Screw Sense Differentiating Polymerization of Achiral Isocyanides

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Polymerization of achiral isocyanides p-XC$_6$H$_4$NC (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-XC$_6$H$_4$NC]$_n$ 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]

$$\underset{(\mathbf{1})}{n\,\mathrm{R{-}\overset{+}{N}{\equiv}\overset{-}{C}}} \xrightarrow{\mathrm{Ni^{II}}} \underset{(\mathbf{2})}{[\mathrm{R{-}N{=}C{<}}]_n}$$

a; R = (S)-Me$_2$CHCH(CO$_2$Me)
b; R = (S)-Me$_2$CHCH(CO$_2$Bu^t)
c—**f**; R = p-XC$_6$H$_4$
c; X = MeO
d; X = Me
e; X = H
f; X = Cl

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**)[7] were mixed with (**1a**) or (**1b**) and polymerized neat with anhydrous NiC$_2$.§ After work up, polymer samples with $\bar{M}_v$ = 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

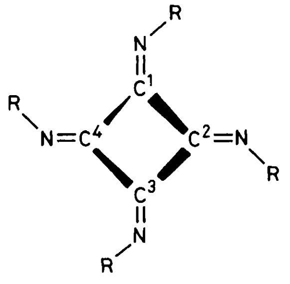

Figure 1. Helical configuration of a poly(iminomethylene). Repeating unit: C-5 is behind C-1, C-6 behind C-2, *etc.*

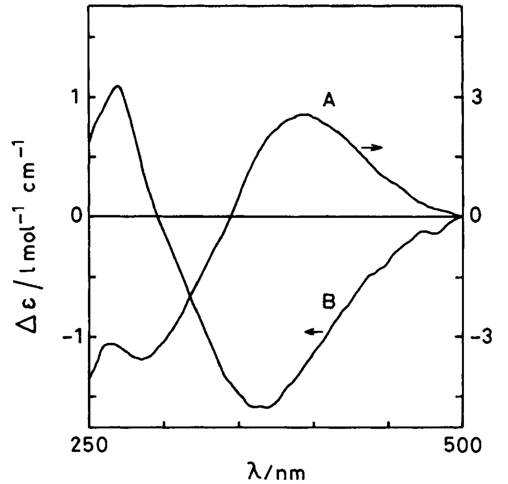

Figure 2. C.d. spectra of polymer (**2b**) (curve A) and polymer (**2c**) (curve B) in acetonitrile and methylene chloride, respectively. Curve A points to a left-handed helix, curve B to a right-handed helix.

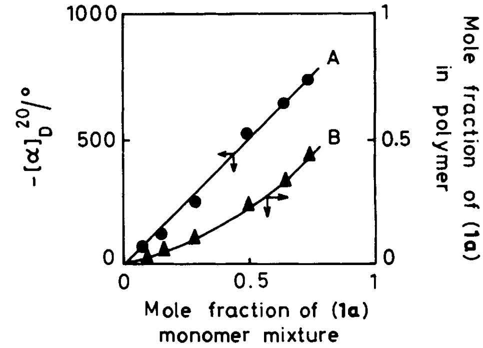

Figure 3. Stereo-differentiating polymerization of p-methoxyphenylisocyanide (**1c**) in the presence of (S)-2-isocyanoisovaleric acid methyl ester (**1a**). Specific optical rotation of the polymer samples as a function of the mole fraction of (**1a**) in the initial monomer mixture (A). Mole fraction of units from (**1a**) in the polymer samples as a function of the mole fraction of (**1a**) in the starting mixture (B).

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† 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 D-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 NiCl$_2$ (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, CHCl$_3$) and contained 23% of units derived from (**1a**) (elemental analysis and ^{1}H n.m.r.).

Table 1. Stereo-differentiating polymerization of achiral isocyanides p-XC_6H_4NC in the presence of chiral 2-isocyanoisovaleric acid esters (**1a**) or (**1b**).[a]

	(**1a**)		(**1b**)	
	$-[\alpha]_D^{20}$ [b]/°	% Incorporation[c]	$-[\alpha]_D^{20}$ [b]/°	% Incorporation[c]
(**2c**)	510	23	350	15
(**2d**)	550	31	485	22
(**2e**)	610	30	540	21
(**2f**)	660	35	445	20
(**2a**)[d]	110	100	—	—
(**2b**)[d]	—	—	−33	100

[a] Reaction conditions: neat at 20 °C; XC_6H_4NC/(**1a**) or (**1b**) = 1 mmol/mmol; 1—10 mol% of $NiCl_2$; molecular weights of products are (X, $\bar{M}_v$) : MeO, 42 000; Me, 36 000; H, 44 000; Cl, 31 000. [b] Optical rotation (c 0.02, $CHCl_3$) of (**2c**)—(**2f**). [c] % Incorporation of (**1a**) or (**1b**) in (**2c**)—(**2f**) as calculated from elemental analyses and ^1H n.m.r. [d] Reaction conditions for preparation of homopolymers: (**2a**), neat, 10 mol% of $NiCl_2$, 20 °C; (**2b**), neat, 0.5 mol% of $NiCl_2$; 45 °C.

were visible in the region of 300—350 nm. These couplets are due to the n–π* 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° and +33°, 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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