The following full text is a publisher's version.

For additional information about this publication click this link.
http://hdl.handle.net/2066/16517

Please be advised that this information was generated on 2017-08-07 and may be subject to change.
Screw Sense Differentiating Polymerization of Achiral Isocyanides

Tadao Harada, Marco C. Cleij, Roeland J. M. Nolte, Alfonso M. F. Hezemans, and Wiendelt Drenth

Laboratory of Organic Chemistry and Laboratory of General Chemistry, University at Utrecht, Croesestraat 79, 3522 AD Utrecht, The Netherlands

Polymerization of achiral isocyanides \( p-XC_6H_4NC \) \((X = \text{MeO, Me, H, Cl})\) by nickel(0) chloride in the presence of \((S)-2\)-isocyanoisovaleric acid methyl or t-butyl ester gives rise to optically active polymers \([p-XC_6H_4NC]_n\) with an excess of right-handed screw sense.

Poly(iminomethylene)s, (2), are atropisomeric polymers with a rigid helical structure (Figure 1). They are prepared from isocyanides, e.g., (1), by the catalytic action of nickel(0) salts.

When enantiomers of chiral isocyanides are polymerized, optically active polymers are formed with predominantly one screw sense. Depending on the chiral side chain \( R \) this screw sense may be either right-handed (\( P \)) or left-handed (\( M \)). Achiral isocyanides are converted into racemic mixtures of right-handed and left-handed screws. Stereo-differentiating polymerization of achiral isocyanides has not yet been reported.* We describe here that \((S)-2\)-isocyanoisovaleric acid methyl \((1a)\) or t-butyl \((1b)\) ester induces a screw sense differentiating polymerization of achiral aryl isocyanides \((1c)-(1f)\).

Compounds \((1a)\) and \((1b)\) were prepared from \( L \)-valine by esterification, \( N \)-formylation, and subsequent dehydration steps, according to standard procedures. The optical rotations of the compounds amounted to \([\alpha]_D^{20} (1a) = 27.6^\circ\) and \([\alpha]_D^{20} (1b) = 29.5^\circ\) (c 1, benzene). Aaryl isocyanides \((1c)-(1f)\) were mixed with \((1a)\) or \((1b)\) and polymerized near with anhydrous \( \text{NiCl}_2 \). After work up, polymer samples with \( \bar{M}_n = 30\,000-40\,000 \) were obtained which consisted mainly of \((2c)-(2f)\) and showed high negative optical rotations (Table 1). In the c.d. spectra of \((2c)-(2f)\) strong negative couplets

![Figure 1. Helical configuration of a poly(iminomethylene). Repeating unit: C-5 is behind C-1, C-6 behind C-2, etc.](image)

* Atropisomerism is stereoisomerism due to restricted rotation around single bonds, cf. ref. 1. Polymers (2) show restricted rotation around the single bonds connecting the main chain carbon atoms.

** In addition to the procedure described here, we tried without success the stereo-differentiating polymerization of achiral isocyanides with chiral catalysts (nickel \( b \)-tartrate, nickel \( l \)-alaninate, nickel \( l \)-valinate), chiral additives \([l\text{-borneol}, (S)-\text{a-phenylethyamine, cinchonine}]\), and a chiral solvent \([\text{(S)-butan-2-ol}]\).

\*§ In a typical procedure monomer \((1c)\) (133 mg, 1.0 mmol) was mixed with \((1a)\) (144 mg, 1.02 mmol) and stirred under a nitrogen atmosphere with anhydrous \( \text{NiCl}_2 \) (13.2 mg, 0.1 mmol) for 16 h. The reaction mixture was treated with \( \text{MeOH} \) and the polymer that precipitated was collected, washed with \( \text{MeOH} \) to remove unchanged \((1a)\) and low molecular weight products, and dried. In this way 158 mg \( (90\%) \) of a polymer sample was obtained that had \([\alpha]_D^{20} = -510^\circ\) (c 0.02, CHCl\(_3\)) and contained 23% of units derived from \((1a)\) (elemental analysis and \( ^1\text{H n.m.r.} \)).
This phenomenon suggests that reversible interconversion of carrier molecules. Azobenzene exhibits photoinduced cis-trans isomerism. The geometrical change involved is so large that it has frequently been employed as a photoantenna for photocontrol of functional molecules such as crown ethers,4–8 cyclodextrins, and polymers.10,11

Cations are known to be transported through membranes by synthetic macrocyclic polyethers as well as by antibiotics.1–3 In particular, polyether antibiotics such as nigericin and monensin interconvert between the cyclic and acyclic forms in the membrane phase, a property which is believed to be responsible for rapid ion-transport through the membranes. This phenomenon suggests that reversible interconversion between two states can be responsible for the high efficiency of carrier molecules. Azobenzene exhibits photoinduced reversible cis-trans isomerism. The geometrical change involved is so large that it has frequently been employed as a

**Table 1. Stereo-differentiating polymerization of achiral isocyanides p-NC(CH₂)₆NH in the presence of chiral 2-isocyanoisovaleric acid esters (1a) or (1b).**

<table>
<thead>
<tr>
<th>(1a)</th>
<th>% Incorporation</th>
<th>% Incorporationc</th>
<th>(1b)</th>
<th>% Incorporation</th>
<th>% Incorporationc</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2c)</td>
<td>510</td>
<td>35</td>
<td>(2f)</td>
<td>510</td>
<td>35</td>
</tr>
<tr>
<td>(2d)</td>
<td>560</td>
<td>31</td>
<td>(2f)</td>
<td>560</td>
<td>31</td>
</tr>
<tr>
<td>(2e)</td>
<td>510</td>
<td>35</td>
<td>(2f)</td>
<td>510</td>
<td>35</td>
</tr>
<tr>
<td>(2f)</td>
<td>660</td>
<td>35</td>
<td>(2f)</td>
<td>660</td>
<td>35</td>
</tr>
<tr>
<td>(2a)</td>
<td>110</td>
<td>100</td>
<td>(2b)</td>
<td>110</td>
<td>100</td>
</tr>
<tr>
<td>(2b)</td>
<td>110</td>
<td>100</td>
<td>(2b)</td>
<td>110</td>
<td>100</td>
</tr>
</tbody>
</table>

* Reaction conditions: neat at 20°C; XCH(HNC/N(1a) or (1b) = 1 mmol/mmol; 1–10 mol% of NiCl₂; molecular weights of products are (X, M₁): MeO, 42 000; Me, 36 000; H, 44 000; Cl, 31 000. b Optical rotation (c 0.02, CHCl₃) of (2c)–(2f). c % Incorporation of (1a) or (1b) in (2e)–(2f) as calculated from elemental analyses and H N M.R. d Reaction conditions for preparation of homopolymers: (2a), neat, 10 mol% of NiCl₂, 20°C; (2b), neat, 0.5 mol% of NiCl₂, 45°C.

were visible in the region of 300—350 nm. These couplets are responsible for rapid ion-transport through the membranes. A new photoresponsive crown ether with an ammonium-group tail was synthesised in which the ion-binding ability of the ammonium ion capable of intramolecular ‘tail-biting’ in the cis-form produced by photoisomerisation.

A new photoresponsive crown ether with an ammonium-group tail was synthesised in which the ion-binding ability changes in response to photoirradiation because of competitive intramolecular ‘tail-biting’ in the cis-form produced by photoisomerisation.

**On-Off-switched Crown Ether–Metal Ion Complexation by Photoinduced Intramolecular Ammonium Group ‘Tail-biting’**

Seiji Shinkai,* Midori Ishihara, Kaori Ueda, and Osamu Manabe*

Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan

A new photoresponsive crown ether with an ammonium-group tail was synthesised in which the ion-binding ability changes in response to photoirradiation because of competitive intramolecular ‘tail-biting’ in the cis-form produced by photoisomerisation.

References


Received, 23rd January 1984; Com. 096