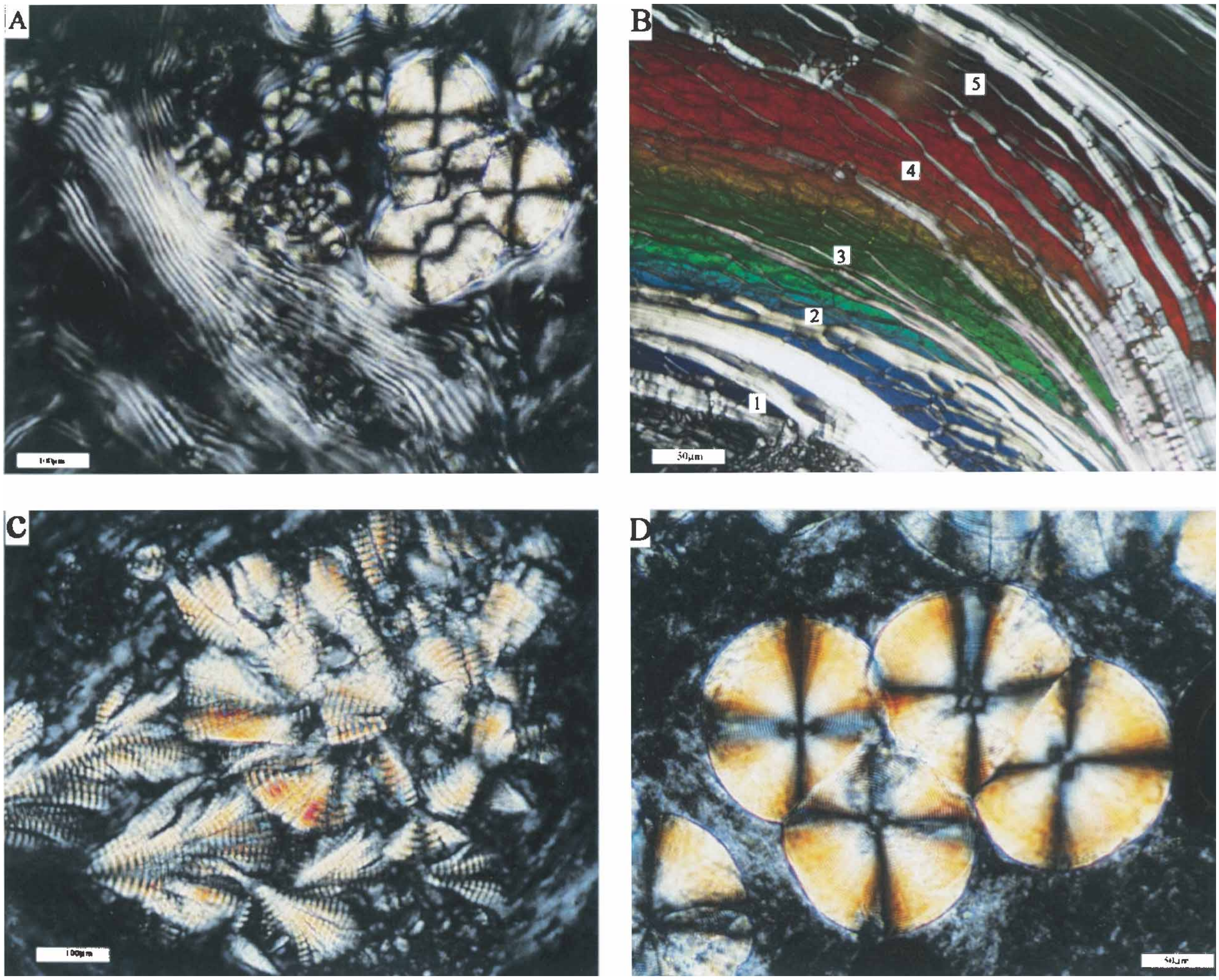


Figure 4. POM textures appearing in sandwiched samples of **Poly-R** solutions of different solvents. A: Cholesteric oily streaky texture with spherulitic structures; B: oily cholesteric texture with reflection colours covering the visible spectrum; C, D: spherulitic structures in concentrated $CHCl_3$ (C) and THF (D) solutions.

concentration, as shown in figure 3. At first, the sandwiched samples exhibit distinct birefringence under POM, perhaps a precholesteric phase as in figure 3A. Near the border of solution droplets, a frozen nematic phase is formed due to the fast evaporation of the solvent, as in figure 3B. At higher concentrations the solutions exhibit a typical cholesteric phase, as shown in figure 4 and by XRD (figure 5). A typical oily streaky cholesteric texture was observed in **Poly-R**, as shown in figure 4B. Reflection colours typical of a cholesteric LC phase were also observed and measured on reflection in the UV-Vis spectrometer; however it is not always easy to prepare samples with a characteristic reflection colour for these observations. The observed colours cover almost the whole visible region from 400 to more than 800 nm, as shown in figure 6, and are related to the cholesteric helix pitch and, changing with solution concentration.

If the concentration in DCM was increased to 26% or over, spherulites were formed gradually in the anisotropic solution and coexisted with the cholesteric phase during storage (figure 4A). Long storage was neccessary for the formation of spherulitic structure. At concentations above 36%, the cholesteric phase almost disappeared and only spherulites remained, under POM observation (figures 4C, 4D).

Because of the self-organization property of liquid crystal systems, the formation of a LLC phase in **Poly-R** and **Poly-S** solutions gives a useful way to prepare ordered polycarbodiimide samples which may be useful for applications as organic electro-optical materials. As we have already discussed, CD spectra of **Poly-R** and **Poly-S** cast films have very large enhancement and large SHG signals compared with solution samples, the enhancement strongly depending on the solvent. These results suggest that the phenomena are related to the formation of LLCs, which act as important amplifying media in enhancing the bulk chirality of the polycarbodiimide samples, due to the formation of the more ordered liquid crystal glass.

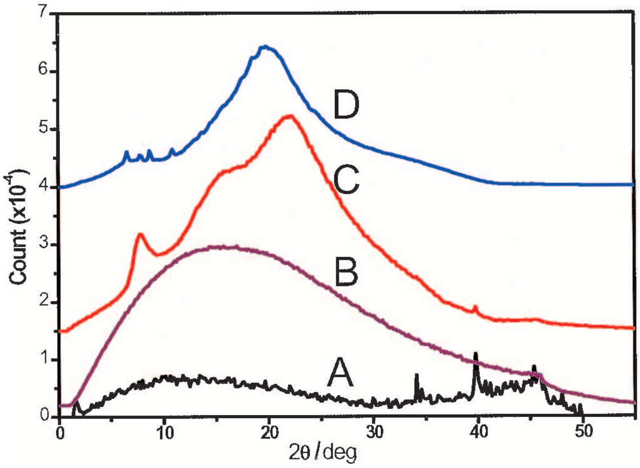


Figure 5. XRD patterns of different solution samples. Curves A to C, with broad peaks at about 2θ, are typical XRD patterns of the cholesteric phase. In curves C and D, the sharp peaks appearing in low angle region correspond to spherulites. A: in DCM 20%; B: in DCM 26%; C: in DCM 35%; D: in THF 30%.

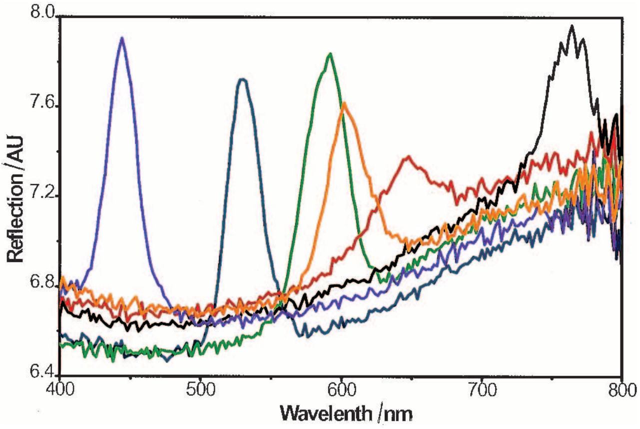


Figure 6. Reflective UV-Vis spectra of cholesteric samples of **Poly-R**/DCM solution exhibiting maximum reflection peaks, and covering almost the whole visible region from 400 to 800 nm.

LLC phase formation also makes it possible to align the chiral helical main chain of polycarbodiimides in the way that has been extensively used to align LCs in LC cells. Studies on the operation of polycarbodiimide samples in LC cells, to obtain ordered films for optical purposes, are in progress.

4. Conclusions

We have synthesized polycarbodiimide compounds with different molecular weight. The polycarbodiimides formed chiral helical structures and their chiro-optical properties were greatly enhanced compared with monomers. Due to the formation of a very rigid backbone, and the presence of bulky phenyl group in the chiral side chain, polycarbodiimides have been found for the first time to form LLC phases in DCM and chloroform. Films cast from LLC solutions exhibit preferential orientation of the molecular helical main chain backbone, and large enhanced circular dichroism and optical rotatory power. In the lyotropic liquid crystal phase, helical main chain polycarbodiimide structures have very good ordering, enabling the preparation of ordered helical polymer films, which may be used as potential optical modulation materials. **Poly-R** and **Poly-S** helical structure segments in LLC solutions can be extensively ordered by standard liquid crystal techniques used in LC cells.

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