Atropisomerism in Polymers. Screw-Sense Selective Polymerization of Isocyanides by Inhibiting the Growth of One Enantiomer of a Racemic Pair of Helices

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Abstract: Isocyanides polymerize under the catalytic activity of Ni(II) to the corresponding poly(isocyanides): $nRN^\equiv 
\begin{align*}
\text{N=C=O} + \text{H}_{2}N\equiv 
\text{C=O} &\rightarrow \text{H}_{2}N\equiv 
\text{C=O} \\
\text{H}_{2}N\equiv 
\text{C=O} &\rightarrow \text{H}_{2}N\equiv 
\text{C=O} \\
\end{align*}

Stereoisomerism resulting from restricted rotation around a single bond (atropisomerism) is a well-known phenomenon in organic chemistry. In polymer chemistry this type of isomerism is very rare. Atropisomerism in polymers was demonstrated for the first time in 1974 in polymers of isocyanides. It was shown that poly(tert-butyl isocyanide) (>C=NC(CH$_3$)$_3$) could be resolved into fractions that displayed positive and negative optical rotations. Subsequent work revealed that the optical rotation is due to a 4:1 helical configuration of the polymer backbone (Figure 1). To date, two other examples of atropisomerism in polymers have been reported. There is evidence that polychlorophenyl, prepared from chloral with a chiral initiator, forms a stable helix with a preference of one helical screw sense over the other. Yuki et al.3a and later Crand and Soga3b showed that bulky methacrylic acid esters polymerize in the presence of chiral anionic catalysts to give optically active polymers.

Poly(isocyanides) more systematically called poly(mino-methylenes) or poly(carbonimidoyls) are prepared from isocyanides by the catalytic action of protonic acids, Lewis acids, or nickel(II) salts.3 The polymers are unusual in the sense that they carry a side chain on each atom of their main chain. This feature causes restricted rotation around the single bonds that connect the main-chain carbon atoms. Two configurations are possible around each of the single bonds, viz. $R$ or $S$.3 If the poly-

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Scheme 1

$RNH_2 \rightarrow RNHCHO \rightarrow RN^\equiv \equiv 
\begin{align*}
R &\equiv 
\text{C=O} \\
R &\equiv 
\text{C=O} \\
\end{align*}

Table I. Chiroptical Properties of Homopolymers of Chiral Isocyanides $[RN\equiv \equiv \equiv 
\begin{align*}
R &\equiv 
\text{C=O} \\
R &\equiv 
\text{C=O} \\
\end{align*}

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(9) If the configurations around the single bonds are alternating $R$ and $S$, a syndiotactic structure arises. If the configurations are randomly $R$ and $S$, an atactic chain is formed. Strictly speaking, the terms isotactic, syndiotactic, and atactic cannot be used for polymers of the type described in this paper, as they refer to polymer chains that contain chiral centers.
The resolution of poly(tert-butyl isocyanide) into enantiomers indicates that polymerization of isocyanides proceeds stereoselectively to isotactic helical molecules. When the monomer is achiral, a racemic mixture of $P$ and $M$ screws is formed. However, when the monomer is one enantiomer of a chiral isocyanide, its polymer will be a mixture of diastereoisomers, and $P$ and $M$ screws will not be obtained in equal amounts. This feature was confirmed when the monomer is one enantiomer of a chiral isocyanide, its polymerization proceeds stereoselectively to isotactic helical molecules. When the monomer is an achiral isocyanide, we expected the screw to grow further in the same direction (see Figure 2). However, a different reaction took place. The bulky optically active monomer selectively inhibited the growth of one of the polymer helices from the achiral isocyanide. Our procedure resembles the procedure used by Berkovitch-Yellin to regulate the growth of crystals by "tailor-made" inhibitors.15

**Results**

Homopolymerization of Chiral Isocyanides. The chiral isocyanides used in this study were synthesized from optically active amines and amino acids as generally outlined in Scheme I. (See also the Experimental Section.) Homopolymerization of these monomers was achieved by adding nickel(II) as catalysts and optically active amines as initiators.13

Here we describe a different procedure for obtaining optically active polymers from achiral isocyanides, i.e., by polymerizing a mixture of an achiral and a bulky optically active isocyanide.14 Our initial objective was to make a living polymer of an optically active isocyanide with one particular screw sense. By adding a large amount of an achiral isocyanide, we expected the screw to grow further in the same direction (see Figure 2). However, a different reaction took place. The bulky optically active monomer selectively inhibited the growth of one of the polymer helices from the achiral isocyanide. Our procedure resembles the procedure used by Berkovitch-Yellin to regulate the growth of crystals by "tailor-made" inhibitors.15

![Figure 1](image1.png) View along the helical axis of a poly(isocyanide) molecule with a right-handed screw sense. Unit 5 is behind unit 1, etc. (A) According to the Cahn–Ingold–Prelog nomenclature rules, the configuration around each of the single bonds connecting the main-chain carbon atoms is $S$; see the Newman projection along $C^2-C^3$. (B) $a-d$ denotes the priority sequence.

![Figure 2](image2.png) Screw-sense selective polymerization by adding an achiral isocyanide to an optically active living polymer.

![Figure 3](image3.png) CD spectra of polymers $3a$ (A), $3b$ (B), $3c$ (C), $3d$ (D), and simulated spectrum of $3a$ (E).
Screw-Sense Selective Polymerization of Isocyanides

<table>
<thead>
<tr>
<th>Table II. Properties of Copolymers of 4-Methoxyphenyl Isocyanide (2k) and Chiral Isocyanides 2a-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>R in chiral monomer</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>2a</td>
</tr>
<tr>
<td>2b</td>
</tr>
<tr>
<td>2c</td>
</tr>
<tr>
<td>2d</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: molar ratio 4-methoxyphenyl isocyanide to chiral monomer, 1:1; catalyst, 1 mol \% NiCl\(_2\); neat; reaction temperature, 20 °C.  
\(^b\)Percent incorporation of chiral monomers in polymer sample as calculated from elemental analysis and \('H NMR.  
\(^c\)Optical rotation of polymer sample (c 0.03, CHCl\(_3\)).  
\(^d\)Derived from the CD spectra of the polymers.  
\(^e\)Determined by measuring intrinsic viscosities (toluene at 30.00 °C). Mark-Houwink relation \(\eta = 1.4 \times 10^4 M^{0.5}.\)  
\(^f\)Optical rotation is probably due to side chains of chiral monomer.  
\(^g\)Not determined.

This \(n \rightarrow \pi^+\) transition is responsible for the CD spectrum in the region 250-500 nm. In polymers of optically active isocyanides both the chiral center in the side chain and the helical structure of the main chain induce rotational power in the imino chromophore. In the spectra of the polymers of Table I, the side-chain contribution is manifested as a negative band in the range 250-350 nm. The screw senses of the polymers are derived from the couplet at \(\sim 350\) nm in their CD spectra. We previously calculated the CD spectra of poly(isocyanides) with Tinoco’s exciton theory and the coupled oscillator theory of De Voe. In this way it was derived that a positive couplet corresponds with an \(M\) helix and a negative couplet with a \(P\) helix. In its CD spectrum polymer 3c clearly shows a positive couplet, indicative of an \(M\) helix. For polymers 3a and 3b, this couplet is partly obscured by the contribution of the chiral side chain (Figure 3). However, the CD spectra of 3a and 3b could be analyzed by simulation. For instance, in Figure 3 the calculated spectrum of 3a is shown, divided into a contribution from the chiral side chain and from the helical main chain. As the resulting calculated curve is almost identical with the experimental curve, we conclude that this polymer also consists of \(M\) helices. The CD spectra of polymers 3e-i have been discussed earlier. For polymer 3e, no definite conclusion about the screw sense could be made, as the couplet is completely obscured by the contribution from the chiral side chain. Even simulated CD spectra could give no decisive answer about the screw sense. The screw senses of polymers 3a-i as derived from the CD spectra are given in Table I.

Copolimerization. The achiral isocyanide 4-methoxyphenyl isocyanide (2k) was polymerized neat by NiCl\(_2\) in the presence of optically active isocyanides 2a-i. The molar ratio of achiral to chiral monomer was 1:1. After workup, yellow to brown polymer samples were obtained, containing varying amounts of optically active monomer (Table II). The molecular weights of these samples amounted to \(M_r \approx 45,000\). The optical rotation of the polymers varied with the type of optically active comonomer used. High negative optical rotations were obtained with the comonomers derived from the amino acids 2a-e (Table II). Relatively low optical rotations were obtained with the comonomers 2f-i (Table II). The CD spectra showed that the polymers derived from the latter comonomers consisted of a racemic mixture of right- and left-handed screws; no couplets were visible in the CD spectra. This suggests that the low optical rotations of the polymers are due to the chirality of the side chains and not to the helical structure of the polymer main chain.

Various achiral isocyanides (2j-i) were polymerized by NiCl\(_2\) in the presence of chiral isocyanate 2a or b as described above

Table III. Properties of Copolymers of Achiral Isocyanides R"("NC") (2j-i) and the Chiral Isocyanides (S)-\(t\)-CH\(_2\)(CH\(_2\))3(CHOOC\(_6\)H\(_4\))NC (2a, 2b)

<table>
<thead>
<tr>
<th>R in achiral monomer</th>
<th>incorp.(^b)</th>
<th>(\delta_0^D,) (\text{deg}^d)</th>
<th>screw sense(^d)</th>
<th>(M_r^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2j</td>
<td>4-(CH(_3))(_2)NC(_6)H(_4)</td>
<td>13</td>
<td>-250</td>
<td>P</td>
</tr>
<tr>
<td>2k</td>
<td>4-CH(_2)OC(_6)H(_4)</td>
<td>13</td>
<td>-520</td>
<td>P</td>
</tr>
<tr>
<td>2l</td>
<td>4-CH(_2)C(_6)H(_4)</td>
<td>31</td>
<td>-550</td>
<td>P</td>
</tr>
<tr>
<td>2m</td>
<td>2-CH(_2)C(_6)H(_4)</td>
<td>31</td>
<td>-340</td>
<td>P</td>
</tr>
<tr>
<td>2n</td>
<td>C(_6)H(_5)</td>
<td>30</td>
<td>-610</td>
<td>P</td>
</tr>
<tr>
<td>2o</td>
<td>C(_6)H(_5)Cl</td>
<td>35</td>
<td>-660</td>
<td>P</td>
</tr>
<tr>
<td>2p</td>
<td>2,6-Cl(_2)C(_6)H(_4)</td>
<td>i-CH(_3)</td>
<td>37</td>
<td>0</td>
</tr>
<tr>
<td>2q</td>
<td>C(_6)H(_5)Cl</td>
<td>68</td>
<td>-93</td>
<td>P</td>
</tr>
<tr>
<td>2r</td>
<td>n-C(_6)H(_5)</td>
<td>i-CH(_3)</td>
<td>58</td>
<td>-58</td>
</tr>
<tr>
<td>2s</td>
<td>i-C(_6)H(_5)</td>
<td>i-CH(_3)</td>
<td>52</td>
<td>-105</td>
</tr>
<tr>
<td>2t</td>
<td>i-C(_6)H(_5)</td>
<td>i-CH(_3)</td>
<td>52</td>
<td>-377</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: molar ratio achiral to chiral monomer, 1:1; catalyst, 1 mol \% NiCl\(_2\); neat; reaction temperature, 20 °C.  
\(^b\)Percent incorporation of achiral monomer in polymer as calculated from elemental analysis and \('H NMR.  
\(^c\)Optical rotation of polymer (c 0.03, CHCl\(_3\)).  
\(^d\)Derived from the CD spectra of the polymers.  
\(^e\)Determined by measuring intrinsic viscosities (toluene at 30.00 °C). Mark-Houwink relation \(\eta = 1.4 \times 10^4 M^{0.5}.\)  
\(^f\)Not determined.

Figure 4. CD spectra of polymers 3k (A, 19% incorporation of 2a), 3n (B, 23% incorporation of 2a), and 3o (C, 35% incorporation of 2a). The observed couplets are indicative of right-handed helices.

(Tab III). All the resulting polymers had negative optical rotations except for the one derived from 2,6-dichlorophenyl isocyanide (2p); for this polymer no optical rotation within experimental error could be measured. CD spectra (e.g. see Figures 4 and 5) confirmed that the negative optical rotations of the samples derived from 2j-o and 2q-s can be ascribed to right-handed helical structures of the polymer main chains. The CD spectra of the polymers resulting from the achiral aromatic isocyanides 2j-o show a very clear negative couplet pointing to a \(P\) helix (Figure 4). For the monomers 2q-s this negative couplet is partly obscured by the contribution from the incorporated chiral monomer (e.g. Figure 5A). The CD spectra of the polymer samples derived from 2q-s and 2b could be analyzed by subtracting the CD spectrum of the homopolymer of 2b, corrected for the amount of incorporation of 2b (see Figure 5B). Figure 5B clearly shows a negative couplet, thereby proving that the aliphatic isocyanides 2q-s also form a \(P\) helix. An exception is the polymer derived from tert-butyl isocyanide (2t) and the chiral comonomer 2b. This polymer showed a negative optical rotation but no couplet in the CD spectrum, indicating that is consists of a racemic mixture of \(P\) and \(M\) screws. The observed optical rotation is probably due to the chirality of the side chains originating from 2b. Also, the polymer obtained from 2,6-dichlorophenyl isocyanide (2p) and

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2b did not show a coulplet in the CD spectrum, indicating it to be a racemic mixture of screws as well.

The extent of asymmetric induction in the polymerization of 4-methoxyphenyl isocyanide (2k) by the chiral comonomer 2a was measured as a function of the initial ratio of these isocyanides in the monomer mixture. The optical rotation of this polymer sample increased with increasing mole fraction of 2a (f2a) in the starting mixture up to a maximum value of 740° at f2a = 0.75 and thereafter decreased. The percentage of monomeric units of 2a that is incorporated in these samples increased with increasing f2a. In Figure 6A the optical rotation of the polymer sample is presented as a function of the incorporation of the chiral comonomer. For comparison, the optical rotation of a mixture of homopolymers 3a and 3k is also presented (Figure 6B). From these curves the contribution of the achiral monomer to the optical rotation can be calculated (Figure 6C). Figure 6C also includes a number of corrected optical rotation values for the copolymerization of 2k with 2b and 2k with 2c. These values match the curve of 2k and 2a. As the CD spectrum is a better method for measuring the chiral induction, we determined the differential dichroic absorption coefficient (Δε) at 366 nm as a function of the incorporation of 2a (Figure 6D). Both the optical rotation and the Δε values show a maximum at about 50% incorporation of 2a.

The copolymer mixture derived from 4-methoxyphenyl isocyanide (2k) and (S)-2-isocyanovaleric acid isopropyl ester (2b) was analyzed by chromatography over a Sephadex LH-20 column. Subsequently, the low molecular weight fractions were separated over a Sephadex H-20 column. The results are presented in Table IV. The copolymer mixture consisted of high molecular weight fractions with a low content of chiral monomer and a high optical rotation and low molecular weight fractions with a high content of chiral monomer and a low optical rotation.

**Discussion**

A convenient procedure for obtaining optically active polymers from achiral monomers is by copolymerization with optically active comonomers. By the inductive effect of the chiral comonomer units, the achiral monomers can assume as secondary structure that corresponds to the structure of the main chain of the optically active homopolymer.

The data presented in the Results section indicate that an unusual reaction had taken place. The homopolymers from isocyanides 2a-e form a left-handed helix (see Table II). We explain these results as follows. The optically active isocyanides 2a-e are bulky, slowly polymerizing monomers. From kinetic measurements we estimate their second-order rate constants in ε = k2[NIL[RNC] to be <10⁻³ M⁻¹s⁻¹. These monomers preferentially form an M screw (Figure 7A). The achiral monomers 2j-o and 2k-s polymerize rapidly. Their second-order rate constants are in the range k2 = 0.2–12 M⁻¹s⁻¹. These monomers form a racemic mixture of M and P screws (Figure 7B). When an achiral isocyanide, e.g., phenyl isocyanide (2n),...
Screw-Sense Selective Polymerization of Isocyanides

![Figure 8. Mechanism of polymerization of isocyanides with Ni(II) as catalyst.](image)

**Table IV.** Gel Permeation Chromatography of the Copolymer Mixture from 4-Methoxynphenyl Isocyanide and (S)-2-Isocyanosovalaric Acid Isopropyl Ester

<table>
<thead>
<tr>
<th>fraction</th>
<th>inc of monomer</th>
<th>$[\alpha]_D^{19} \text{deg}$</th>
<th>$M_n^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-9</td>
<td>17</td>
<td>-460</td>
<td>58 600</td>
</tr>
<tr>
<td>10-14</td>
<td>20</td>
<td>-440</td>
<td></td>
</tr>
<tr>
<td>15-21</td>
<td>21</td>
<td>-450</td>
<td>47 000</td>
</tr>
<tr>
<td>21a'</td>
<td>24</td>
<td>-430</td>
<td></td>
</tr>
<tr>
<td>21b'</td>
<td>27</td>
<td>-440</td>
<td></td>
</tr>
<tr>
<td>21c'</td>
<td>30</td>
<td>-360</td>
<td></td>
</tr>
<tr>
<td>21d'</td>
<td>49</td>
<td>-170</td>
<td></td>
</tr>
<tr>
<td>22'</td>
<td>100</td>
<td>-25</td>
<td>8800</td>
</tr>
</tbody>
</table>

*Sephadex LH 60 column unless otherwise indicated; eluent CHCl3.

| *a* Percent incorporation of chiral monomer as derived from 1H NMR.
| *b* Optical rotation of polymer sample (c 0.02, CHCl3).
| *c* Determined by measuring intrinsic viscosities (toluene at 30.0 °C). Mark-Houwink relation $[\eta] = 1.4 \times 10^3 M_0^{1.75}$. *d* Fraction 21 was subsequently separated on Sephadex LH 20.
| *e* Not determined, due to small size of the samples. From the retention times the rank order of molecular weight is estimated to be 21a > 21b > 21c > 21d.

is polymerized in the presence of a chiral one, e.g., (S)-2-isocyanosovalaric acid methyl ester (2a), the former isocyanide will start to form a racemic mixture of left- and right-handed screws. Monomer 2a will have a preference for incorporation in the M helix of 2n, and as a result, the growth of this helix will be slowed down. As far less of 2a will be incorporated in the P helix of 2n, this screw can grow relatively unhindered. Eventually, the P helix will consume most of the achiral phenyl isocyanide, and this screw sense will be predominantly formed (Figure 7C). This mechanism is supported by the fact that no chiral induction is observed when a combination of a fast polymerizing chiral (2f-g) and a fast polymerizing achiral monomer (2k) is used (Table II). Also, a combination of a slowly polymerizing chiral (2h) and a slowly polymerizing achiral monomer (2p, 2i) yields a racemic mixture of P and M helices (Table III).

According to the mechanism shown in Figure 7, the copolymer sample is expected to have the following composition: high molecular weight fractions with high optical activity and a low content of chiral monomer; low molecular weight fractions with a high content of chiral monomer (which will eventually add up to 100%) and an optical rotation that will approach that of the homopolymer of the chiral isocyanide. Table IV shows that the results of the chromatography experiments are in line with the suggested mechanism.

Table II and Figure 6B reveal that the substituent R in the ester function COOR of isocyanides 2a-e has no appreciable effect on the chiral induction, whereas the alkyl group at the chiral carbon atom does. We explain this in the following way. Prior-}

Figure 9. Intermediate in the polymerization of isocyanides 2a-e.

vously, we have shown that the mechanism of polymerization of an isocyanide is a consecutive insertion process around the nickel(II) center.2 The reaction starts from a square-planar nickel-isocyanide complex by attack of a nucleophile X on one of the coordinated isocyanides (see Figure 8). In the resulting complex (Figure 8B) the plane of the ligand C(X)=NR is approximately perpendicular to the plane of the isocyanide carbons and nickel, with R in either the E or the Z configuration. There is no free rotation around the bond from C1 to Ni for sterical reasons. Carbon atom C1 in Figure 8B has gained in nucleophilicity and can now attack a neighboring ligand. Such an attack is facilitated when a new isocyanide ligand C5=NR is substituted for C(X)=NR. In the case of an achiral isocyanide the possibilities of attack on C1 or C2 are equal. In the case of a chiral isocyanide one of these attacks will predominate. In Figure 8C it has occurred on C2. When the sequence of attack continues in the direction C1 → C2 → C3 → C4, a left-handed helix is obtained. In a similar way, the sequence of attacks C1 → C4 → C3 → C2 results in a right-handed helix.

For isocyanides 2a-e the complex as shown in Figure 8B will have the E configuration, as these isocyanides have large substituents. The alkyl group at the chiral carbon atom is the most bulky substituent and will point away from the bulky nickel center (see Figure 9).23 As a consequence, the ester function COOR' is directed toward C1 and the hydrogen atom toward C2. This will result in the formation of a left-handed helix, as was experimentally confirmed. For sterical reasons, the substituent R' in COOR' will point away from the reaction center and is expected to have no effect on the chiral induction. When the methyl group in 2e is replaced by an isopropyl (2a) or sec-butyl (2d) group, an increase in stereoselectivity will be the result, in agreement with experiments.

As far as we know, the copolymerization mechanism presented here has no precedent in literature. It would be interesting to see whether our procedure can be applied to other copolymerization systems.

**Experimental Section**

**Analytical Techniques.** Infrared (IR) spectra were recorded on Perkin-Elmer 297 and 293 spectrophotometers. Ultraviolet (UV) spectra were obtained on a Perkin-Elmer 200 spectrophotometer. CD spectra were recorded on a Perkin-Elmer 241 polarimeter. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. 1H NMR spectra were obtained on a Varian EM 390 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 Mettler FP5/FP51 photoelectric melting point apparatus. Solution viscosity data were obtained with a Cannon-Ubbelohde viscometer.

**N-Formyl-L-valine Methyl Ester (1a).** According to a literature procedure 1-valine was esterified with methanol and freshly distilled SOCl2 in quantitative yield.26 Subsequent reaction with formic acid, sodium formate, and acetic anhydride,27 gave N-formyl-1-valine methyl ester.

(25) As a relative measure of steric hinder, the $\lambda$ steric parameter can be used. See also: Kagan, H. B. Stereochemistry; Thieme: Stuttgart, 1977, Vol. 3, p. 26. (R. AR); $\lambda$: 0.00; CH1, 1.00; CH(CH3)2, 1.27; $\lambda$: COO, 0.90.


ester: yield 80%; white crystals after recrystallization from CCl$_4$; $\delta$ 16.78, 10.46, 3.79 ppm (c 5, CH$_2$OH); mp 62.1 °C; IR (KBr) 1660 (N-C), 1740 (C=O) cm$^{-1}$; H NMR (CDCl$_3$) $\delta$ 1.0 (2 d, 6 H, CH$_2$), 1.9-2.6 (m, 1 H, CH), 3.85 (3 s, 3 H, OCH$_3$), 4.2 (8 d, 2 H, CH$_2$), 6.75 (s, br, 1 H, CHO), 7.35 (3 s, 3 H, CHO), 8.24 (s, 1 H, CHO).

(S)-2-Isoanisolaevic Acid Methyl Ester (2a). This isocyanide was prepared from 1a according to a modification of the procedure of Skorna and Ugi. Into a round-bottomed flask, equipped with a magnetic stirrer and a CO$_2$/acetone reflux condenser kept at -30 °C, were brought 2140 (N=C) cm$^{-1}$; H NMR (CDCl$_3$) $\delta$ 1.05 (t, 3 H, C(CH$_3$)$_3$), 1.25-1.90 (m, 8 H, C$_2$H$_5$CH(CH$_3$)$_2$), 3.58 (m, 3 H, OCH$_3$), 3.85 (s, 3 H, CHO) ppm (c 2, CH$_3$), 2.0 (1 d, 3 H, CH$_3$), 4.22 (q, 2 H, CH$_2$), 4.61 (m, 2 H, CH$_2$), 7.75 (s, br, 1 H, CHO), 8.24 (s, 1 H, CHO).

(S)-2-Isoanisolaevic Acid Methyl Ester (2b). This compound was obtained from N-formyl-L-valine methyl ester with an excess of LiAlH$_4$ in boiling diethyl ether. Subsequently, the mixture was refluxed for 2 h. After workup, the desired compound was obtained from Ar-formyl-L-isoleucine methyl ester as a colorless liquid; bp 33 °C (0.5 mmHg); yield 5.2 g (74%) of a colorless liquid; bp 44 °C (0.2 mmHg); $\alpha$ 1.9-2.6 ppm (m, 1 H, CH), 3.75 (s, 3 H, OCH$_3$), 4.1 (d, 1 H, CH) ppm (c 3, CH$_2$CO$_2$); IR (neat) 1750 (C=O), 2145 (C=N) cm$^{-1}$; 'H NMR (CDCl$_3$) $\delta$ 1.1 (2 d, 6 H, CH$_2$), 2.0-2.7 (m, 1 H, CH), 3.9 (s, 3 H, CHO) ppm (c 2, CH$_3$), 1.37 (t, 3 H, CH$_3$), 1.43 (d, 3 H, CH$_3$), 4.22 (q, 2 H, CH$_2$), 4.61 (m, 2 H, CH$_2$), 7.75 (s, br, 1 H, CHO), 8.24 (s, 1 H, CHO).

(41) Reference 40, p. 316.

Polyl[(15,2S)-1-carboxymethoxy-2-methylbutyl isocyanide] (3d). Isocyanide 2d was polymerized neat with 1 mol % NiCl₂ at 45 °C. After 5 days, methanol/water (3:1, v/v) was added to the reaction mixture. The yellow polymer was collected by filtration, washed with methanol/water, and dried under reduced pressure at 50 °C: yield 75%; [α]²⁰D –82° (c 0.5, CHCl₃); IR (KBr) 1745 (C=O), 1625 (N=CH) cm⁻¹; 1H NMR (CDCl₃) δ 1.15-2.70 (br, 9 H, CH₃), 2.5-3.3 (br, 5 H, C₆H₅). Poly[(S)-1-carboxethoxyl isocyanide] (3e). Isocyanide 2e was polymerized neat with 0.2 mol % NiCl₂·H₂O at ambient temperature. After 5 days, the glassy reaction mixture was dissolved in a small amount of chloroform and added dropwise to an excess of vigorously stirred methanol/water (4:1, v/v). The precipitated yellow polymer was collected by filtration, washed with methanol/water, and dried under reduced pressure at 50 ºC: yield 75%; [α]²⁰D –28° (c 0.36, CHCl₃); IR (KBr) 1745 (C=O), 1625 (N=CH) cm⁻¹.

Poly[(S)-1-phenyl-ethyl isocyanide] (3g). Isocyanide 2g was polymerized neat with 0.015 mol % NiCl₂·H₂O at 0-5 °C: yield 90%; [α]²⁰D –350° (c 1.0, CHCl₃); IR (KBr) 1745 (C=O), 1605 (N=CH) cm⁻¹; 1H NMR (CDCl₃) δ 1.15 (br, 3 H, CH₃), 3.0 (br, 1 H, CH), 6.9 (br, 5 H, C₆H₅).

Poly[(S)-1-acetoxy-1-phenylisocyanide] (3h). Isocyanide 2h was polymerized with 0.15 mol % NiCl₂·H₂O in methanol at ambient temperature. The polymer was obtained as a bright yellow powder: yield 75%; [α]²⁰D –16.7° (c 0.5, CHCl₃); IR (KBr) 1745 (C=O), 1625 (N=CH) cm⁻¹.

Poly[(R)-1,2-dimethylpropyl isocyanide] (3i). Monomer 2i was polymerized with 0.1 mol % NiCl₂·H₂O in methanol at ambient temperature: yield 75%; [α]²⁰D –16.7° (c 0.5, CHCl₃); IR (KBr) 1745 (C=O), 1625 (N=CH) cm⁻¹.

Registry No. 1a, 3154-46-9; 1b, 99065-94-8; 1c, 71738-70-0; 1d, 3154-48-1; 1e, 21683-14-7; 1f, 61852-43-5; 1g, 19145-06-3; 1h, 87281-05-8; 1i, 75240-52-7; 2a, 63472-88-8; (2a)(2k) (copolymer), 112138-45-1; (2a)(2j) (copolym), 112128-27-2; (2a)(2i) (copolym), 112128-25-3; (2a)(2h) (copolym), 112129-24-9; (2a)(2g) (copolym), 112115-20-7; (2b)(2h) (copolym), 112115-18-1; (2b)(2g) (copolym), 112138-46-2; (2b)(2q) (copolym), 112131-38-1; (2b)(2r) (copolym), 112132-92-2; (2b)(2s) (copolym), 112115-33-0; (2b)(2t) (copolym), 112115-34-1; 2c, 112115-12-5; (2c)(2k) (copolym), 112119-19-2; 2d, 63463-94-8; (2d)(2k) (copolym), 112120-25-0; 2e, 68778-13-2; (2e)(2k) (copolym), 112122-27-2; 2f, 21872-32-2; (2g)(2q) (copolym), 112123-23-8; 2h, 87281-06-9; (2h)(2k) (copolym), 112124-29-4; 2i, 75236-36-1; (2i)(2k) (copolym), 112125-25-0; 3a, 112114-17-4; 3b, 112115-15-8; 3c, 112116-19-9; 3d, 112115-17-0; 3e, 68778-14-3; 3f, 53368-89-1; 3g, 26714-26-1; 3h, 87281-24-1; 3i, 75236-37-2; 3j, 77188-54-9; (1j)-valine, 72-18-4; (1j)-isoleucine, 73-32-5; (1k)-lysine, 56-41-7; (2k)-2-amino-2-phenylethanol, 56613-80-0; (R)-N-formyl-2-aminophenylethanol, 87281-04-7; N-benzoyl-L-valine, 5699-79-6; N-benzoyl-L-valine methyl ester, 10512-91-1; N-benzyl-L-valine, 42807-42-1; (1l)-valinol, 2026-48-4; (S)-1-bromo-3-methyl-2-butanamine, 112113-11-6; (R)-3-methyl-2-butanamine.