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Notes

Synthesis and CD Spectra of Isocyanide Polymers: Some New Aspects about Their Stereochemistry

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Introduction

The polymerization of isocyanides, catalyzed by either protonic acids[1] or Ni(II) salts,[2] provides an unusual class of polymers, which are assigned the poly-Schiff base structure, on the basis of their infrared spectra analogous to those of model compounds and the known mode of reactivity of the functional group. Assuming that this structural assignment is correct in all cases, these materials can be defined as poly(iminomethylenes).[3]

Millich and co-workers observed that the polymerization of optically active α-phenylethyl isocyanide[4] provided a polymer that exhibited a large increase in optical rotation over the monomer. This result was related to the preference for an ordered conformation for the polymer and the structural regularity of the poly[[(α-phenylethyl)imino]methylene] was shown to be consistent with a 4/1 helix by X-ray studies in the solid state.[5]

Drenth and co-workers synthesized a wide range of poly(iminomethylenes) and studied their structural properties. They resolved into optically active fractions the poly[(*tert*-butylimino)methylene].[6] On the basis of the circular dichroism spectrum, these authors concluded that the earlier proposed 4/1 helix structure was applicable also to poly[(*tert*-butylimino)methylene] and they later obtained, by polymerizing chiral isocyanides, optically active poly(iminomethylenes) that were also assigned the 4/1 helix structure.[7,8] Circular dichroism measurements were used to support this assumption, and Drenth and co-workers suggested that the succession of negative to positive bands in the range 300–250 nm of the CD spectrum of the poly[(*tert*-butylimino)methylene] is a couplet due to the coupling of the $n \rightarrow \pi^*$ transition of the imino chromophores of the polymer. On the basis of theoretical calculations this couplet would be consistent only with a 4/1 helix. By comparing the sign of the CD band near 300 nm, assumed as the lower energy part of the exciton couplet, with the corresponding CD band of the poly[(*tert*-butylimino)methylene], they assigned the prevalent screw sense to several optically active poly(iminomethylenes).[7,8]

The existence of a polyimine structure for the isocyanide polymers makes it possible, in principle, to have syn–anti isomerism around the carbon–nitrogen double bond and syn–anti isomerism could prevent a high stereoregularity of the polymers. This possibility was excluded on the basis of the space-filling models of the 4/1 helix,[3-5] which was assumed to be the unique structure of the poly(iminomethylenes). However, in recent years, Green and co-workers[9] carried out high-field ^{13}C NMR studies on some poly(iminomethylenes) and obtained evidence for some stereoirregularity of the backbone chains.

In the present work, we report on the synthesis of the polymers of two aliphatic isocyanides. The chiro-optical properties of these polymers were determined to obtain information on the stereoregularity of the macromolecular chains and on the occurrence of a helicoidal conformation. Suitable imines were also prepared as low molecular weight structural models for the corresponding polymers and the UV and CD analysis of these compounds were a great aid to the chiro-optical study and the structural characterization of the polymers.

Results and Discussion

The isocyanides, **2**, were obtained by dehydration of the corresponding formamides with thionyl chloride in dimethylformamide,[10] and the formamides were prepared by *N*-formylation[11] of the amines 1 as shown in Scheme I. The polymerization of these monomers was carried out according to a reported procedure[3] by adding 1 mol % of $NiCl_6 \cdot 6H_2O$, as the catalyst, to the isocyanide dissolved in methanol and maintaining the reaction temperature at 65 °C for 15 h. After reprecipitation, the polymers, **3a** and **3b**, were obtained as yellow solids in good yields. An increase of the polymer optical rotation with respect to the monomer was always obtained. The molecular weights were rather low with an $\bar{M}_n$ of 2600 for **3a** and 1790 for **3b**. Attempts to obtain higher molecular weights by using 0.1% of catalyst were not successful.

The ^{13}C NMR spectrum of the polymer **3b** (Figure 1), recorded at 75.4 MHz in $CDCl_3$ as solvent, showed between 10 ppm and 70 ppm a group of broad signals arising from the resonances of the carbon nuclei of the pendant groups; the broad absorption centered at 164 ppm is due to the N=C function. The same trend was observed for the polymer **3a**.

UV and CD Analysis. In the aliphatic poly(iminomethylenes), **3a** and **3b**, the imino group is the only chromophore absorbing in the studied range (190–600 nm). In order to obtain evidence for the assignments in the UV and CD spectra for the macromolecular structure, we have examined first the UV and CD spectra of the low molecular weight compounds. As low molecular weight structural model compounds of polymers, the (*E*)-*N*-neopentylidene derivatives, **4**, of amines 1 were synthesized[12,13] from pivalaldehyde and 1 as shown in Scheme II. The electronic spectra reported in the literature[14] for an isolated azomethine group in a purely aliphatic environment contains two bands, the first at about 240 nm ($\epsilon \approx$ 100–200) is assigned to the $n \rightarrow \pi^*$ transition, while the second at about 170 nm is assigned to a $\pi \rightarrow \pi^*$ transition. (ϵ and $\Delta\epsilon$ of the polymers were based on one monomeric unit.) The UV spectra of the model compounds, **4a** and **4b** (Figures 2 and 3), showed a weak band at 245 nm ($\epsilon \approx 100$), which is attributable to the $n \rightarrow \pi^*$ transition. Both imines are optically active, and then this transition is asymmetrically perturbed by the chiral environment to give a simple Cotton effect in the CD spectrum (Figures 2 and 3) in correspondence to the aforementioned absorption band.

The UV spectrum of poly[(menthylimino)methylene] (**3a**) (Figure 2) showed a relatively stronger absorption at

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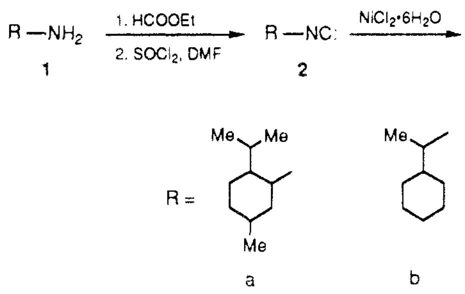
Scheme I



215 nm (ϵ = 4000) and a band at 315 nm ($\epsilon \approx$ 1000) on a long tail extending up to 400 nm. In the CD spectrum (Figure 2), in addition to a long tail extending up to 400 nm, two well-defined bands were present, the first one at 310 nm ($\Delta\epsilon$ = −1.6) and a second one at 235 nm ($\Delta\epsilon$ = +2). As far as compound **3b** is concerned, in the absorption spectrum (Figure 4) were present bands at 210 nm ($\epsilon \approx$ 5200), followed by a long tail going up to 400 nm. The CD spectrum (Figure 4) showed four bands at 350 nm ($\Delta\epsilon$ = −0.22), at 285 nm ($\Delta\epsilon$ = +0.5), at 230 nm ($\Delta\epsilon$ = +0.6), and at 210 nm ($\Delta\epsilon$ = −3.5).

The CD spectrum of resolved poly[(*tert*-butylimino)methylene] has been reported in the literature:[6] the succession of two opposite sign bands, the first one at 300 nm and the second one at 260 nm, was interpreted as an exciton couplet arising from the coupling of the n → π* transition of the imino chromophores, and the sign of this couplet was believed to be related to the polymer screw sense. Drenth and co-workers also interpreted the positive sign of the band at 300 nm as being caused by the preference for the left-handed helix, and this feature has been extrapolated to indicate the helical preference in a series of asymmetric α-substituted aliphatic-pendant poly(iminomethylenes), by assuming that all the polymers had the 4/1 helix structure. Furthermore, the $\Delta\epsilon$ value of 0.2 for the CD band at longer wavelengths in the spectrum of poly[(*tert*-butylimino)methylene] was assumed as the value corresponding to a single screw sense having 4/1 helix structure, independent of the chemical nature of the aliphatic residue of the monomeric unit.

The spectroscopic data of **3a** and **3b** cannot be interpreted following the above reasoning, in fact (i) the CD spectrum of the polymers studied in this investigation show intensity values at 300 nm higher than 0.2, which has been attributed as the value of a pure 4/1 helix; (ii) by analogy with the interpretation of the CD spectrum of poly[(*tert*-butylimino)methylene], the couplet diagnostic of the 4/1 helix structure of **3a** and **3b** should be that centered between 300 and 260 nm (no detectable UV band is present in the absorption spectrum of both the polymers (Figures 2 and 3) in this range as expected for an exciton couplet); (iii) in a typical couplet of an ordered polymer the $\Delta\epsilon$ values are higher than the $\Delta\epsilon$ values of the corresponding transition of the structural model compound,[15] on the contrary a decrease in intensity of the polymer CD bands with respect to the monomer can be observed for the present polymers.

In the spectra of **3a** and **3b** are present absorptions that are shifted toward longer wavelengths with respect to the absorption of the corresponding model compound. The absorptions at longer wavelengths can be related to some extent of conjugation of the imino group of the polymeric chains, which can give rise to a red shift of the n → π* transition.[16] The conjugation is not compatible with a 4/1 helix because, in this structure, the dihedral angle between two repeting units must be 90° and, if so, conjugation should be prevented.[6] It seems reasonable to admit that the aliphatic polymers **3a** and **3b** do not have a regular 4/1 helix geometry, but segments of conjugated structures could exist in solution and then we can say that a 4/1 helix is not the unique structure of asymmetric α-substituted aliphatic-pendant poly(iminomethylene)s.[17] Even if a multiplicity of sources exists, which, in principle, can cause broadening of NMR signals,[18] taking into account the CD results, the remarkable broadening of the N=C signal in the ^{13}C NMR spectrum can be reasonably attributed to a the coexistence of a multiplicity of local conformations due to the lack of stereoregularity.

In conclusion, on the basis of the results obtained, we believe, in accordance with Green,[9] that caution must be taken in extrapolating the stereoregular 4/1 helix structure to all poly(iminomethylenes) apart from the nature of the monomer polymerized. In addition, taking into account the nature of the transition involved and the complexity of the CD spectra, we feel unreliable the assignment of the stereochemistry of the poly(iminomethylenes) based only on the sign of the 300-nm CD band.

Experimental Section

Analytical Techniques. Ultraviolet (UV) spectra were obtained on a Jasco Uvidec-710 spectrophotometer. CD spectra were recorded on a Jasco J-600 apparatus. Optical rotations were measured on a Jasco DIP-360 polarimeter. ^{1}H NMR spectra were obtained on a Gemini 200 instrument and ^{13}C NMR spectra were obtained on a Varian 300 instrument: chemical shifts (δ) are given downfield from internal tetramethylsilane. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Melting points were determined on a Kofler melting point apparatus and are uncorrected. Molecular weights $\bar{M}_n$ were determined with a vapor pressure osmometer Model Osmomat 070 (Gonotec). Microanalyses were performed at Laboratorio di Microanalisi, Istituto di Chimica Organica, Facoltá di Farmacia, Universitá di Pisa.

(−)-*N*-Formylmenthylamine. This compound was obtained, after recrystallization from CCl_4–pentane, in 75% yield from **1a** (Carlo Erba) and from a 25% excess of ethyl formate, according to a standard procedure. Mp 100–101 °C; $[\alpha]_D^{25}$ = −84.4 (c = 2, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 8.2 (s, 1 H, CHO, syn); 8.0 (d, 1 H, CHO, anti); 5.85 (s, 1 H, NH anti); 5.55 (s, 1 H, NH, syn); 3.85 (m, 1 H, CHN, syn); 3.15 (m, 1 H, CHN, anti); 2–0.8 (m, 18 H, cyclohexyl and methyl). Anal. Calcd: C, 72.13%; H, 11.48; N, 7.65%, O, 8.74%. Found: C, 72.08%; H, 11.36%; N, 7.53%; O, 8.71%.

(−)-Menthyl Isocyanide (2a). This isocyanide was prepared from the corresponding formamide by the method of Walborsky in 86% yield. Bp 45–46 °C/0.1 mmHg; $[\alpha]_D^{25}$ = −56.1 (c = 1.55; CH_3CN). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 3.3 (m, 1 H, CHNC); 2.3–0.9 (m, 18 H, cyclohexyl and methyl). Anal. Calcd: C, 80.00%; H, 11.51%; N, 8.49%. Found: C, 79.98%; H, 11.53%; N, 8.42%.

(*S*)-(−)-*N*-Formyl(α-cyclohexylethyl)amine. This compound was prepared from **1b** (Fluka) in 95% yield, as described for (−)-*N*-Formyl-*N*-menthylamine. $[\alpha]_D^{19}$ = −17.84 (c = 0.98, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 8.15 (d, 1 H, CHO, syn); 8.05 (d, 1 H, CHO, anti); 6.9 (br, 1 H, NH, anti); 6.7 (br, 1 H, NH, syn); 4.0 (m, 1 H, CHN, syn); 3.75 (q, 1 H, CHN, anti); 3.5 (q, 1 H, CH); 2.1–0.8 (m, 10 H, cyclohexyl); 1.2 (d, 3 H, CH_3, syn); 1.1 (d, 3 H, CH_3, anti). Anal. Calcd: C, 69.67%; H, 10.96%; N, 9.03%; O, 10.34%. Found: C, 69.58%; H, 10.94%; N, 9.00%; O, 10.43%.

(*S*)-(−)-α-Cyclohexylethyl Isocyanide (2b). This compound was prepared in 50% yield from the corresponding formamide as described for **2a**. Bp 45 °C/0.1 mmHg; $[\alpha]_D^{18}$ = −30 (c = 1.53, CH_3CN). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 3.7 (m, 1 H, CHNC); 1.9–0.8 (m, 11 H, cyclohexyl); 1.1 (d, 3 H, CH_3). Anal. Calcd: C, 78.83%; H, 10.94%; N, 10.23%. Found: C, 78.79%; H, 10.95%; N, 10.21%.

Poly[(menthylimino)methylene] (3a). Isocyanide **2a** was polymerized with 1 mol% of $NiCl_2{\cdot}6H_2O$ in MeOH solution, at 65 °C. After 15 h, MeOH was added to the reaction mixture. The

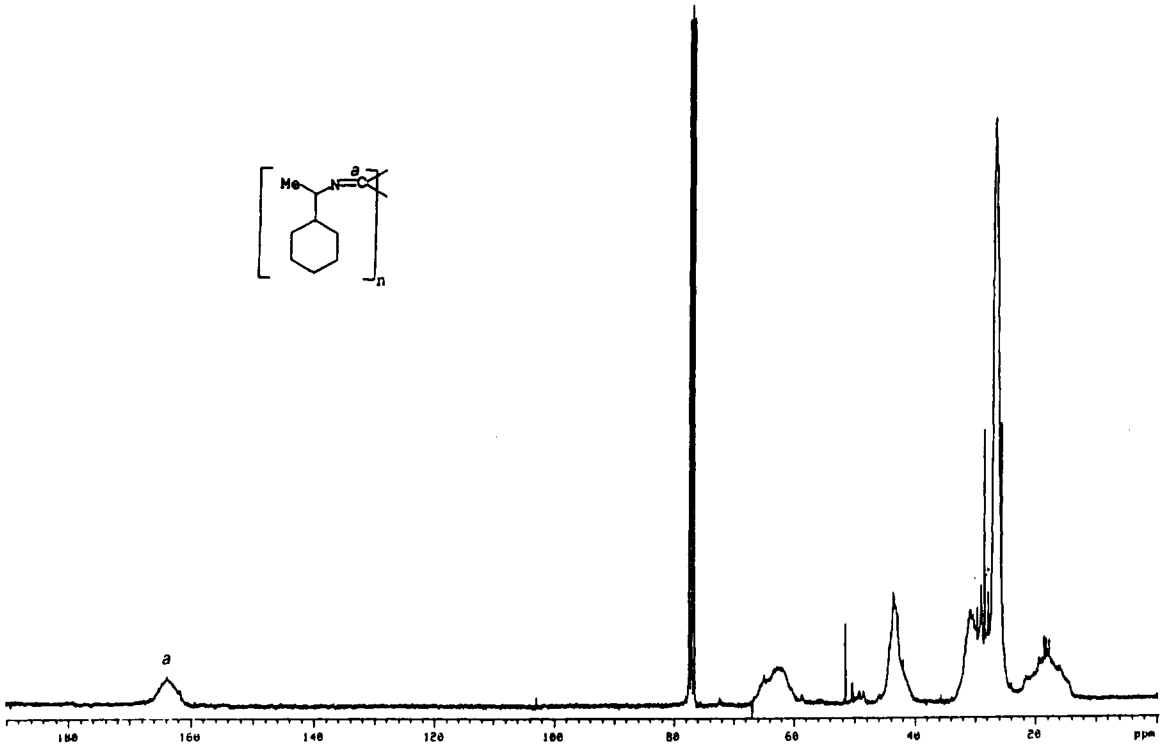


Figure 1. ^{13}C NMR spectrum (300 MHz, $CDCl_3$) of **3b**.

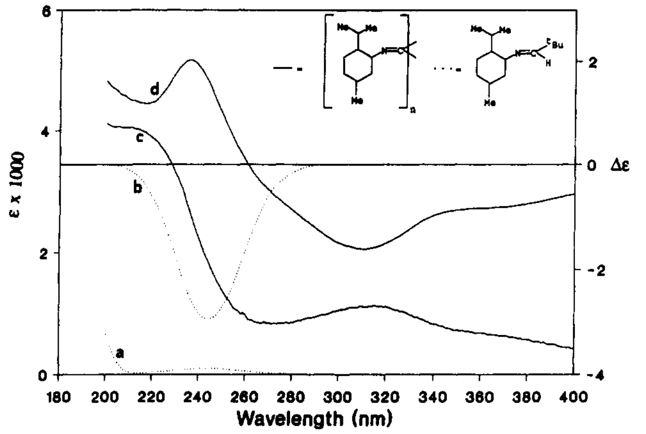
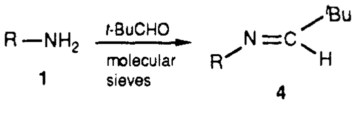


Figure 2. Absorption (a) and circular dichroism (b) spectra of **4a**; absorption (c) and circular dichroism (d) spectra of **3a**.

Scheme II



R = a, b (see Scheme I)

yellow polymer was washed with MeOH, dissolved in $CHCl_3$, reprecipitated with MeOH, and dried at 70 °C. $[\alpha]_D^{20} = -207$ ($c = 0.044$; hexane). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 3.9–3.2 (br, 1 H, CHNC); 2.3–0.5 (br, 18 H, cyclohexyl and methyl). IR (film cast from $CHCl_3$): 1640 cm^{-1} (N=C). Anal. Calcd: C, 80.00%; H, 11.51%; N, 8.49%. Found: C, 79.89%; H, 11.47%; N, 8.50%.

Poly[[(α-cyclohexylethyl)imino]methylene] (3b). Isocyanide **2b** was polymerized neat with 1 mol% of $NiCl_2 \cdot 6H_2O$ at 65 °C. After 15 h, MeOH was added to the reaction mixture; the yellow polymer was washed with MeOH, dissolved in $CHCl_3$, reprecipitated with MeOH, and dried at 70 °C. $[\alpha]_D^{24} = -295$ ($c = 0.0159$; THF). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 3.8–2.8 (br, 1 H, HCNC); 2.2–0.5 (br, 14 H, cyclohexyl and methyl). IR (film cast from $CHCl_3$): 1635 cm^{-1} (N=C). Anal. Calcd: C, 78.83%; H, 10.94%; N, 10.23%. Found: C, 78.04%, H, 10.96%; N, 10.22%.

(−)-*N*-Neopentylidenementhylamine (4a). To a solution of menthylamine (9.2 mmol) in CH_2Cl_2 were added 9.2 mmol of pivalaldehyde and the reaction mixture was stirred at room temperature overnight on molecular sieves. The molecular sieves were filtered off, the CH_2Cl_2 was evaporated at reduced pressure, and the imine was obtained, after distillation, in 88% yield. Bp 132–134 °C/20 mmHg; $[\alpha]_D^{25} = -106.4$ ($c = 1.7$; hexane). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.5 (s, 1 H, =CH); 2.75 (m, 1 H, HC-N); 1–0.6 (m, 18 H, cyclohexyl and methyl); 1.05 (s, 9 H, *t*-Bu). Anal. Calcd: C, 80.72%; H, 13.00%; N, 6.28%. Found: C, 80.69%; H, 12.97%; N, 6.31%.

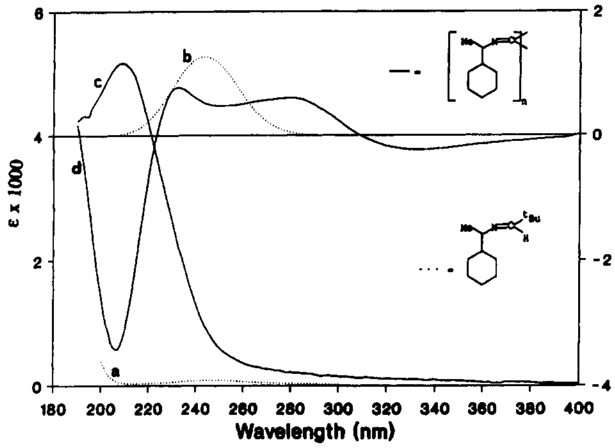


Figure 3. Absorption (a) and circular dichroism (b) spectra of **4b**; absorption (c) and circular dichroism (d) spectra of **3b**.

(*S*)-*N*-Neopentylidene(α-cyclohexylethyl)amine (4b). This compound was obtained from **1b**, in 85% yield, as described for **4a**. Bp 103–105 °C/20 mmHg; $[\alpha]_D^{20} = +27.4$ ($c = 1.7$, hexane). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.4 (s, 1 H, =CH); 2.65 (q, 1 H, CHN); 1.8–1.1 (m, 11 H, cyclohexyl); 1.05 (d, 3 H, CH_3); 1 (s, 9 H, *t*-Bu). Anal. Calcd: C, 80.00%; H, 12.82%; N, 7.18%. Found: C, 80.02%, H, 12.80%; N, 7.19%.

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(17) Even if the molecular weights of our poly(iminomethylenes) are very low, we exclude that their chirooptical properties are attributable to the effect of the end groups. As a matter of fact, we obtained two samples of polymers having higher molecular weights (poly[(menthylimino)methylene] with $\bar{M}_n$ = 14 000 and poly[[(cyclohexylethyl)imino]methylene] with $\bar{M}_n$ = 3100) by polymerization of the neat monomers: the CD spectra of these polymers are unchanged (as far as position, intensity, and number of the bands are concerned) with respect to those of the poly(iminomethylenes) having lower molecular weights.
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Registry No. **1a**, 2216-54-8; **1b**, 17430-98-7; **2a**, 143144-53-0; **2a** (homopolymer), 143144-57-4; **2b**, 143144-54-1; **2b** (homopolymer), 143144-58-5; **4a**, 143144-55-2; **4b**, 143234-72-4; (−)-*N*-formylmenthylamine, 34048-58-3; ethyl formate, 109-94-4; (*S*)-(−)-*N*-formyl(α-cyclohexylethyl)amine, 138785-77-0; pivalaldehyde, 630-19-3.