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POLY(IMINOMETHYLENES).
9. INDUCTION OF SCREW SENSE IN THE NICKEL(II)-CATALYZED POLYMERIZATION OF CHIRAL ISOCYANIDES

A. J. M. van BEIJNEN, R. J. M. NOLTE, J. W. ZWIKKER and W. DRENTH
Laboratory for Organic Chemistry of the University, Croesestraat 79, Utrecht (The Netherlands)
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Summary

A rule is presented which predicts the screw sense of the polymers obtained in a nickel(II)-catalyzed reaction from chiral isocyanides of the type \( \text{R}^1\text{R}^2\text{R}^3\text{C—N=C} \). It is based on the steric effects and on the ligand properties of \( \text{R}^1, \text{R}^2 \) and \( \text{R}^3 \). The optical rotation data on ten chiral isocyanides and their polymers verify this rule. The results suggest that the asymmetric induction of screw sense is controlled kinetically at the catalyst center. A thermodynamically controlled process appears to be less likely.

Introduction

In the preceding paper [1] we described a mechanism for the polymerization of isocyanides at a nickel(II) center

\[
\text{n R—N=C } \xrightarrow{\text{Ni(II)}} \left[ \text{R—N=C<} \right]_n
\]

The polymers are helical [2] and their screw sense is determined by the direction of the circular sequence of ligand insertion around nickel. With achiral isocyanides the chances of getting right- and left-handed screws are equal. This equality does not hold for chiral isocyanides. We now present a rule which predicts the preferred helical screw sense for the polymer of a chiral isocyanide of the type \( \text{R}^1\text{R}^2\text{R}^3\text{C—N=C} \).

Results and discussion

First, we consider molecules of isocyanides of which the substituents \( \text{R}^1, \text{R}^2 \) and \( \text{R}^3 \) are not able to coordinate to nickel, e.g. sec-butyl isocyanide, \( \text{C}_2\text{H}_5\text{CH(CH}_3\text{)—N=C} \). We distinguish the substituents \( \text{R}^1, \text{R}^2 \) and \( \text{R}^3 \) by their steric effects and we designate them as S, M and L, which stand for small, medium and large.
The polymerization starts from a square-planar nickel(II) complex, \([\text{Ni}^{II}(\text{C}=\text{N—R})_4]^{2+}\). The initiation step consists of attack by a nucleophile, \(X^-\), on one of the coordinated isocyanides, producing intermediate I [1]. The plane of \(\text{C}^1(\text{X})=\text{N—C}^\equiv\) is approximately perpendicular to the ligand plane \(\text{C}^1\text{C}^2\text{C}^3\text{C}^4\), while the nickel center and the group \((\text{SML})\text{C}\) will be in the (Z)-position just as in similar platinum complexes [3]. It is conceivable that the largest substituent, \(L\), will be in the exo position. Consequently, \(S\) and \(M\) point inwards.

The next step of the reaction, the first propagation step, involves attack of either \(\text{C}^2\) or \(\text{C}^4\) by \(\text{C}^1\). We suggest that the preferred direction of attack is on the side of the smaller substituent, \(S\). Thus, in structure I, the attack will occur on \(\text{C}^2\). As explained in the preceding article [1], concomitantly with this attack an isocyanide monomer, which had entered apically from above, substitutes for \(\text{C}^1(\text{X})=\text{N—C}^\equiv\), while the latter group shifts down. Once the propagation has started, it continues in the same direction, which in the sequence \(\text{C}^2 \rightarrow \text{C}^3 \rightarrow \text{C}^4\) gives rise to a left-handed screw. For clarity, a Newman projection of I along the \((\text{SML})\text{C—N=}\) bond is given in II. This picture leads to the following rule:

Isocyanides \((\text{SML})\text{C—N=}\text{C}\) which have no coordinating substituent groups, polymerize preferably to a right-handed \((P)\) screw if the sequence \(S \rightarrow M \rightarrow L\) is clockwise. A left-handed \((M)\) screw is preferred if this sequence is anti-clockwise.

The derivation of this rule is a kinetic one because it is based on the transition state of the reaction, more specifically, its first propagation step. Another means of approach is a thermodynamic one. It gives an answer to the question which screw, \(P\) or \(M\), is more favorable once the polymer has been formed. Let again the side chain of the polymer be \((\text{SML})\text{C—N=}\). The projection of such a side chain along the \(\text{C—N=}\) bond is given in III. In this
### TABLE 1
Predicted screw sense and optical rotation of polymers obtained from chiral isocyanides R–N=C

<table>
<thead>
<tr>
<th>Compound</th>
<th>R*</th>
<th>S</th>
<th>M</th>
<th>L</th>
<th>Y</th>
<th>Predicted</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Screw sense</td>
<td>Sign of rotation of main chain</td>
</tr>
<tr>
<td>1</td>
<td>(S)–C₂H₅CH(CH₃)</td>
<td>H</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td>M</td>
<td>+</td>
<td>+41.4°</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>O</td>
<td>COBz</td>
<td>M</td>
<td>+</td>
<td>+74.3°</td>
<td>&gt; +85°</td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>O</td>
<td>COBz</td>
<td>P</td>
<td>–</td>
<td>+46.5°</td>
<td>0.0°</td>
</tr>
<tr>
<td>4</td>
<td>(S)–H₂C=CHCH(C₂H₅)</td>
<td>H</td>
<td>C₂H₅</td>
<td>H₂C=CH</td>
<td>P</td>
<td>–</td>
<td>+94°</td>
</tr>
<tr>
<td>5</td>
<td>(S)–HC=CCH(C₂H₅)</td>
<td>H</td>
<td>C₂H₅</td>
<td>HC=C</td>
<td>P</td>
<td>–</td>
<td>-12.8°</td>
</tr>
<tr>
<td>6</td>
<td>(S)–C₆H₅CH(CH₃)</td>
<td>H</td>
<td>CH₃</td>
<td>C₆H₅</td>
<td>P</td>
<td>–</td>
<td>-42.0°</td>
</tr>
<tr>
<td>7</td>
<td>(S)–C₆H₅CH₂CH(CH₃)</td>
<td>H</td>
<td>CH₃</td>
<td>C₆H₅CH₂</td>
<td>P</td>
<td>–</td>
<td>+44.4°</td>
</tr>
<tr>
<td>8</td>
<td>(S)–C₆H₅OC(O)CH(CH₃)</td>
<td>H</td>
<td>CH₃</td>
<td>C₆H₅OC(O)</td>
<td>P</td>
<td>–</td>
<td>+16.7°</td>
</tr>
<tr>
<td>9</td>
<td>(S)–CH₃CO(O)CH₂CH(CH₃)</td>
<td>H</td>
<td>CH₃</td>
<td>CH₃CO(O)CH₂</td>
<td>P</td>
<td>–</td>
<td>+58.3°</td>
</tr>
<tr>
<td>10</td>
<td>(S)–CH₂CH[CH₂OC(N–Tos(O)CH₃)]</td>
<td>H</td>
<td>CH₃OC(N–Tos(O)CH₃)</td>
<td>P</td>
<td>–</td>
<td>-7.4°</td>
<td>-16.9°</td>
</tr>
</tbody>
</table>


**Compound (conc. in g/100 ml, solvent): 1 (neat); 2 (1.5, CHCl₃); 3 (2.5, CHCl₃); 4 (neat); 5 (neat); 6 (5, CH₃OH); 7 (1.8, CCl₄); 8 (1.0, CHCl₃); 9 (3.0, CHCl₃); 10 (2.1, CHCl₃).

***Isocyanide from which polymer has been obtained (conc. in g/100 ml, solvent): 2 (0.4, CHCl₃); 3 (0.75, CHCl₃); 4 (0.25, CHCl₃); 5 (0.005, CHCl₃); 6 (3.3, toluene); 7 (0.4, CHCl₃); 8 (0.35, CHCl₃); 9 (1.3, CHCl₃); 10 (0.15, CHCl₃).

††Not measured, see text.

†††Bz = benzyol.

†††Tos = p-CH₃-C₆H₄SO₂.
projection the main chain carbon atoms $C^1$ and $C^3$ are on top of each other. The next carbon atom attached to $C^3$, atom $C^4$, will preferably point in the direction of $S$ because of the lesser steric hindrance. The sequence $C^1 - C^4$ constitutes an $M$-screw. Thus, the thermodynamic and kinetic derivations lead to the same rule.

This rule predicts for $\text{(S')-(+)-sec-butyl isocyanide (1)}$ an $M$-screw polymer (Table 1). This screw sense fits into our experiments on the resolution of poly(tert-butyliminomethylene) over a column of poly[($\text{S}-\text{sec-butyliminomethylene}$)] [2]. The optical rotation of poly[($\text{S}-\text{sec-butyliminomethylene}$)] itself could not be observed because of its insolubility.

Recently, we prepared [4] poly(iminomethylenes) from $\alpha$- and $\beta$-2,3,4,6-tetra-O-benzoyl-$\alpha$-D-glucopyranosyl isocyanide. According to our rule their screw senses will be $M$ and $P$, respectively (Table 1, compounds 2 and 3). In an earlier paper [2] we showed that an $M$-screw gives rise to a (+)-contribution to the optical rotation at 578 nm. The side chain of the polymer from 2,3,4,6-tetra-O-benzoyl-$\alpha$-D-glycopyranosyl isocyanide will also contribute to the optical rotation. We do not know its exact value but it seems reasonable to assume that its sign will not be much different from the sign of the monomer itself, i.e. (+) [5]. Thus, the optical rotation by the main chain of the polymer derived from the $\alpha$-anomer is reinforced by the side chain. Experimentally, for this polymer $[\alpha]_{578}^{20} > 85 ^\circ$, which indeed is relatively large. On the contrary, for the polymer from the $\beta$-anomeric isocyanide $[\alpha]_{578}^{20}$ is immeasurably small (Table 1). In this polymer the contributions to the optical rotation by the main chain and the side chain are opposed.

The picture described above will be disturbed when the conformation of the ligand $C^1(X)=N-CR^1R^2R^3$ is not determined exclusively by the size of the substituents $R^1$, $R^2$ and $R^3$. This situation occurs when one of these substituents, denoted as $Y$, has ligand properties. Since nickel(II) is able to expand its coordination sphere from tetra- to penta- and further to hexacoordination, it is conceivable that a structure like IV may be present instead of $I^*$. The direction of insertion is now determined by the relative sizes, $S$ and $L$, of the remaining substituents: see also Newman projection V. From the projections II and V the following general rule can be derived:

Isocyanides (SML)C—N=C which have no coordinating substituent groups, polymerize to preferably a right-handed screw if the sequence $S \rightarrow M \rightarrow L$ is clockwise. A left-handed screw is preferred if this sequence is anti-clockwise. When in (SYL)C—N=C the substituent $Y$ coordinates to nickel(II), a right-handed screw is preferred if the sequence $S \rightarrow Y \rightarrow L$ is clockwise and a left-handed screw if it is anti-clockwise.

*One of the referees remarked that hexacoordination might be unfavorable in our system. When, indeed, hexacoordination does not occur, on addition of an incoming ligand to nickel the nickel —$Y$ bond should be broken. If attack by $C^1$ on $C^2$ is faster than conformational rotation around (SYL)C—N, our conclusions are still valid.
We have applied this rule to predict the preferred screw sense of the polymers in Table 1. Again it was assumed that:

(i) a P-helix gives rise to a (—)-sign and an M-helix to a (+)-sign of optical rotation;

(ii) the contribution to the optical rotation by the polymer side chain is of a sign equal to the sign of the monomer itself.

In each case the predicted screw sense was found to be in agreement with the optical rotation data.

The screw sense of the polymers from α- and β-glucopyranosyl isocyanide (2 and 3) was assigned by considering the relative sizes and not the coordinating properties of the substituents on the anomeric carbon atoms. This procedure was preferred because models showed that the bulky benzyloxy groups in the glucopyranosyl ring cause less steric hindrance in I than in IV. However, if IV is followed and the ring oxygen coordinates to nickel, the same screw senses are obtained.

An analogous situation exists for compounds 4 and 5 of Table 1. Again, the same screw senses are predicted if one considers either the steric effects exclusively or includes coordinating properties of the unsaturated groups. For compounds 6 - 9 of Table 1, both approaches lead to opposed screw senses. In e.g. 8 the ester substituent C(O)OC₂H₅ can act either as the largest group (L) in I or as the coordinating group (Y) in IV. Apparently, as one can conclude from the optical rotation data of the polymer of this compound, the latter possibility is preferred. Although nickel(II)-arene complexes are unknown [6], a π-interaction between metal and aromatic ring in compounds 6 and 7 is not unlikely [7]. The more so since the nickel center has gained softness by coordination of isocyanide ligands [8]. Models reveal that an interaction of the phenyl group with the nickel center is less easily attained for compound 7 than for compound 6. This fact is in line with the optical rotations of these polymers which suggest an appreciably lower chiral induction in the former case than in the latter.

In isocyanide 10 both imidazole and carbonyl groups are able to coordinate to nickel. Therefore, the screw sense will depend on the relative sizes and coordinating abilities of the CH₂Im(Tos) and CH₂OC(O)CH₃ substituents. The data suggest a small excess of P-screws.

Summarizing, the data of Table 1 suggest that the induction of screw sense in the polymerization of chiral isocyanides is controlled kinetically at the catalyst center. The thermodynamic stability seems to be of less importance in this context.

Experimental

Optical rotations were measured on a Perkin-Elmer polarimeter, type 141.

The synthesis and polymerization of compounds 1 - 3 of Table 1 have been published in earlier papers [2, 4]. Those of the remaining monomers
and polymers will be described separately [9]. All compounds were characterized satisfactorily by elemental analysis and spectroscopic data. The molecular weights of the polymers were estimated from viscosity data to be in the range of 5 000 - 70 000. Optical rotations expressed per repeating unit of the polymers were independent of molecular weight.

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References