Hindered Rotation in Poly(N-acyl)iminoalkylenes – A $^{13}$C Nuclear Magnetic Resonance Study

Bernabé L. Rivas*, Klaus Albert, Kurt E. Geckeler, Ernst Bayer*

Institut für Organische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

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Polyn(N-acetyl)iminoethylene, polyn(N-propionyl)iminoethylene and polyn(N-acetyl)-2,2-di-methyliminoethylene were prepared by cationic polymerization in solution of 2-methyl-2-oxazoline, 2-ethyl-2-oxazoline, and 2,4,4-trimethyl-2-oxazolone respectively. The $^{13}$C NMR spectra of the polymers obtained showed different sets of shifts for the carbon atoms of the backbone as well as for the N-acylimino side chain due to the restricted rotation of the N-acylimino group. The temperature dependence of the N-acylimino side chain signals showed a different coalescence behaviour depending on the substituents at both the main and the side chain.

Introduction

It is well known that the electron delocalization in an amide leads to a partial double bond character of the central carbon-nitrogen bond. This is confirmed by the relatively large energy barriers which have been observed for rotation around this bond in various amides [1–4].

Nuclear magnetic resonance spectroscopy provides a most convenient method of investigating the hindered rotation around a covalent bond. This principle was demonstrated for N,N-di-methylformamide as a low molecular weight analogue [3–6]. As a result of the partial double bond character of the carbon-nitrogen bond, the rotation around that bond is relatively slow at room temperature. Therefore the magnetic nonequivalence of the hydrogen atoms in the methyl groups cis and trans to the carbonyl oxygen leads to two signals in the $^1$H NMR spectrum.

On the other hand, long-chain polymer molecules such as polyamides exhibit a large variety of conformations in solution. There is only little information about the rate of interconversion of the various accessible conformations. Interconversion processes have been investigated for the special case of helix-coil transitions of polypeptides and polynucleotides [7, 8] as well as for the case of helix-helix transition in polyn(L-proline) [9–11].

Investigations on polyn(N-acetyl)iminoethylene and particularly for polyn(N-acetyl)iminoethylene by low resolution NMR spectroscopy have been reported [12–15]. The aim of this study was to investigate the effect of the substituent at the side and the main chain of polyn(N-acylimino)-alkylenes on the coalescence temperature. To this purpose, polyn(N-acetyl)iminoethylene, polyn(N-propionyl)iminoethylene, and polyn(N-acetyl)-2,2-di-methyliminoethylene were synthesized and their temperature-dependent $^{13}$C NMR spectra recorded.

Experimental Section

Polymers: Polyn(N-acetyl)iminoethylene [16], polyn(N-propionyl)iminoethylene [17], and polyn(N-acetyl)-2,2-dimethyl iminoethylene [18] were synthesized by cationic polymerization in solution of 2-methyl-2-oxazoline, 2-ethyl-2-oxazoline, and 2,4,4-trimethyl-2-oxazoline respectively, using boron trifluoride etherate as initiator (1-mol%). The polymers were purified by precipitation from dichloromethane.

Poly(N-acetyl)iminoethylene:

Analysis for ($C_4H_9NO_x$)$_n$

Calcd C 56.44 H 8.45 N 16.23%,

Found C 56.71 H 8.31 N 16.38%.

$M_n$ = 4,300 (vapor pressure osmometry).

Poly(N-propionyl)iminoethylene:

...
Analysis for \((C_5H_9NO)_n\)

Calcd C 60.63 H 9.08 N 14.13%.
Found C 60.58 H 9.11 N 14.13%.

\[ [\eta] = 0.83 \text{ [dl/g]}, \]

Poly(N-acetyl)-2,2-dimethyl iminoethylene:

Analysis for \((C_6H_{11}NO)_n\)

Calcd C 63.72 H 9.73 N 12.39%.
Found C 63.68 H 9.68 N 12.37%.

\[ [\eta] = 0.040 \text{ [dl/g]}, \]

13C NMR Spectra were recorded on a Bruker AC 250 spectrometer with a variable-temperature probe. In the absence of an external source of heat, the temperature of the samples was 296–297 K. Chemical shifts were specified with reference to tetramethylsilane (TMS). All the other conditions are described in the legends.

Results and Discussion

In order to study and compare the hindered rotation around the amide bond, poly(N-acetyl)iminoethylene 1, poly(N-propionyl)iminoethylene 2, and poly(N-acetyl)-2,2-dimethyl iminoethylene 3, were synthesized.

The carbonyl, methylene and methyl signals of the 13C NMR spectra of 1, 2, and 3 were used to investigate whether the interactions of the substituent groups at the side and main chain lead to a change in the hindered rotation around the amide bond.

Generally, the spectra were recorded at 5–15 K intervals from 296–348 K and in the range of the coalescence temperature, \( T_c \), at 1–5 K intervals. \( T_c \) was determined as the lowest temperature at which the two (for 3) and four (for 1 and 2) signals coalesce to give a single signal (see Figs. 1, 2, and 5).

The spectrum of 1 shows signals (from down-field) at \( \delta = 175.1–175.4 \) ppm (C=O); at \( \delta = 52.0–48.0 \) ppm (N–CH2); and at \( \delta = 27.7–26.0 \) ppm (CH3). The spectrum of 2 exhibits signals at \( \delta = 173.3–173.1 \) ppm (C=O); at \( \delta = 46.0–42.9 \) ppm (N–CH2); at \( \delta = 25.1–25.0 \) ppm (CH2–C=O) and at \( \delta = 9.9–8.8 \) ppm (CH3). The 13C NMR spectrum of 3 shows the following signals: \( \delta = 170.1–169.5 \) ppm (C=O); \( \delta = 69.9–66.4 \) ppm (quaternary carbon), \( \delta = 54.4–52.4 \) ppm (N–CH2), and at highest field the signal at \( \delta = 23.6–22.2 \) ppm (CH3).

The presence of an ethyl group bonded to the carbonyl group in the side chain of 2 as well as two methyl groups in the main chain of 3 shifts the carbonyl carbon signal to higher field with respect to 1. This is explained by steric perturbation of the carbon nuclei, known as steric compression shifts [19, 20].

Miron et al. [13] postulated a splitting of the methyl proton absorption of 3 into four signals. They used low-resolution 1H NMR spectroscopy (60 MHz) but did not prove their postulate. The spectrum showed a broad signal corresponding to the methylene protons, which could not be resolved and a COCH3 doublet separated by 7 Hz coalescing at 79 ± 2°C.

The spectra of the three compounds show a different temperature-dependent behaviour. At room temperature, the carbonyl signal of 1 is split into four signals with an intensity ratio of 40:28:15:17 which can be observed up to 323 K (see Fig. 1). At 336 K the two low-field as well as the two high-field signals merge into two resonances which coalesce at 340 K. A similar behaviour is observed for the methyl signals. Four main signals are present at room temperature, at temperatures higher than 336 K only one resonance can be detected.

Substitution of acetyl by a propionyl substituent results only in modest changes in the coalescence temperature. For 2, \( T_c \) of the carbonyl resonances is lowered to 338 K (see Fig. 2), whereas \( T_c \) of the methyl signals is changed to 328 K. In addition the methylene groups coalesce at 323 K.

The greater mobility of the polymer molecule as a result of an increase of temperature is also reflected in the temperature-dependent line widths of the methylene and methyl signals in 1 and 2. Whereas in 1 a significant decrease in signal line width is observed at temperatures higher than 333 K (see Fig. 3), in 2 a linear decrease of the methylene and methyl signal line widths from 8–10 Hz to 2 Hz is observed (see Fig. 4).

For compound 3, at room temperature, two main carbonyl signals in an intensity ratio of 70:30 are observed, the chemical shift difference of
which gradually decreases with higher temperatures (see Fig. 5).

For 1 and 2, $T_c$ was determined directly from the spectra. In the case of 3 it was determined from the plot of $\Delta v$ versus $T$ (see Fig. 6) for safety precautions with respect to temperatures higher than 373 K.

Fig. 7 shows the temperature dependent behavior of the methyl signals of 2. The signal intensity decreases with increasing temperature up to the coalescence of the resonances into only one signal (328 K). Higher temperatures result in reduced signal line width. Thus the exchange process among the different structures resulting from the hindered rotation around the amide bond can be monitored in the temperature range between 297-348 K.

A rough estimation of the energy barriers in the polymers investigated was made using the chemical shift differences of the distinct carbonyl methylene and methyl groups together with the observed $T_c$ values. In the case of the methyl groups of 2 an almost equal population is observed in the room temperature spectrum. Therefore the rate constant $k_c$ for hindered rotation at $T_c$ can be determined using the following equation:

$$k_c = \frac{\pi \Delta v_c}{\sqrt{2}}$$

where $\Delta v_c$ corresponds to the true chemical shift difference at the coalescence temperature. It was assumed that the effect of the chemical exchange on the apparent chemical shift difference $\Delta v_e$ is negligible and it was approximated to the true chemical shift difference $\Delta v$. The activation energy $\Delta G^e_c$ was then calculated according to [21]:

$$\Delta G^e_c = 4.57 T_c (10.32 - \log k_c/T_c)$$

The value of 17.5 kcal/mol fits well those obtained from data from the carbonyl and the methylene group (Table 1), despite the very rough estimation used for the calculation of these values. It is interesting to observe that $T_c$ for 2 is generally lower than that of 1.

For 3, e.g. considering the carbonyl signal with a chemical shift difference between both signals of 35.1 Hz, a coalesce temperature of 406 K can be
determined from the plot of $\Delta \nu$ versus $T$. This temperature is 66 and 68 K higher compared to 1 and 2, respectively. Due to the increased chemical shift difference $\Delta \nu$ together with the raising coalescence temperature a higher $\Delta G_c^\#$ value results. A direct comparison of activation energies of 1, 2 on

Fig. 2. $^{13}$C NMR spectra (62.9 MHz) recorded at different temperatures for the carbonyl carbon signals of poly(N-propionyl)iminoethylene 2. 16% solution in DMSO-d$_6$.

![Fig. 2](image)

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Fig. 3. Relationship between the line widths of the methyl signal and the temperature for poly(N-acetyl)iminoethylene 1.

![Fig. 3](image)

Fig. 4. Relationship between the line widths of the methylene (●) and methyl (○) signals and the temperature for poly(N-propionyl)iminoethylene 2.

![Fig. 4](image)
the one hand and 3 on the other is difficult, because these values were obtained at different coalescence temperatures. Nevertheless, the presence of two methyl groups at the backbone chain strongly increases the coalescence temperature for hindered rotation.

Table I. Parameters for the hindered rotation around the amide bond for poly(N-acetyl)iminoethylene, poly(N-propionyl)iminoethylene and poly(N-acetyl)2,2-dimethyl iminoethylene.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\Delta v$ (Hz)</th>
<th>$T_c$ (K)</th>
<th>$\Delta G^*$ (kcal mol$^{-1}$)</th>
<th>$k_c$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $R_1=CH_3$; $R_2=R_3=H$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C=O)</td>
<td>19.7</td>
<td>340 ± 1</td>
<td>17.4</td>
<td>43.89</td>
</tr>
<tr>
<td>(CH$_3$)</td>
<td>8.4</td>
<td>336 ± 2</td>
<td>17.8</td>
<td>18.76</td>
</tr>
<tr>
<td>2 $R_1=CH_2CH_3$; $R_2=R_3=H$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C=O)</td>
<td>16.4</td>
<td>338 ± 1</td>
<td>17.4</td>
<td>36.43</td>
</tr>
<tr>
<td>(CH$_3$)</td>
<td>7.1</td>
<td>328 ± 5</td>
<td>17.5</td>
<td>15.77</td>
</tr>
<tr>
<td>(CH$_2$)</td>
<td>8.4</td>
<td>323 ± 5</td>
<td>17.1</td>
<td>18.76</td>
</tr>
<tr>
<td>3 $R_1=R_3$; $R_2=CH_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C=O)</td>
<td>35.1</td>
<td>406$^a$</td>
<td>20.3</td>
<td>78.20</td>
</tr>
<tr>
<td>(CH$_3$)</td>
<td>36.0</td>
<td>–</td>
<td>20.5</td>
<td>80.14</td>
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<tr>
<td>(CH$_2$)</td>
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<td>20.4</td>
<td>91.35</td>
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<tr>
<td>(C$_q$)</td>
<td>24.3</td>
<td>–</td>
<td>20.8</td>
<td>54.16</td>
</tr>
</tbody>
</table>

$^a$ Determined from a plot of $\Delta v$ vs T.

Fig. 5. $^{13}$C NMR spectra (62.9 MHz) for the carbonyl carbon signals of poly(N-acetyl)-2,2-dimethyliminoethylene 3 recorded at different temperatures. 16% solution in DMSO-d$_6$.

Fig. 6. Plot of $\Delta v$ (Hz) vs T(K) for poly(N-acetyl)-2,2-dimethyl iminoethylene 3.
This significant effect of the substituent on the hindered rotation of these polyamides (1, 2, and 3) was not observed for other polyamides such as poly(succinylpiperazine), poly(adipylpiperazine) and poly(sebacylpiperazine), which did not show an effect of the substituent on the coalescence temperature $T_c$ [14]. Bovey and Tiers [22] found that the attachment of the amide bond to the backbone in poly(acrylamide) and poly(methacrylamide) did not strongly influence the rate of rotation around the amide bond.

In general the splitting of signals has been also observed with poly(N-formyl)imino-ethylene [15] and poly(N-formyl)imino-propylene [12]. This may be explained by assuming the presence of syn and anti conformations with respect to the carbonyl oxygen of the amide bond, and that these conformations exchange slowly.

If one considers an isolated monomer unit or only the closest neighborhood of the alkyl group, rotation around the carbon-nitrogen bond could not be expected to change the environment of the carbonyl carbons. Also it should not be possible to explain the splitting of the signals. However, it might be explicable in terms of four possible dyad structures in which each of the two acyl groups take up either the anti or syn conformation. Accordingly, four distinguishable situations with respect to the conformation of the amide group are possible (see Scheme 1).

By analogy with low molecular weight compounds [23, 24] for 1 and 2 the most intense peaks for each group may be assigned to structure 4, with the majority of the population possessing this dyad structure was the greatest. The upfield signal is attributed to the carbonyl carbon identified as $O=C^1-R_1$ and the downfield signal to the $O=C^2-R_1$ carbon. For 3 it is assigned to structure 1, which has the more intense peak at up-field which is attributed to the steric effect.
Conclusions

All polymers showed hindered rotation around the amide bond. The observed type of splitting of the signal could arise if the backbone chain acquires a preferred helical conformation producing a temperature dependent nonequivalence between two rotamers [14]. This nonequivalence disappears at the coalescence temperature $T_c$. It was shown for each polymer that $\Delta G_{c}^{\delta}$ values are very similar for the different carbon signals analysed. The hindered rotation seems to depend more strongly on the presence of the methyl groups at the $\alpha$-carbon of the backbone chain than on the methyl or ethyl substituent at the side chain. The steric and the electronic effects increase the rotational barrier for the hindered rotation around the amide bond.

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