Screw Sense Differentiating Polymerization of Achiral Isocyanides

Tadao Harada,* Marco C. Cleij,* Roeland J. M. Nolte,** Alfons 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-XC₆H₄NC (X = MeO, Me, H, Cl) by nickel(II) chloride in the presence of (S)-2-isocyanoisovaleric acid methyl or t-butyl ester gives rise to optically active polymers \( [p-XC₆H₄NC]_n \) with an excess of right-handed screw sense.

Poly(iminomethylenes), (2), are atropisomeric† polymers with a rigid helical structure (Figure 1).2,3 They are prepared from isocyanides, e.g., (1), by the catalytic action of nickel(II) salts.2

When enantiomers of chiral isocyanides are polymerized, optically active polymers are formed with predominantly one screw sense.4 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.5 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.4,6 The optical rotations of the compounds amounted to \([\alpha]_D^{20}\) (1a) + 27.6° and \([\alpha]_D^{20}\) (1b) + 29.5° (c 1, benzene). Aryl isocyanides (1c)—(1f) were mixed with (1a) or (1b) and polymerized neat with anhydrous NiCl₂.§ After work up, polymer samples with \(M_w = 30\,000—40\,000\) 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)

![Figure 2. C.d. spectra of polymer (2b) (curve A) and polymer (2c) (curve B) in acetonitrile and methylene chloride, respectively. Curve A points to a left-handed helix, curve B to a right-handed helix.](image)

![Figure 3. Stereo-differentiating polymerization of p-methoxyphenylisocyanide (1c) in the presence of (S)-2-isocyanoisovaleric acid methyl ester (1a). Specific optical rotation of the polymer samples as a function of the mole fraction of (1a) in the initial monomer mixture (A). Mole fraction of units from (1a) in the polymer samples as a function of the mole fraction of (1a) in the starting mixture (B).](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-borneol, (S)-α-phenylethylamine, cinchonine], and a chiral solvent [(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 NiCl₂ (13.2 mg, 0.1 mmol) for 16 h. The reaction mixture was treated with MeOH and the polymer that precipitated was collected, washed with 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° (c 0.02, CHCl₃) and contained 23% of units derived from (1a) (elemental analysis and \(^1\)H n.m.r.).
were visible in the region of 300–350 nm. These couples are due to the \( n \rightarrow \pi^* \) transition of the imino functions of the polymer main chains and point to right-handed helices.\(^4,8\) An example is given in Figure 2.

The extent of asymmetric induction by (1a) was measured by varying the initial ratio of isocyanides (1a) and (1c) in the monomer mixture. Figure 3 shows that the optical rotation of the polymer samples increases with increasing mole fraction of (1a) in the starting mixture. The number of monomeric units from (1a) that are incorporated in these samples increases simultaneously.

We also polymerized optically active isocyanides (1a) and (1b) separately with NiCl\(_2\). The resulting homopolymers (2a) and (2b) showed optical rotations of \([\alpha]_{D}^{20} = -110^\circ\) and \([\alpha]_{D}^{20} = +33^\circ\), respectively (Table 1). Remarkably, the c.d. spectra of (2a) and (2b) revealed that these polymers have a screw sense opposite to that of (2c)–(2f) i.e. a left-handed screw (see Figure 2). This result suggests that polymerization of aryl isocyanides (1c)–(1f) in the presence of (1a) or (1b) is not a common copolymerization reaction, in which a left-handed helix would have been expected as in the homopolymers. We explain our results in the following way. Isocyanides (1a) and (1b) are bulky, slowly polymerizing isocyanides. They have a preference for inclusion into left-handed helices and thus may retard the formation of these helices from monomers (1c)–(1f). The right-handed helices may continue to grow on and ultimately consume all the achiral monomer. We are currently verifying this hypothesis.

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References


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.

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 photoantenna for photocontrol of functional molecules such as crown ethers,\(^4–8\) cyclodextrins,\(^9\) and polymers.\(^10,11\)

Recently, Nakatsuji et al.\(^12\) reported a new synthetic ionophore having a crown ether ring and an attached ammonium ion capable of intramolecular complexation. Herein we report on a new photoresponsive crown ether (1H\(^+\)) with an ammonium-group tail. This ‘tail-biting’ crown ether is designed so that the crown ether ring can bind intramolecularly to the ammonium group only when it is photoisomerised to the cis-form. The Corey–Pauling–Koltun (CPK) model of (1H\(^+\)) shows that the hexamethylenespacer