SCREW SENSE OF POLYISOCYANIDES

A. J. M. Van Beijnen, R. J. M. Nolte and W. Drenth*
Laboratorium voor Organische Chemie of the University, Croesestraat 79, Utrecht, The Netherlands

and

A. M. F. Hezemans*
Laboratorium voor Algemene Chemie of the University, Padualaan 8, Utrecht, The Netherlands

Abstract—From steric considerations as well as from an analysis of CD spectra a (*P*)-screw configuration could be attributed to the (−)-rotating molecules of poly(t-butyl isocyanide).

INTRODUCTION

In the presence of a transition metal ion, isocyanides easily polymerise to poly-Schiff bases, nickel(II) being particularly active[1,2]

$$n \; RNC \xrightarrow{\text{Ni}^{II}} \begin{array}{c} RN=C \diagup \\ \diagdown \\ C=NR \\ RN=C \diagup \\ \diagdown \end{array}$$
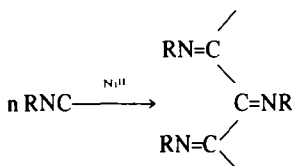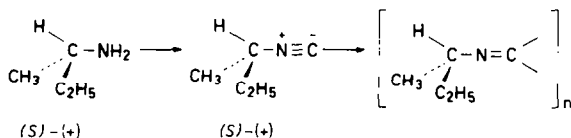
Models reveal that the polymer molecule is not planar but could have the configuration of a tightly coiled helix, especially when the substituent R has large steric requirements, like t-butyl. A helix is a chiral species. Chirality is indeed a property of poly(t-butyl isocyanide) as could be concluded from its partial resolution into fractions with (+)- and (−)-sign of rotation.[3]

Thus, the chirality of poly(t-butyl isocyanide) probably is the result of a helical configuration of its main chain. In this paper we answer the question which screw sense can be attributed to the (+)-rotating and which to the (−)-rotating molecules.

RESULTS AND DISCUSSION

The problem of the screw sense was approached from two independent directions. The first approach is based on the method of resolution. Resolution was achieved by chromatography of a solution of racemic poly(t-butyl isocyanide) in chloroform over a column of a chiral support. The support itself is also a polyisocyanide, viz. poly(sec-butyl isocyanide), synthesized from optically active sec-butyl isocyanide, which had been prepared from the corresponding sec-butyl amine. The absolute configuration of the amine is known.[4]

$$\begin{array}{c} H \\ \diagdown \\ CH_3 \diagup C-NH_2 \\ \diagup \\ C_2H_5 \end{array} \longrightarrow \begin{array}{c} H \\ \diagdown \\ CH_3 \diagup C-\overset{+}{N}\equiv \overset{-}{C} \\ \diagup \\ C_2H_5 \end{array} \longrightarrow \left[\begin{array}{c} H \\ \diagdown \\ CH_3 \diagup C-N=C \diagdown \\ \diagup \\ C_2H_5 \end{array} \right]_n$$

$(S)-(+)$ $(S)-(+)$

Two space filling models were built: one in which (*S*)-sec-butyl-N= units were attached to a right handed (≡*P*) carbon helix and one in which (*S*)-sec-butyl-N= units were attached to a left handed (≡*M*) carbon helix. It appeared that the steric fitting is more favourable with the (*M*)-helix. Assuming the steric hindrance in the polymer

to be the controlling configurational parameter, we propose that our support prepared from (*S*)-(+)-sec-butyl amine, consists of an excess of (*M*)-helices.

The next question is: does (*P*)- or does (*M*)-poly(t-butyl isocyanide) have a greater adhesion to this support? We assume it is the (*P*)-enantiomer because parallel screws have a smoother mutual fit when they are of opposing sense than when they are of the same sense. According to this view the last fraction of poly(t-butyl isocyanide) eluted from the column has an excess of (*P*)-helices. Experimentally, this fraction has the (−)-sign of rotation.

The assignment of (*P*)-screw sense to the (−)-fraction was supported by a second approach based on circular dichroism (CD) spectra. The CD spectra of the (+)- and (−)-fractions of poly(t-butyl isocyanide) have, apart from sign inversion, similar shape. The CD spectrum of a (−)-fraction (Experimental) in cyclohexane solution (1.875 mmol/l, expressed in monomer units) is presented in Fig. 1 together with the UV absorption spectrum. We attribute the absorption, that is visible as a shoulder at 280 nm on the onset of a much larger absorption in the far UV region, to the $n \rightarrow \pi^*$ transition in the $\diagdown C=N$-t-butyl group. This $n \rightarrow \pi^*$ transition is also responsible for the CD spectrum in the region of 240–400 nm. From these spectra we infer the following data. The electronic transition moment is approximately 0.60 Debije. Because of the overlapping much stronger transition in the far UV this value is a rough estimate and an uncertainty of 10% is quite possible. The rotational strength[5] is -1.37×10^{-41} c.g.s. units and the difference between rotational oscillator strength[5] and the product of the rotational strength and frequency is 1.11×10^{-37} c.g.s. units. The latter quantities measure the so-called non-conservative and conservative contributions to the CD[6], respectively.

According to Tinoco[5] the CD of a helical polymer can be described by a two-term equation:

$$\Delta \epsilon (\nu) = \frac{2.458 \times 10^{38} \nu e^{-(\nu - \nu_a)^2/\theta^2}}{\theta N}$$

$$\times \left[\sum_{K=1}^{N} R_K + \frac{2(\nu - \nu_a)}{\theta^2} \sum_{K=1}^{N} R_K(\nu_K - \nu_a) \right] \quad (1)$$

in which ν_a is the frequency at the maximum monomer absorption, θ the bandwidth, ν_K the frequency and R_K the rotational strength of the K-th component of the exciton band in the polymer, which consists of N monomers. The first term in eqn (1) represents the non-conservative
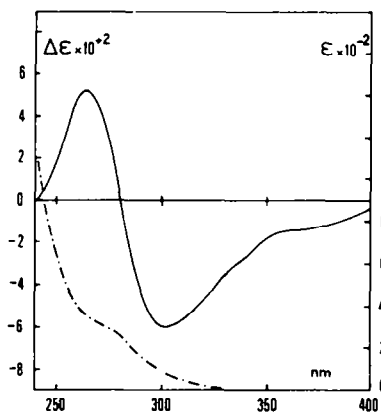
Fig. 1. Absorption---- and circular dichroism—— as a function of
wave length of (−)-poly(t-butyl isocyanide).

contribution and the second term the conservative con-
tribution. Both terms may be calculated with the help of a
model of the polymer. In this model the monomer unit is
represented by the doubly bonded carbon–nitrogen moi-
ety of the $\diagdown$C=N-t-butyl group, which is always perpen-
dicular to the axis of the helix formed by the carbon atoms
of the main chain. The number of monomer units per turn
lies necessarily between two, which is the non-helical
zig-zag chain, and six, which is a planar 6-membered ring.
Both extrema do not show any chirality, of course. The
plane of a monomer unit is defined by the nitrogen atom
and two carbon atoms, which are part of the main chain.
The normal to this plane makes an angle with the helix
axis, which varies from 180° at two units per turn to 0° at
six units per turn. Two assignments for the 280 nm band
are considered: a $\pi \to \pi^*$ transition, polarized parallel to
the carbon–nitrogen bond and a n $\to \pi^*$ transition, polar-
ized normal to the plane of the monomer. Tinoco[5] gives
expressions for $\Sigma_K R_K$ for the non-conservative contribu-
tion and for $\Sigma_K R_K (\nu_K - \nu_s)$ for the conservative contribu-
tion. With these expressions we calculated the non-
conservative contribution to the CD spectrum for the
$\pi \to \pi^*$ and the n $\to \pi^*$ assignments, assuming a (P)-helix,
as a function of the number of monomer units per turn.
The data are plotted in Fig. 2. Figure 3 gives the same data
for the conservative contribution. In the calculation we
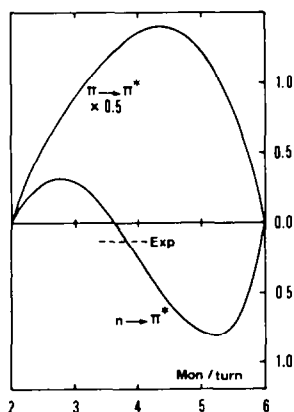used for the monomer a transition moment of 0.60 Debije

Fig. 2. Non-conservative contribution to the CD spectrum of (P)-
poly(t-butyl isocyanide) as a function of the number of monomers
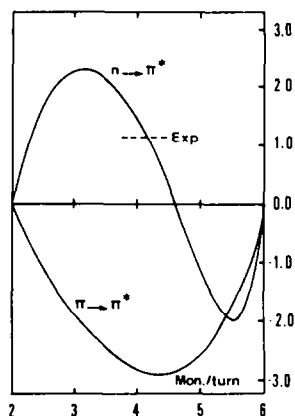per turn, in c.g.s. units × 10⁴⁰.

Fig. 3. Conservative contribution to the CD spectrum of (P)-
poly(t-butyl isocyanide) as a function of the number of monomers
per turn, in c.g.s. units × 10³⁷.

for the transition at 280 nm and a polarizability of 0.00264
nm³ in the plane and of 0.00091 nm³ perpendicular to
the plane of the monomeric unit. The results for a
(M)-helix are obtained by merely inverting all curves in
Fig. 2 and 3. In view of the uncertainty in the electronic
transition moment, the curves for the conservative con-
tribution, which contains this moment to the fourth
power, and those for the non-conservative contribution,
which is proportional to the square of this moment, may
vary considerably, say some 40 and 20%, respectively.
The experimental values of our partly resolved polymer
are indicated by horizontal dotted lines in Figs. 2 and 3.
These experimental data are consistent only with a (P)-
helix, where the n $\to \pi^*$ transition is responsible for the
CD. The number of monomer units per turn is confined to
the region between 3.6 and 4.6. We estimate a value of 4.0
monomer units per turn and in Table 1 we list the relevant
conformational parameters for this helical structure.

Table 1. Conformational parameters of poly(t-butyl isocyanide)

Number of monomers per turn	4.0
Angle between two units	90.0°
Angle between normal to unit plane and helix axis	73.64°
Height increment per unit	0.1039 nm
Dihedral angle of two neighbouring units	90.0°
Radius of helix from centre to chain carbon atoms	0.0305 nm

EXPERIMENTAL

UV spectra were obtained on a Perkin–Elmer, EPR-3T instru-
ment. Optical rotations were measured on a Zeiss polarimeter or a
Cary-60 spectropolarimeter. CD spectra were recorded on a
home-built instrument. The sensitivity of this instrument is better
than 1×10^{-6} in absorbance units. Molecular weight measurements
were performed by means of a Mechrolab osmometer, model
301A in benzene at 25°C.

Poly(t-butyl isocyanide). t-Butyl isocyanide (52.5 mmol) was
polymerised heterogeneously by anhydrous nickel chloride
(2.85 mmol) without solvent at 25°, as previously reported.[1] A
chloroform soluble fraction ($\bar{M}_n = 1280$) was used for the resolu-
tion experiments.

Support preparation. sec-Butyl amine was resolved into optical
antipodes by a standard method[7] ([α]²⁰_D + 7.14°, neat; optical purity
96%) and converted with 10% excess of ethyl formate[8] into (+)-N-
sec-butyl formamide ([α]²⁰_D + 14.05°, neat). (+)-sec-Butyl
isocyanide was obtained from the latter by dehydration with
p-toluenesulfonyl chloride[9] at a lower pressure than recommended
(yield 90%, lit. 45%; [α]²⁰_D + 39.6°, neat).

Table 2. Chromatographic resolution[a] of poly(t-butyl isocyanide)

Fraction	Fraction weight/g	$[\alpha]_{578}^{20}$ [b]
1	0.053	$+4.7°$
2	0.035	$+2.9°$
3	0.035	$0.0°$
4	0.044	$-10.2°$

[a] Supporting medium poly[(+)-sec.-butyl isocyanide]. Eluent chloroform, at 25°C. [b] In chloroform.

Poly[(+)-sec-butyl isocyanide] was synthesized from the optically active monomer (91 mmol) by $NiCl_2·6H_2O$ (0.45 mmol) in ethanol (100 ml) at 25°C, as previously reported.[1] The polymer was highly insoluble in organic solvents and water; its optical rotation and molecular weight could not be measured.

Chromatographic resolution. A column (height 17 cm, inner diameter 1 cm) was packed carefully with 7 g of the support and rinsed thoroughly with chloroform. Poly(t-butyl isocyanide) (0.15–0.30 g), dissolved in a small amount of chloroform, was introduced into the column and eluted with the same solvent. A typical example of a resolution is given in Table 2. The procedure was repeated in order to obtain additional amounts of the partly resolved fractions. The combined first and the combined fourth fraction were further purified over the column. Two samples were used for recording the CD spectra. Their rotations are: $[\alpha]_{578}^{20}$ $-12.0°$; $[\alpha]_{400}^{20}$ $-71°$ (c 0.78 g/100 ml, chloroform) and $[\alpha]_{578}^{20}$ $+6.8°$; $[\alpha]_{400}^{20}$ $+58°$ (c 2.0 g/100 ml, chloroform).

REFERENCES

[1] R. J. M. Nolte, R. W. Stephany and W. Drenth, *Rec. Trav. Chim.* **92**, 83 (1973).
[2] R. J. M. Nolte and W. Drenth, *Ibid.* **92**, 788 (1973).
[3] R. J. M. Nolte, A. J. M. van Beijnen and W. Drenth, *J. Am. Chem. Soc.* **96**, 5932 (1974).
[4] A. Kjaer and E. Hansen, *Acta Chem. Scand.* **11**, 898 (1957).
[5] I. Tinoco, *J. Chim. Phys.* **65**, 91 (1968).
[6] C. A. Bush and J. Brahms, *J. Chem. Phys.* **46**, 79 (1967).
[7] L. Thomé, *Chem. Ber.* **36**, 582 (1903).
[8] J. Moffat, M. V. Newton and G. J. Papenmeier, *J. Org. Chem.* **27**, 4058 (1962).
[9] R. E. Schuster, J. E. Scott and J. Casanova, Jr., *Org. Synth.* **46**, 75 (1966).