POLYISOCYANIDES II
Kinetics and mechanism of the polymerization

BY
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The kinetics of polymerization of various isocyanides by nickel(II) compounds has been studied. The data suggest that reaction occurs by means of successive isocyanide insertions at a positive nickel centre.

Introduction

Polymerization of isocyanides to poly-Schiff bases has been achieved mainly with cationic catalysts or acid coated glass systems. Less attention has been paid to the coordination polymerization by metal complexes. Although suggestions for a mechanism for the different types of polymerization have been made no kinetic study has been published.

Recently we reported on the polymerization of isocyanides by nickel(II) compounds. The present paper deals with the kinetics and mechanism of this reaction.

Results

Catalysis by Ni(Acac)$_2$. Polymerization of isocyanide by nickel acetyl-acetonate, Ni(Acac)$_2$, is very slow in benzene, toluene or dioxane.

requiring reaction temperatures above 100°C. In these solvents as well as in chloroform the rate of polymerization is independent of monomer concentration up to high conversions. In contrast, the polymerization in a polar solvent is fast and the order in monomer varies according to the initial isocyanide-catalyst ratio. E.g. in case of isopropyl isocyanide in sec-butanol a first order dependence of the rate of polymerization on monomer concentration is found if the isocyanide-catalyst ratio is between approximately 80 and 800. If the ratio exceeds 800 the order in monomer approaches zero. A ratio below 80 gives rise to an order of two.

The dependence of the rate of polymerization on catalyst concentration was examined for three isocyanides. The rate constants are summarized in Table I. From these data the following empirical rate equations can be derived (v in mol.l⁻¹.s⁻¹, concentrations in mol.l⁻¹).

\[
\text{Table I}
\]

<table>
<thead>
<tr>
<th>Ethyl isocyanide in chloroform at 39.9°C³</th>
<th>tert-Butyl isocyanide in dioxane at 150.0°Cb</th>
<th>Isopropyl isocyanide in sec-butanol at 30.00°Cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cat] (\times 10^2) mol.l⁻¹</td>
<td>(k_0 \times 10^5) mol.l⁻¹.s⁻¹</td>
<td>[Cat] (\times 10^2) mol.l⁻¹</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.26</td>
<td>6.5</td>
<td>0.790</td>
</tr>
<tr>
<td>2.84</td>
<td>8.5</td>
<td>3.16</td>
</tr>
<tr>
<td>4.72</td>
<td>13</td>
<td>4.73</td>
</tr>
<tr>
<td>10.2</td>
<td>20</td>
<td>6.95</td>
</tr>
<tr>
<td>7.94</td>
<td>25.0</td>
<td>4.64</td>
</tr>
</tbody>
</table>

³ Initial [C₂H₅NC] 2.5 mol.l⁻¹
b Initial [t-C₄H₉NC] 2.0 mol.l⁻¹
c Initial [i-C₅H₇NC] 0.87 mol.l⁻¹.

Ethyl isocyanide in chloroform at 39.9°C
\[v = (6.23 \pm 0.4) \times 10^{-4}[\text{Ni(Acac)}_2]^{0.5}.\]

tert-Butyl isocyanide in dioxane at 150.0°C
\[v = (1.08 \pm 0.03) \times 10^{-2}[\text{Ni(Acac)}_2]^{1.5}.\]

Isopropyl isocyanide in sec-butanol at 30.00°C
\[v = k_1[RNC]\]
A plot of $k_1$ of the last reaction against $[\text{Ni}(\text{Acac})_2]^{0.5}$ is linear and has a slope of $(7.21 \pm 0.2) \times 10^{-4}$ mol$^{-0.5}$,mol$^{-0.5}$,s$^{-1}$. This plot does not pass the zero point because at low concentrations of catalyst the first order dependence in monomer is lost.

Polymerization of isocyanide by Ni(Acac)$_2$ is accelerated by acid$^1$. The influence of the concentration of trichloroacetic acid was investigated quantitatively for the polymerization of isopropyl isocyanide in sec-butanol at 30.00°C. The concentration of Ni(Acac)$_3$ was kept constant at a value of $6.40 \times 10^{-3}$ mol.l$^{-1}$: the initial concentration of isocyanide amounted to 0.87 mol.l$^{-1}$. As mentioned above, the rate is first order in isocyanide under these conditions. Increasing concentrations of trichloroacetic acid not only increased the rate of polymerization but also caused a gradual change from first order behaviour in monomer to second order behaviour. This change of order is not a consequence of some acid-catalysed side reaction because the monomer was still being converted quantitatively into polymer. Rate constants were calculated by assuming the following rate equation for the concentration range investigated.

$$\frac{d[RNC]}{dt} = k_1[RNC] + k_2[RNC]^2$$

This equation integrates to

$$\frac{1}{[RNC]} = \frac{k_1 + k_2[RNC]_0}{k_1[RNC]_0} \exp(k_1t) - \frac{k_2}{k_1}$$  \[2\]

$[RNC]_0$ represents the initial isocyanide concentration. The constant $k_1$ is supposed to be equal to the rate constant for reaction without acid; $k_1 7.12 \times 10^{-5}$s$^{-1}$. Consequently, $k_2$ can be obtained from the slope and from the intercept of a plot of $1/[RNC]$ versus $\exp(k_1t)$. Rate constants calculated both ways agreed within experimental error. The average values are given in Table II. These values of $k_2$ are proportional to the concentration of acid $k_2 = k(\text{Cl}_3\text{CCOOH}) \times [\text{Cl}_3\text{CCOOH}]$; $k(\text{Cl}_3\text{CCOOH}) 0.19 \pm 0.01$ 12.mol$^{-2}$,s$^{-1}$.

Catalysis by NiCl$_2$ and Ni(ClO$_4$)$_2$. Anhydrous nickel dichloride is practically unsoluble in ethanol. Therefore the complex$^8$ NiCl$_2$(C$_2$H$_5$OH)

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Table II

Influence of trichloroacetic acid on the rate of polymerization of isopropyl isocyanide by nickel(II)- compounds at 30.00°C.

<table>
<thead>
<tr>
<th>[Cl\textsubscript{3}C\textsubscript{COOH}] \times 10\textsuperscript{3} mol.l\textsuperscript{-1}.</th>
<th>Ni(Acac\textsubscript{2})\textsuperscript{a}</th>
<th>1\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k_2 \times 10^4), l.mol\textsuperscript{-1}.s\textsuperscript{-1}.</td>
<td>(k_2), l.mol\textsuperscript{-1}.s\textsuperscript{-1}.</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.273</td>
</tr>
<tr>
<td>0.416</td>
<td>0.310</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>2.11</td>
<td>3.62</td>
<td></td>
</tr>
<tr>
<td>2.79</td>
<td>4.73</td>
<td></td>
</tr>
<tr>
<td>3.35</td>
<td>6.90</td>
<td>0.246</td>
</tr>
<tr>
<td>3.72</td>
<td></td>
<td>0.213</td>
</tr>
<tr>
<td>9.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) In sec-butanol; \(k_2\) was calculated from eq. [2] with \(k_1\) 7.12 \times 10\textsuperscript{-5} s\textsuperscript{-1}, estimated error 5%; \([\text{Ni(Acac)}\textsubscript{2}]\) 6.40 \times 10\textsuperscript{-3} mol.l\textsuperscript{-1}; initial \([i-C_\textsubscript{3}H_7NC]\) 0.87 mol.l\textsuperscript{-1}.

\(b\) In ethanol; \(1 = \text{NiCl}_2(C_\textsubscript{2}H_5OH)(t-C_\textsubscript{4}H_9NC); [1] 2.20 \times 10\textsuperscript{-4} \text{ mol.l}\textsuperscript{-1}; initial \([i-C_\textsubscript{3}H_7NC]\) 0.87 mol.l\textsuperscript{-1}.

\((t-C_\textsubscript{4}H_9NC), 1, \) was used as the actual catalyst. With excess isocyanide both \text{NiCl}_2 and 1 are converted into \text{NiCl}_2(RNC)_4, 2. Compounds 2 are very unstable both as a solid and in solution, because of a rapid polymerization of the ligand. Its existence in ethanolic solutions could be proved in case of tert-butyl isocyanide, which shows a low rate of polymerization.

The rate of polymerization of isopropyl isocyanide by 1 was measured in ethanol at 30.00°C. The reaction was first order in monomer to a high degree of accuracy. In contrast to the behaviour of Ni(Acac\textsubscript{2}) the order in isocyanide did not vary on changing the concentration of the catalyst. The first order rate constant was proportional to the concentration of catalyst, the reaction showing an overall second order behaviour (Table III). This second order rate constant for catalysis by 1 is \(k_2(1) 0.273 \pm 0.015 \text{ l.mol}^{-1}.\text{s}^{-1}\) at 30.00°C.

Polymerization of isopropyl isocyanide by 1 was not accelerated by trichloroacetic acid. The value of \(k_2(1)\) slightly decreases with increasing acid concentration (Table II).

Rates of polymerization of isopropyl isocyanide by 1 in ethanol were measured at different temperatures. The enthalpy and entropy of activation are \(\Delta H^\ddagger 61.4 \pm 4 \text{ kJ.mol}^{-1}\) and \(\Delta S^\ddagger -54 \pm 13 \text{ J.mol}^{-1}.\text{K}^{-1}\), respectively.
Table III

Rate constants for the polymerization of isopropyl isocyanide by 1 and by nickel(II) perchlorate at 30.00°C.

<table>
<thead>
<tr>
<th>[1] × 10^4 mol.l⁻¹</th>
<th>k₁ × 10⁵ s⁻¹</th>
<th>[Ni(ClO₄)₂] × 10³ mol.l⁻¹</th>
<th>k₉ × 10⁵ mol.l⁻¹.s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.82</td>
<td>5.81</td>
<td>0.406</td>
<td>1.53</td>
</tr>
<tr>
<td>3.47</td>
<td>10.2</td>
<td>4.07</td>
<td>2.15</td>
</tr>
<tr>
<td>7.23</td>
<td>17.6</td>
<td>14.2</td>
<td>2.09</td>
</tr>
<tr>
<td>9.05</td>
<td>22.7</td>
<td>27.2</td>
<td>2.59</td>
</tr>
<tr>
<td>12.2</td>
<td>31.5</td>
<td>41.4</td>
<td>2.71</td>
</tr>
</tbody>
</table>

a In ethanol; 1 = NiCl₂(C₂H₅OH)(α-C₄H₉NC); initial [i-C₃H₇NC] 0.87 mol.l⁻¹.
b In sec-butanol; for the range 0–60% conversion; initial [i-C₃H₇NC] 0.87 mol.l⁻¹.

The rate of polymerization of isopropyl isocyanide by Ni(ClO₄)₂·6H₂O was measured in sec-butanol at 30.00°C. The reaction was zero order in monomer up to approximately 60% conversion. In this region the concentration of nickel perchlorate affected the rate relatively little (Table III). Strangely enough, after approximately 60% conversion the rate of polymerization increased rapidly, becoming roughly inversely proportional to the concentration of monomer.

During polymerization of isopropyl isocyanide by nickel perchlorate a yellow solid was precipitated from the reaction mixture simultaneously with the polyisocyanide polymer. The compound was identified as the complex Ni(ClO₄)₂(i-C₃H₇NC)₄, 3.

Substituents effects. Various isocyanides were polymerized by Ni(Acac)₂ in sec-butanol and by 1 in ethanol at 30.00°C. The results are summarized in Table IV. The following features have been observed.

i. The reactions are first order in monomer except for polymerization of cyclohexyl isocyanide and phenyl isocyanide by Ni(Acac)₂. Under the experimental conditions these isocyanides show zero and second order behaviour in monomer, respectively.

ii. With some combinations of isocyanide and catalyst induction periods are observed.

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Table I
First order rate constants for the polymerization of isocyanides, RNC, by nickel(II)-compounds at 30.00°C.

<table>
<thead>
<tr>
<th>R</th>
<th>Ni(Acac)$_2$</th>
<th>1$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1 \times 10^5$, s$^{-1}$</td>
<td>$k_1 \times 10^5$, s$^{-1}$</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>0.810</td>
<td>~8$^f$</td>
</tr>
<tr>
<td>C$_2$H$_5$</td>
<td>7.01$^c$</td>
<td>35.7$^c$</td>
</tr>
<tr>
<td>n-C$_4$H$_9$</td>
<td>8.24</td>
<td>57.1</td>
</tr>
<tr>
<td>i-C$_4$H$_9$</td>
<td>9.71</td>
<td>60.4</td>
</tr>
<tr>
<td>i-C$_3$H$_7$</td>
<td>7.06</td>
<td>12.4</td>
</tr>
<tr>
<td>s-C$_4$H$_9$</td>
<td>5.98</td>
<td>10.2</td>
</tr>
<tr>
<td>c-C$<em>6$H$</em>{11}$</td>
<td></td>
<td>4.39</td>
</tr>
<tr>
<td>CH$_3$CH(C$_6$H$_5$)</td>
<td>2.58</td>
<td>1.67$^e$</td>
</tr>
<tr>
<td>t-C$_4$H$_9$</td>
<td>0.00</td>
<td>0.0011</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>$^d$</td>
<td></td>
</tr>
<tr>
<td>p-CH$_3$OC$_6$H$_4$</td>
<td>3.70</td>
<td>5.3$^g$</td>
</tr>
<tr>
<td>p-CH$_2$C$_6$H$_4$</td>
<td></td>
<td>8.5</td>
</tr>
<tr>
<td>p-ClC$_6$H$_4$</td>
<td></td>
<td>60$^g$</td>
</tr>
</tbody>
</table>

$^a$ In sec-butanol; [Ni(Acac)$_2$] $6.40 \times 10^{-3}$ mol.l$^{-1}$; initial [RNC] 0.9 mol.l$^{-1}$.
$^b$ In ethanol; $1 = \text{NiCl}_2(\text{C}_2\text{H}_5\text{OH})(t$-C$_4$H$_9$NC); [1] $4.54 \times 10^{-4}$ mol.l$^{-1}$; initial [RNC] 0.9 mol.l$^{-1}$.
$^c$ Induction period observed.
$^d$ Reaction zero order in cyclohexyl isocyanide.
$^e$ Reaction second order in phenyl isocyanide.
$^f$ Polymerization is inhibited after a short time. No reliable rate constant can be calculated.
$^g$ Polymerization slows down after 40–50% conversion. The rate constant is calculated from initial data.

iii. With some isocyanides, especially aromatic ones, the rate of polymerization slows down or becomes negligible shortly after initiation. The induction period and low rate of polymerization probably arise from an inactivation of the catalyst$^7$.

With the exception of methyl isocyanide there is a linear relationship between log $k_1$(Ni(Acac)$_2$) and log $k_1$(1) for the various isocyanides. This indicates similar reaction mechanisms for both catalysts.

The rate data of Table IV were analyzed in terms of the Hammett and Taft equations$^{10}$. A plot of log $k_1$(1) versus Hammett $\sigma$ constants for

the para-substituted phenyl isocyanides is linear with \( p = 2.15 \pm 0.06 \), correlation coefficient 0.99. The relationships between \( \log k_1 \) of the various isocyanides, except the substituted aromatic ones, and the Taft polar and steric parameters, \( \sigma^* \) and \( E_s \), were determined by regression analysis\(^{11}\). The following equations represent the best fit of data\(^*\)

\[
\text{Ni(Acac)}_2 \quad \log k_1(R) = -(1.08 \pm 0.07) \sigma^* + (0.203 \pm 0.005) E_s - (4.221 \pm 0.004) \\
\text{correlation coefficient 0.98}
\]

\[
\text{NiCl}_2 \quad \log k_1(R) = -(1.83 \pm 0.5) \sigma^* + (0.84 \pm 0.06) E_s - (3.59 \pm 0.02) \\
\text{correlation coefficient 0.86}
\]

**Discussion**

Nickel acetylacetonate is trimeric in the solid state\(^{13}\) as well as in non-donor solvents\(^{14-16}\). In this trimeric structure the nickel atom is surrounded by six oxygen atoms in a slightly distorted octahedron\(^{13}\). In coordinating solvents nickel acetylacetonate is monomeric\(^{14}\).

In sec-butanol both isocyanide and solvent compete for coordination to nickel. Therefore, an equilibrium will be present

\[
\text{Ni(Acac)}_2S_2 \xrightarrow{\text{S}} \text{Ni(Acac)}_2S(RNC) \xrightarrow{\text{S}} \text{Ni(Acac)}_2(RNC)_2 \rightarrow \text{polymerization}
\]

Compound 6 has been isolated previously\(^1\). At very low concentrations of isocyanide the nickel is mainly present as 4 and two molecules of RNC have to enter in order to start polymerization. At higher isocyanide concentrations the equilibrium shifts to 5 and to 6, giving rise to lower

\( * \) Methyl isocyanide, isobutyl isocyanide and tert-butyl isocyanide are omitted in the calculations. For phenyl isocyanide the value\(^{12}\) of \( E_s \) 1.24 is used, which gives the best results.

orders in isocyanide. In the presence of trichloroacetic acid this species also competes for the ligand positions and the shift to lower order occurs at higher isocyanide concentrations. From rate equation [1] it follows that the actual polymerization catalyst is not a complex such as 6. The half power in catalyst concentration suggests that the catalytic species is a dissociation product. A conceivable dissociation is

\[
\text{Ni(\text{Acac})}_2(\text{RNC})_2 \rightleftharpoons \text{Ni(\text{Acac})(RNC})_2^\oplus + \text{Acac}^\ominus
\]

Radical fission of a ligand, as has been found for other polymerizations with metal acetylacetonates\textsuperscript{17}, is less likely because radicals just like anions fail to polymerize isocyanides\textsuperscript{2}.

In the more weakly coordinating\textsuperscript{18} dioxane, monomeric and trimeric nickel acetylacetonate will be in equilibrium. Apparently, in this solvent the catalyst is a dissociation product of the trimer

\[
\text{Ni}_3(\text{Acac})_6(\text{RNC})_n \rightleftharpoons \text{Ni}_3(\text{Acac})_5(\text{RNC})_n^\oplus + \text{Acac}^\ominus \quad [3]
\]

If the trimer is the predominant species in solution, dissociation according to [3] gives rise to a half power in nickel acetylacetonate concentration in the rate equation. This behaviour will probably be found in chloroform, which is a non-donor solvent.

Support for the ionic dissociation mechanism is afforded by the solvent effect on the polymerization, on which we reported earlier\textsuperscript{1}. In polar solvents the reaction proceeds much faster than in benzene, toluene and dioxane. Support also comes from the fact that polymerization by Ni(\text{Acac})\textsubscript{2} is accelerated by acid.

Dissociation of acetylacetone anion from its metal complex is known to occur by steps\textsuperscript{19}. One end of the chelate dissociates fast and the remaining metal oxygen bond is broken slowly. Dissociation is accelerated by mechanisms, which are called "solvent path" and "acid path". In the former case solvent molecules add to the vacant coordination side on the metal and prevent reclosing of the half opened chelate. In the latter case recombination is prevented by protons which trap the
free end of the chelate. Both mechanisms find expression in the kinetic equation\textsuperscript{20,21}

\[
\text{Rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{acid}].
\]

This equation is similar to the one we observed for the polymerization of isopropyl isocyanide by Ni(ACac\textsubscript{2}) in the presence of trichloroacetic acid.

Further support for a mechanism involving ionic dissociation of a Ni(ACac\textsubscript{2}) complex is afforded by the kinetic results of the experiments with nickel chloride. In catalysis by the latter compound neither a half power in catalyst concentration, nor a dependence of the rate of polymerization on concentration of trichloroacetic acid is found. The data suggest that the active catalyst is compound 2, which is probably sufficiently cationic to start polymerization\textsuperscript{7}.

On account of its even more ionic character Ni(Clo\textsubscript{4})\textsubscript{2} is expected to have a higher catalytic activity than NiCl\textsubscript{2}. Just the reverse was found. The most reasonable explanation for this behaviour is the low solubility of the complex Ni(Clo\textsubscript{4})\textsubscript{2}(RNC)\textsubscript{4} in the reaction medium. During polymerization solid 3 is in equilibrium with dissolved 3, which in turn equilibrates with its various dissociation products

\[
\begin{align*}
\text{Ni(Clo}_4\text{)}_2(\text{RNC})_4 & \rightleftharpoons \text{Ni(Clo}_4\text{)}_2(\text{RNC})_4 + \text{Ni(Clo}_4\text{)}_2(\text{RNC})_3 + \text{RNC} \\
\text{Ni(Clo}_4\text{)}_2(\text{RNC})_3 & \rightarrow \text{Ni(Clo}_4\text{)}_2(\text{RNC})_2 + \text{RNC}
\end{align*}
\]

When the concentration of isocyanide decreases more solid 3 will dissolve through displacement of the equilibria to the right. The gradual dissolution of 3 has a rate accelerating effect on the polymerization. Assuming \(v = k[\text{Ni}][\text{RNC}]\) to be the actual rate equation and substituting for [\text{Ni}] the total concentrations of dissolved 3 and its first two dissociation products the rate equation becomes (S solubility of 3)

\[
v = k(\text{Ni(Clo}_4\text{)}_2) S \left\{ [\text{RNC}] + K_1 + \frac{K_1 \cdot K_2}{[\text{RNC}]} \right\} \tag{4}
\]

Equation [4] accounts for both the independence of polymerization rate on Ni(ClO₄)₂ concentration and the low and changing order in monomer; the latter because the terms between braces gain importance from left to right during polymerization.

Zero valent dicobalt octacarbonyl is equally effective as a catalyst in the polymerization of isocyanides as Ni(Acac)₂¹. This behaviour is not in contrast with the cationic mechanism above. On treating the former compound with isocyanides it is converted into the 1:1 electrolyte²² [Co(RNC)₅][Co(CO)₄]⁹.

Isocyanides as ligands in metal complexes have been compared with carbon monoxide²². Both compounds have comparable electronic structures. Insertions of carbon monoxide into metal-carbon bonds are known and have been studied extensively²³. Recently, similar reactions have been found for isocyanide complexes²⁴. Even successive insertions of isocyanide molecules have been reported, a behaviour not observed for carbonyl compounds. These findings suggest that the polymerization of isocyanides by nickel(II) involves an insertion mechanism at the nickel atom. An insertion mechanism has also been proposed by Otsuka⁴,²⁴ for the polymerization of tert-butyl isocyanide by a complex formed by alkylation of Ni(t-C₄H₉NC)₄ with methyl iodide.

A general scheme for isocyanide insertion reactions has been presented by Loew²⁵; it is based on a quantum chemical study of hydrogen isocyanide. Adopting this scheme the polymerization might be depicted as follows.

In the propagation stage of the reaction the polymer chain is attached to the positive nickel centre. Coordination of a new monomer to the catalyst is initiated by an attack of the isocyanide carbon lone pair on nickel. As bond formation proceeds electron density will flow via nickel towards the metal-polymer bond. This facilitates a nucleophilic attack

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of the polymer chain on the isocyanide carbon, which has become less electron rich. An electron deficient anti-bonding \( pi \) orbital on the isocyanide carbon participates in formation of the new carbon-carbon bond.

The reaction steps may be either sequential or concerted. The kinetics of reactions carried out on palladium(II)-isocyanide complexes with amines\(^{26}\) are also consistent with a mechanism which involves a nucleophilic attack on the isocyanide group. Electron withdrawing substituents on isocyanide and electron donating substituents on the attacking amine were found to increase the reaction rate.

From the literature it is known that coordinated carbon monoxide is also susceptible to nucleophilic attack on carbon\(^{27-31}\).

Polyisocyanides are likely to accept the configuration of a tightly coiled helix structure\(^1,2\). This requires a rigid transition state of propagation. The value of \( \Delta S^\neq \) is not decisive at this point.

The substituent effects we observed suggest that polymerization of isocyanides is subject to both steric and polar influences. In case of aryl isocyanides the reaction rate is increased by electron withdrawing substituents. The reverse seems to be true for alkyl isocyanides where the Taft equation is in line with an increase in rate with electron donation of the substituent.

The mechanism discussed above predicts that electron withdrawing substituents on coordinated isocyanide and electron donating substituents in the polymer chain increase the rate of polymerization. The mechanism is in agreement with the substituent effect we observed if in polymerization of aryl isocyanides the substituent effect in the monomer predominates over the effect in the polymer chain. In the polymerization of alkyl isocyanides the reverse is true if the observed Taft correlations are valid, which is subject to some discussion\(^{10}\).

**Kinetic scheme\(^7\).** Polymerization of isocyanide by Ni(Acac)\(_2\) in sec-butanol can be described by the following kinetic scheme

\[
\text{Complex formation} \quad \text{Ni(Acac)}_2 + 2 \text{RNC} \xrightleftharpoons{K_1} 6
\]

\( K_1 \)
Initiation

\[ 6 \rightarrow k_i \rightarrow M_i^\ominus + \text{Acac}^\ominus \]

Propagation

\[ M_n^\ominus \xrightarrow[]{k_p} m_n^\ominus + 1 \]

Termination

\[ M_n^\ominus, m_n^\ominus + \text{Acac}^\ominus \xrightarrow[]{k_t} \ldots \]

\[ m_n^\ominus + 1 + \text{RNC} \xrightarrow[]{K_p} M_n^\ominus + 1 \]

\[ M_n^\ominus \text{ represents an active catalyst, which has a monomer molecule and a } \]

\[ \text{polymer chain of } n \text{ units in its ligand shell; } m_n^\ominus \text{ is the same species but } \]

\[ \text{without a monomer molecule; } k_i, k_p \text{ and } k_t \text{ are rate constants for } \]

\[ \text{initiation, propagation and termination, respectively; } K_1 \text{ and } K_p \text{ are } \]

\[ \text{dissociation constants.} \]

Assuming a rapid coordination of isocyanide, the rate of disappearance of monomer is given by \( v = -d[\text{RNC}]/dt = k_p \sum_n [M_n^\ominus]. \) Application of the steady-state treatment leads to

\[ v = k_p \left( \frac{k_i}{k_t} \right)^{\frac{1}{2}} [\text{Ni(Acac)}_2]_0^{\frac{1}{2}} \left[ \frac{[\text{RNC}]}{K_p + [\text{RNC}] \left( \frac{[\text{RNC}]^2}{K_1 + [\text{RNC}]^2} \right)^{\frac{1}{2}}} \right] \]

\[ [\text{Ni(Acac)}_2]_0 \text{ represents the total nickel concentration.} \]

At high ratios of isocyanide to catalyst the equilibria in the scheme are to the right; thus probably \([\text{RNC}] > K_p; [\text{RNC}]^2 > K_1 \) and the order in isocyanide will be zero. At low ratios of isocyanide to catalyst the equilibria shift to the left; \([\text{RNC}] < K_p \) and \([\text{RNC}]^2 < K_1 \) and the order is two. In intermediate cases the apparent order is between zero and two.

In other solvents than sec-butanol slight modifications of this scheme are necessary.

**Experimental part**

The isocyanides and \( \text{NiCl}_2(\text{C}_2\text{H}_5\text{OH})(\text{it-C}_4\text{H}_9\text{NC}) \) were prepared as described previously. Nickel acetylacetonate, nickel chloride and nickel perchlorate were purified commercial products. Solvents were of Analar grade and dried and distilled before use.

Kinetic measurements were carried out in a thermostated vessel or in sealed ampules, placed in a thermostated bath. At regular intervals samples were drawn. The polymer was precipitated by centrifugation, the supernatant diluted tenfold with solvent and an infrared spectrum recorded in the range of 2400–2000 cm\(^{-1}\) on a Perkin-Elmer 457 spectrometer; the reference cell contained solvent. Supernatants from reactions in
ethanol and sec-butanol were diluted with benzene to reduce the NC absorption of hydrogen-bonded isocyanide. The concentration of isocyanide in solution was obtained from a calibration plot of extinction of NC stretching vibration versus concentration. Rate constants were calculated by least squares analysis of the zero, first and second order reaction plots. In general the relative error in \( k \) values amounts to 5%.

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