Epimerization and NMR Spectra of Poly(2-vinylpyridine)

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(Received August 20, 1984)

ABSTRACT: Isotactic poly(2-vinylpyridine) was epimerized by the action of *t*-BuOK in DMSO solution. The course of the reaction was followed by 300 MHz ¹H NMR as well as 20 and 90 MHz ¹³C NMR spectroscopy. It was found that the polymer epimerized until equilibrium was reached had essentially the same microstructure ($\sigma \sim 0.5$) as the polymer obtained by radical polymerization. Monte-Carlo simulation was used to calculate *n*-ad stereosequence distributions for the partially and completely epimerized polymers. Isotactic (*mm*) contents of the polymers measured from the methine proton and aromatic C₂-carbon resonances, were in excellent agreement with those calculated by the Monte-Carlo method. The (*mm*)-aromatic C₂-carbon resonance patterns were interpreted in terms of heptad stereosequence resonances. CSMP programming, coupled with an optimization routine was used to evaluate rate constants for the epimerization reaction. When studied at 90 MHz all aromatic carbon resonances were sensitive to stereosequence effects. Several of these were interpreted in terms of pentad resonances.

KEY WORDS Epimerization / Poly(2-vinylpyridine) / Stereosequence Distribution / Tacticity / ¹H NMR / ¹³C NMR / CSMP / Monte Carlo / Simulation /

Epimerization of stereoregular vinyl polymers and their models provides a convenient route to materials with known and controllable stereosequence distributions.^{1–14} Such polymers are useful for studies on the physical, chemical, and spectroscopic behavior of polymers containing pseudo-asymmetric atoms. Epimerized polypropylene and epimerized polystyrene samples have been very helpful in studies on the NMR spectra of polypropylene^{3–5} and in studies on the NMR spectra, glass transition temperatures and crystallinity of polystyrene,^{8–11,15,16} for example. In general, vinyl polymers can be epimerized under conditions that permit the reversible removal of hydrogen (or other) atoms or ions from the polymer backbone, leaving monomer radicals or ions that can change their configuration, *viz.*

Rather severe conditions are necessary for the epimerization of polypropylene and the epimerization of polystyrene has the disadvantage that the isotactic polymer can be epimerized homogeneously only in hexamethyl phosphotriamide (HMPA), a potentially carcinogenic solvent.

The present paper describes studies on the epimerization and NMR spectra of poly(2-vinylpyridine). Due to the acidity of the protons present on this polymer, its epimerization can be achieved under much milder conditions than are required for the epimerization of polystyrene or polypropylene. In addition, isotactic poly(2-vinylpyridine) is readily soluble in DMSO, so the reaction could be conducted without the necessity

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of working with a hazardous solvent. Hogen-Esch and coworkers^{12,13} have reported mechanistic studies on the epimerization of 2-vinylpyridine oligomers, but no studies on the epimerization of poly(2-vinylpyridine) have been reported. By studying the ¹H- and ¹³C NMR spectra of partially epimerized poly(2-vinylpyridine) samples, we hoped to evaluate assignments previously made for the NMR spectra of these polymers, as well as to make additional assignments and to improve our general understanding of the NMR spectra of vinyl polymers containing aromatic rings.

EXPERIMENTAL

Polymer Synthesis

Isotactic poly(2-vinylpyridine) was prepared from carefully dried monomer in toluene solution at 0°, using phenyl magnesium bromide prepared in benzene as the initiator.¹⁶ ¹³C NMR analysis of the polymer indicated it to contain the following triad concentrations: (*mm*) = 0.92; (*mr* + *rm*) = 0.06; (*rr*) = 0.02. Data of Natta *et al.*,¹⁷ indicate that a similar procedure yields polymer having a molecular weight of approximately 10,000.

Epimerization Reaction

Equal amounts of solutions of isotactic poly(2-vinylpyridine) (0.38 M in vinylpyridine units) and of *t*-BuOK (0.50 M) were mixed and sealed in glass vials under vacuum. The vials were then heated for different times in a constant temperature bath maintained at 40 ± 0.5°C. The contents of the vials were then poured into water to precipitate the epimerized polymers. These were then reprecipitated from CHCl₃ solution into petroleum ether and dried. The recoveries after two purifications generally ranged from 70–80%.

Computer Simulation of Epimerization Reaction

The Monte-Carlo method previously described^{8,11} was used to calculate dyad through heptad stereosequence distributions for the epimerized polymers as a function of relative time and *m*-content. The program was modified to operate on initial chains that were generated by the following conditional probabilities: $p(m/r) = 0.61$ $p(r/m) = 0.06$. These probabilities were obtained from the *mm*, (*mr* + *rm*) and *rr* estimates made from the starting polymer, as is discussed above. The same

effect could be obtained by assuming a perfectly isotactic polymer at the start and then shifting the time axis so that the appropriate *mm* value prevailed at time zero. An *R*-value of 0.50 was used in the Monte-Carlo calculations.

A CSMP program¹⁸ was also used to calculate dyad and triad stereosequence distributions for the epimerized polymers. It provided results equivalent to those obtained by the Monte-Carlo method. The CSMP program was combined with STEPIT¹⁹ to obtain a routine for selecting the rate constants that provided the best agreement between calculated and observed stereosequence distributions.

NMR Measurements

300 MHz ¹H NMR spectra of the polymers in CDCl₃ solution at 50°C were recorded using a Varian HR-300 spectrometer operated in CW mode. 20 MHz ¹³C NMR spectra of the polymers in CD₃OD solution at 50°C were recorded by a Varian CFT-20 spectrometer using the following acquisition parameters: sweep width 300 Hz, acquisition time 6.83 s, pulse width 14 μs, digital points 4096, 20–80 K transients. The digital resolution was 2 Hz/point for recording whole spectra or 0.15 Hz/point for expanded aromatic signals. 90 MHz ¹³C NMR spectra of the polymers in 15% CH₃OD solution were recorded using a Nicolet NIC-360NB spectrometer and the following typical acquisition parameters: sweep width 7246 Hz, pulse width 21 μs, acquisition time 2.26 s, digital points 32768, 2000 transients. Aromatic carbon patterns were assigned to specific ring carbons based on analogy to published interpreted spectra and based on chemical shift calculations. All chemical shifts are referenced to tetramethylsilane.

For determination of peak areas, different methods were used. Well resolved signals (aliphatic ¹H resonances) were cut and weighed. 20 MHz resonance patterns of aromatic protons and carbons were digitized using a Tetronix digitizer coupled with a PDP-11 computer and peaks were resolved numerically using the LGFIT2 program of von Meerwall.²⁰ The error of this line area determination depended on the degree of overlapping, but it is estimated not to exceed 3% between the *mr* and *rr* regions for highly epimerized samples.

Spectrum simulations were done using a Calcomp plotter and a program written by Dr. W. L. Brunner of The University of Kentucky. Line intensities for

simulations are equal to stereosequence distributions calculated for the polymers, based on their *mm*-contents, as determined by ^1H NMR spectroscopy. A constant half-width and a line shape that was a combination of Lorentzian and Gaussian curves were used.

Gel Permeation Chromatography

The molecular weights of isotactic poly(2-vinylpyridine) and of epimerized samples derived from it were estimated by gel permeation chromatography, using 0.25% solutions of the polymers in THF solution and a 7-column Styragel® series having a porosity range that varied from $2 \times 10^3 \text{ \AA}$ to $5 \times 10^6 \text{ \AA}$. A Waters Ana-prep instrument equipped with a differential refractive index detector and a calibration based on monodisperse polystyrene samples were used. The measurements were conducted at 30°C .

RESULTS AND DISCUSSION

Epimerization Studies

The conditions used to epimerize poly(2-vinylpyridine) are essentially those used by Hogen-Esch and coworkers in studies on the epimerization of 2-vinylpyridine oligomers.¹²⁻¹⁴ The reaction proceeded at a convenient rate if a solution of isotactic poly(2-vinylpyridine) (0.19 M in repeat units) and *t*-BuOK (0.25 M) in dimethyl sulfoxide (DMSO) was heated at 40°C . Under these conditions, the epimerization proceeds to equilibrium in about ten hours.

The reaction is accompanied by the development of a deep red color that increases in intensity with time. This color disappears when the reaction mixtures are poured into water. The color is not believed to be due to anions of structure I, which should not be red. The color may be due to anions of type II, which can result from a small amount of backbone degradation, *viz.*

A similar phenomenon has been observed in studies on the epimerization of polystyrene.⁸⁻¹¹ The polymers isolated from epimerizations were light yellow in color.

In support of the chain degradation reaction discussed above, gel-permeation chromatography showed that the molecular weight of the polymer fell by a factor of 2 every 1.5 h under the epimerization conditions employed in this study. This means that about 4% of the monomer units will have been affected by this reaction after epimerization is almost complete ($\sim 6 \text{ h}$). Figure 1 shows a plot of $1/M_n - 1/M_n^0$ versus time, where M_n^0 and M_n are the number-average molecular weights of the isotactic and epimerized polymers, respectively. Based on the slope of this plot, and the concentrations of base and vinylpyridine units present in the reaction mixture, the rate constant for degradation is estimated to be $9.2 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$.

To determine whether or not spectroscopically significant side reactions accompany the epimerization reaction, a sample of atactic poly(2-vinylpyridine) prepared by free radical polymerization was submitted to the epimerization conditions for 160 h. The infrared, ^1H NMR and ^{13}C NMR spectra of the original and recovered polymers were practically the same, indicating that the epimerization reaction is a rather clean reaction. Although bases are known to react with pyridine rings, this does not seem to be a complication under the conditions employed in this study.

Figure 1. Plot of $1/M_n - 1/M_n^0$ versus time for epimerized poly(2-vinylpyridine) samples.

Figure 2. 300 MHz ^1H NMR spectra of epimerized isotactic poly(2-vinyl pyridine) samples in CDCl_3 at 50°C . The reaction times and *mm*-contents of the samples are indicated on the figure.

Figures 2–4 show the ^1H and ^{13}C NMR spectra of epimerized polymers isolated after various reaction times. Expansions of the aromatic carbon resonance regions are provided in Figures 3 and 4. The ^1H and ^{13}C NMR spectra of poly(2-vinylpyridine) have been the subject of several studies^{20–27} and it seems to be well established that the methine proton resonance signal at $\delta = 2.25$ ppm and the aromatic C-2 (quaternary) carbon resonance occurring between $\delta_{\text{C}} = 165.05$ and $\delta_{\text{C}} = 165.5$ ppm provide measures of the *mm*-contents of the polymers. Figure 5 shows a plot of the *mm*-contents of the epimerized polymers *versus* time. The experimental points fall nicely on a curve that can be generated by either Monte-Carlo⁸ or CSMP¹⁸ simulation of the epimerization reaction.

^1H NMR Spectra

Figure 2 shows the 300 MHz ^1H NMR spectra of

several partially epimerized poly(2-vinylpyridine) samples along with the spectrum of the atactic polymer prepared by free radical initiation and the spectrum of the completely epimerized polymer. The latter two spectra are essentially identical, suggesting that atactic poly(2-vinylpyridine) should be considered to be completely epimerized.

The aliphatic proton resonances of the isotactic and atactic polymers are essentially the same as those reported previously, and the aliphatic proton resonance patterns of the epimerized polymers progress gradually from one extreme to the other. Unless polymers derived from 2-(β , β -dideuteriovinyl)pyridine can be studied, this region can only provide information about *mm*-contents.

The aromatic proton resonances of poly(2-vinylpyridine) are all observed separately, and are influenced by streosequence distribution effects. This is particularly true of the resonances of the

Figure 3. 20 MHz ^{13}C NMR resonance patterns of quaternary aromatic (C-2) carbons of epimerized isotactic poly(2-vinylpyridine) samples in CD_3OD at 50°C . The *mm*-contents of the samples are indicated on the figures. Simulated resonance patterns for the *mm*-region are shown in dotted lines on each spectrum.

protons in the 6-position of the pyridine ring, ($\delta = 8.0\text{--}8.4$ ppm) which are well separated from the other aromatic proton resonances and which are rather well defined. At least six separate signals are evident in this region, indicating a sensitivity to pentad or higher *n*-ads, and the pattern in the spectrum of the atactic (or fully epimerized) polymer is almost symmetrical. The *mmmm* (or *mmmmmm*) resonance is clearly assigned to the signal at $\delta = 8.22$ ppm and the spectrum of the

polymer having an *mm*-content of 0.50 suggests that *mrrm* and *mmrr* resonances should occur downfield and upfield, respectively, of the *mmmm* line.

Based on spectra simulations and the use of empirical chemical shift rules, the resonance observed in this region has been assigned as shown in Figure 6. The spectra can be accounted for by pentad resonances that are considerably overlapped when their central triads are considered. Figure 7 compares the H-6 proton resonance patterns ob-

Figure 4. 90 MHz ^{13}C NMR aromatic carbon resonance spectra of epimerized isotactic poly(2-vinylpyridine) samples in CH_3OD solution. The *mm*-contents of the polymers are indicated in the central portion of each spectrum. Individual resonance patterns are identified by numbers placed in the middle of the figure. Components of each pattern are identified by letters placed on the second spectrum from the top. The relative intensities of these components are compared with calculated stereosequence functions in Table III.

served for the polymers with simulated spectra based on these assignments and on pentad stereosequence distributions calculated for the polymers by Monte-Carlo simulation. The agreement is very good, indicating the validity of the assignments.

20 MHz ^{13}C NMR Spectra

^{13}C NMR spectra of the epimerized polymers in CD_3OD solution at 40° were initially studied with a 20 MHz spectrometer. In all previous reports, the resonance of the quaternary aromatic carbons (C-2) is claimed to be the one most sensitive to tacticity.

An effort was therefore made to use the epimerized polymers to learn more about this region.

Figure 3 shows expanded 20 MHz aromatic C-2 carbon spectra for a series of epimerized poly(2-vinylpyridine) samples. The three areas assigned previously to *mm*-, *mr*-, and *rr*-triads are designated I, II, and III, respectively. The relative intensities of these areas were estimated using the curve-fitting program of von Meerwall.²⁰ The error involved in separating the II and III areas by the procedure employed is estimated to be less than 0.03 in relative intensity. Taking the I, II, and III areas as measures of *mm*-, *mr*-, and *rr*-triad concentrations, the data

Figure 5. Triad stereosequence distributions determined for epimerized isotactic poly(2-vinylpyridine) by ^1H NMR (*mm*) and ^{13}C NMR (all sequences) spectroscopy. The curves were calculated by CSMP simulation with $k_0 = 8.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, $k_1 = 7.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, and $k'_0 = 7.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. Monte-Carlo simulation generates equivalent curves after appropriate scaling.

Figure 6. Assignment of H-6 aromatic proton resonance pattern (CDCl_3 , 60°C) of atactic poly(2-vinylpyridine). The *rm*-centered pentad resonances are distinguished by having a small circle placed at their tops. A digitized spectrum of atactic poly(2-vinylpyridine) is included to show the agreement between the observed (—) and simulated (---) spectrum.

Figure 7. Observed and simulated H-6 aromatic proton resonance (300 MHz) patterns of epimerized isotactic poly(2-vinyl pyridine) samples. The line positions are based on the assignments given in Figure 6, and the line intensities are based on Monte-Carlo simulation of the epimerization reaction ($R=0.50$). *mm*-Contents based on methine proton resonance patterns are indicated on the spectra.

were analyzed using a combination of CSMP¹⁸ and STEPIT¹⁹ programs to determine k_0 , k'_0 , and $k_1 = k'_1$ in the following epimerization reactions:

The values obtained are listed below

$$k_0 = 8.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

$$k'_0 = 7.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

$$k_1 = k'_1 = 7.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

An R value appropriate for Monte-Carlo simulation of the epimerization process can be calculated as follows: $R = k_0/(k_0 + k'_0) = 0.53$. Use of this value with the Monte-Carlo program (and appropriate time scaling) or use of the k values listed above in CSMP simulation of the epimerization process yielded the curves shown in Figure 5. The mr - and rr -resonance areas, although close to the calculated curves are systematically below and above them, respectively, indicating that the II and III areas may not be due solely to mr - or rr -triads.

Fine structure is observed within the general I-, II-, and III-resonance areas and several groups^{23,24,27} ventured to interpret this in terms of pentad stereosequences. It is not surprising that different assignments were made since the fine structure is poorly defined and limited information is available for evaluating or generating such assignments. The presently available data enable several heptad assignments to be made. A general procedure for doing this was discussed previously.¹¹ Unfortunately, the presence of mr - and rr -resonances of unknown origin in the starting polymer frustrated this approach, but a set of assignments and empirical chemical shift parameters that cover the mm -region has been developed. The parameters and assignments are shown in Table I. These enabled simulated spectra to be constructed that matched satisfactorily the observed spectra in region I, as is shown in Figure 3. We plan to continue studies on the C-2 resonance patterns

Table I. Empirical chemical shift parameters for the C-2 aromatic carbons of poly(2-vinylpyridine) and heptad assignments for the mm -region based on these parameters

Empirical chemical shift parameters ¹¹		
	Poly(2-vinylpyridine)	Polystyrene ¹¹
Δmmm^a	-0.07 ppm	-0.080
Δmrm	-0.09 ppm	-0.288
Δmrr	-0.12 ppm	-0.196
mm -Region heptad assignments		
Heptad	δ	Method of calculation
$mmmmmm$	165.29 ppm	Observed
$mmmmmr$	165.22 ppm	$165.29 + \Delta mmmr$
$mmmmrr$	165.17 ppm	$165.29 + \Delta mrr$
$mmmmrm$	165.20 ppm	$165.29 + \Delta mrm$
$rmmmmr$	165.15 ppm	$165.20 + 2\Delta mmmr$
$rmmmrr$	165.10 ppm	$165.20 + \Delta mmmr + \Delta mrr$
$rmmmrm$	165.05 ppm	$165.20 + 2\Delta mrm$
$mrmmrr$	165.08 ppm	$165.29 + \Delta mrm + \Delta mrr$
$rmmmrm$	165.13 ppm	$165.29 + \Delta mmmr + \Delta mrm$
$mrmmrm$	165.11 ppm	$165.29 + 2\Delta mrm$

$$\begin{aligned}
 {}^a \Delta mmmr &= \delta mmmmmmr - \delta mmmmmmm \\
 &= \delta rmmmmmr - \delta rmmmmmm \\
 &= \delta rmmmmmr - \delta rmmmmmm, \text{ etc.}
 \end{aligned}$$

using spectra measured at 90- and 100-MHz.

90 MHz ¹³C NMR Spectra

Figure 4 shows 90 MHz aromatic carbon resonance spectra of the various poly(2-vinylpyridine) samples in CH₃OD solution. All five aromatic carbons are observed in separate regions and all show sensitivity to stereosequence distribution effects. As is the case with the 20 MHz spectra, the C₂- (quaternary) carbon resonance region consists of three broad, somewhat overlapped resonances that provide measures of triad stereosequence distributions. These distributions are plotted on Figure 5, along with results obtained in the ¹H NMR and 20 MHz ¹³C NMR studies.

Surprisingly, the resonances of other aromatic carbons in poly(vinylpyridine)s provide more detailed stereosequence information than does the C-2 carbon region. Thus, the resonances of the C₃- and C₆-carbons contain 4 or 5 signals that can be assigned to combinations of pentads, as is shown in

Table II. C₃-carbon resonance assignments for epimerized isotactic poly(2-vinylpyridine)

Resonance region ^a and assignment		Epimerization time =	Observed and (calculated) resonance areas			
			40 min	100 min	180 min	Atactic
A	<i>mrrm</i>		0.06 (0.07)	0.09 (0.09)	0.08 (0.09)	0.05 (0.06)
B	<i>rrrm</i>		0.03 (0.02)	0.07 (0.09)	0.07 (0.09)	0.11 (0.12)
C	<i>rrrr</i> <i>rmrr</i> $\frac{1}{2}$ <i>mrrmr</i>		0.06 (0.04)	0.13 (0.10)	0.18 (0.19)	0.26 (0.25)
D	$\frac{1}{2}$ <i>mrrmr</i> <i>rrrm</i> <i>mrrmm</i> <i>rmmr</i>		0.20 (0.20)	0.25 (0.27)	0.34 (0.31)	0.26 (0.25)
E	<i>mmmr</i> <i>mmmm</i>		0.68 (0.68)	0.46 (0.52)	0.33 (0.34)	0.19 (0.19)

^a Refer to Figure 4 to identify resonance region.**Table III.** C₆-carbon resonance assignments for epimerized isotactic poly(2-vinylpyridine)

Resonance region ^a and assignment		Epimerization time =	Observed and (calculated) resonance areas			
			40 min	100 min	180 min	Atactic
A	<i>mrrm</i>		0.05 (0.06)	0.08 (0.09)	0.07 (0.09)	0.08 (0.06)
B	<i>rrrm</i>		0.02 (0.02)	0.06 (0.05)	0.09 (0.09)	0.13 (0.12)
C	<i>rrrr</i> <i>mmrr</i> <i>rmrr</i>		0.17 (0.17)	0.21 (0.22)	0.24 (0.26)	0.30 (0.31)
D	<i>mrrmr</i> <i>mrrmm</i> <i>mmmm</i> <i>mmmr</i> <i>rmmr</i>		0.74 (0.72)	0.65 (0.61)	0.60 (0.54)	0.49 (0.50)

^a Refer to Figure 4 to identify resonance region.

Tables II and III. The resonance areas observed in these patterns are in good agreement with those calculated by the Monte-Carlo technique. Assignments have not been made for the C₄- and C₅-aromatic carbon resonance as of this writing, but it should be possible to interpret them also. The

C₅-patterns are quite interesting; they resemble the aromatic H₆-proton patterns in that the *mmmm* (or *mmmmmm*) signal occurs in the center of the pattern. They can probably be interpreted in the same manner as the H₆-aromatic proton resonance patterns.

A very interesting feature of these spectra is the ordering of the resonances with respect to stereoregularity within each of the aromatic carbon resonance patterns. For example, considering the carbon designations shown below, the *mr*- and *rr*-resonances appear upfield from the *mm*-resonances

for carbons C-2 and C-4 but they are ordered in the opposite direction for carbons C-3 and C-6 and a severely overlapped situation occurs with carbon C-5. The different ordering for carbons C-4 and C-6 is surprising since they are both "meta" to the polymer backbone and might be expected to experience similar shielding effects if the rings are rotating freely. Apparently this is not the case. Dipole-dipole interactions or electrostatic interactions involving the pyridine nitrogen atoms in the acidic solvent employed may cause the relative motions of adjacent pyridine rings to be correlated and may cause the polymer chain to prefer conformations that favor different shieldings of similarly placed nuclei.

Whatever the cause of these effects, they make the resonance patterns of carbons C-3 and C-6 particularly useful for stereosequence studies, as is indicated by the correlations shown in Tables II and III.

CONCLUSIONS

Epimerization of poly(2-vinylpyridine) occurs cleanly, albeit with some chain degradation. The reaction can be simulated by Monte-Carlo or CSMP-programming. ^1H and ^{13}C NMR studies on the epimerized polymers have led to interpretations of some of the aromatic proton and carbon resonances. It seems that additional study will lead to interpretations of other aromatic carbon and proton resonances and of the aliphatic carbon resonances. The unusual shielding effects noted in the aromatic carbon resonance studies merit further investigations. Based on the results obtained in this study and in earlier investigations^{23,24} poly(2-vinylpyridine) prepared by conventional free radical initiated polymerization seems to be atactic.

Acknowledgements. The authors are grateful to Dr. Ernst von Meerwall for assistance in the use of his program, to Mr. Arijit M. Dasgupta for conducting the GPC measurements on the epimerized samples, to Dr. Toshimitsu Suzuki for providing an initial poly(2-vinylpyridine) spectrum and to Messrs. Rick Wiggins and Gayle A. Seymour of the University of Akron Computer Center for helpful advice and assistance. This project was supported by the National Science Foundation (NSF-DMR-80-10709/83-03739) and one of us (A.D.) was the recipient of a Fulbright Fellowship.

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