^{13}C Nuclear Magnetic Resonance Spectra of Poly(*N*-formylpropylenimine) and Some Related Formamide Derivatives

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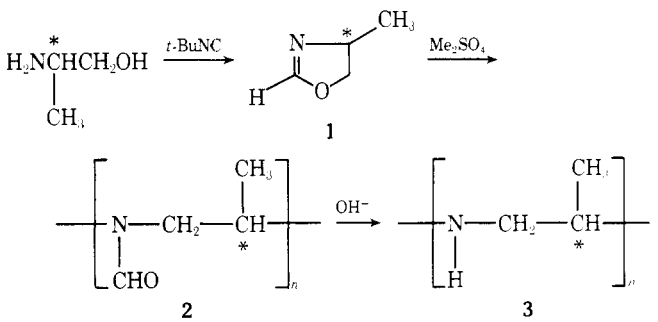
ABSTRACT: Isotactic and atactic poly(*N*-formylpropylenimine)'s were prepared by the polymerization of L- and DL-4-methyl-2-oxazoline, respectively, using dimethyl sulfate as initiator. The tacticity of these polymers was determined from the ^{13}C NMR spectra of the poly(propylenimine)'s (in concentrated HCl) obtained by alkaline hydrolysis. Isotactic poly(propylenimine) gives a single set of shifts for the three carbon atoms but in the *N*-formyl precursor, restricted rotation of the *N*-formyl group gives rise to fine structure for all four carbon atoms, as well as a time-dependent optical rotation of its aqueous solution. ^{13}C NMR spectra of the model compounds *N*-ethyl-*N*-methylformamide and *N*-isopropyl-*N*-*n*-propylformamide were also recorded and the chemical shifts were identified for each pair of conformers.

The following sequence of reactions may be used to produce linear polymers of propylenimine (**3**) and its *N*-formyl precursor (**2**), as shown by Saegusa et al.[1] When the starting material is L-alaninol the resulting polymer is optically active indicating some retention of configuration about the chiral center. If the configuration is totally retained the polymer will be isotactic, and there should be a single set of chemical shifts in the ^{13}C-{^{1}H} NMR spectrum of optically active poly(propylenimine).



We have recently confirmed this,[2] the shifts in water at 60°C being CH_3 20.08, CH_2 53.75, CH 55.11 ppm downfield from TSP (sodium trimethylsilyl-1-propane sulfonate). In concentrated HCl there is a "titration shift"[3] for each resonance, the new positions being CH_3 17.39, CH_2 49.45, CH 55.62 ppm, but without the development of any fine structure. In contrast poly(propylenimine) made from racemic starting material by the same method shows fine structure (when the spectrum is taken in concentrated HCl), the intensity pattern of which shows that the polymer is completely atactic.

In the present paper we report the ^{13}C NMR spectrum of the isotactic precursor **2**, as well as its mutarotation on dissolution in water; both of these properties reflect the restricted rotation about the N–CHO bond.

Experimental Section

L-4-Methyl-2-oxazoline (1). 1 was prepared by Saegusa's method[1] from L-alaninol, $[\alpha]^{25}$D +21.8° (C_2H_5OH), which had been made from L-alanine via the ethyl ester. The neat liquid product had a positive rotation, $[\alpha]^{25}$D 14.4° in a 1-dm cell, but a large negative rotation in ethanol as observed by Saegusa,[1] $[\alpha]^{25}$D −148°. The ^{13}C chemical shifts (in D_2O) were CH_3 22.75, CH 61.94, CH_2 75.19, CH=N 157.99 ppm downfield from TSP. Racemic monomer was made in similar fashion from DL-alanine.

Poly(*N*-formylpropylenimine) (2). After drying 1 over activated molecular sieves 4A for 24 hr, it was sealed off in the presence of 1–3% dimethyl sulfate in the absence of air and kept at 120°C for 24–48 hr. Occasional samples refused to polymerize under these conditions. Successful polymerizations proceeded to 80–90% conversion. The product was poured into ether, filtered, dried, dissolved in methanol, and reprecipitated in ether to give a white solid, $[\alpha]^{25}$D 107° (H_2O) after equilibration; cf. Saegusa,[1] $[\alpha]^{25}$D 130° (MeOH). One product had $[\eta]$ = 16 cm^3 g^{-1} corresponding to a molecular weight of the order of 10^4.

***N*-Ethyl-*N*-methylformamide (4).** This was obtained in a very pure state by heating formamide with ethylmethylamine hydrochloride,[4] followed by extraction with chloroform. A trace of formic acid was removed by washing with sodium hydroxide. ^{1}H NMR (δ ppm relative to TMS, solvent $CDCl_3$; the chemical shift for the more abundant conformer is given first in each case) CH_3CH_2 1.19, 1.12 (J = 7.1 Hz); NCH_3 2.87, 2.96; NCH_2 3.32, 3.39 (J = 7.2 Hz); CHO 8.12, 8.05. A similar but more restricted set of data has been previously reported.[5]

***N*-Isopropyl-*N*-*n*-propylformamide (5).** This was prepared by the following sequence of reactions according to methods described in the literature,[6,7] starting either from *n*-propylamine or isopropylamine, and using the complementary iodide in the final stage.

$$RNH_2 + HCOOEt \longrightarrow RNHCHO + EtOH$$
$$\downarrow \text{NaH/xylene}$$
$$RNNaCHO \xrightarrow{R'I} RR'NCHO$$

The two products had identical ^{1}H NMR spectra; the chemical shift (δ ppm) for the more abundant conformer is given first in each case (solvent $CDCl_3$, reference TMS): CH_3CH_2 0.91 (J = 7.0 Hz); $(CH_3)_2CH$ 1.25, 1.20 (J = 6.9 Hz); CH_3CH_2 1.59, 1.61 (J = 7.6 Hz); NCH_2, complex multiplet centered on 3.14; NCH, 3.70, 4.34 (J = 6.7 Hz); CHO 8.18, 8.05. Anal. Calcd: C, 64.86; H, 11.60; N, 10.77. Found: C, 65.12; H, 11.62; N, 10.85. The boiling point is 45° (0.5 mm). This compound does not appear to have been previously reported.

^{13}C NMR Spectra. These were mostly obtained with a Bruker Fourier transform spectrometer operating at 22.63 MHz; conditions are indicated in the legends. The spectrum of **4** was obtained on a Varian instrument operating at 25.14 MHz.

The ^{13}C NMR Spectrum of Poly(*N*-formylpropylenimine). The isotactic polymer has the decoupled spectrum shown in Figure 1a. When not decoupled from protons by broad-band irradiation the spectrum has the appearance shown in Figure 1b. The decoupled spectrum is much more complicated than for the isotactic poly(propylenimine) produced by hydrolysis (see the introductory section), and each of the four carbon resonances exhibits fine structure. The carbonyl resonance is split into two peaks of unequal intensity. The methyl resonance also splits into two peaks of unequal intensity, with signs of a third weak resonance as a shoulder on the upfield peak. The methylene and methine resonances may be interpreted in terms of two overlapping sets of four peaks as indicated by the stick diagram in Figure 1a.

The fine structure in Figure 1a is explicable in terms of four possible dyad structures, in which each of the two formyl groups may take up either the syn or anti conformation, as is usual for compounds containing the peptide linkage. By analogy with low molec-

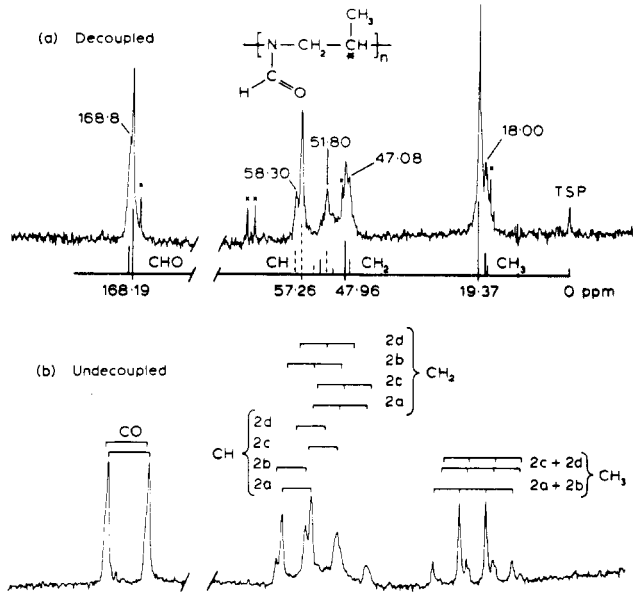
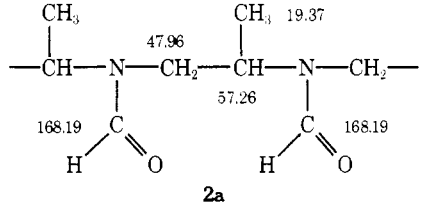
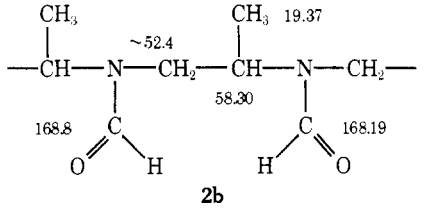


Figure 1. ^{13}C NMR spectrum (22.63 MHz) of isotactic poly(*N*-formylpropylenimine), 10% solution in D_2O. (a) Decoupled from protons by broad-band irradiation, 7750 pulses, pulse width 7 μsec, dwell time 143 μsec, acquisition time 0.7 sec, 4096 points 33°C; (b) undecoupled, 56000 pulses, pulse width 11 μsec, dwell time 143 μsec, acquisition time 1 sec, 4096 points, 60°C. Note that the sharp spikes in (a), marked X, are not present in (b) and are due to low molecular weight impurities. Analysis in terms of four dyad structures **2a–d** is described in the text.

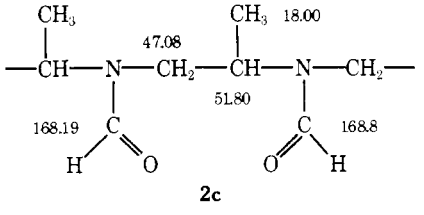
ular weight compounds[5] the most probable structure is assumed to be **2a** in which both carbonyl groups are turned away from the more substituted side of the nitrogen atom. The most intense peak for each group (see abscissa of Figure 1a) is then assigned to structure **2a.**



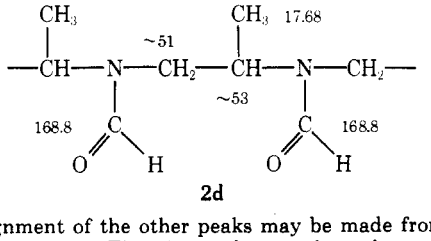
2a



2b



2c



2d

The assignment of the other peaks may be made from the following considerations. First, it may be seen from the carbonyl and methyl resonances that the two *N*-formyl conformations are roughly in the ratio 70:30 so that we may expect the populations of the four dyad structures to be in the order **2a** > **2b** ~ **2c** > **2d** and roughly in the proportions 50:20:20:10, assuming a Bernouilli distribution. Second, carbons which are syn to carbonyl may be expected to be upfield from those which are anti to carbonyl ($\Delta\delta$ = 5 ppm for α carbons, 1–2 ppm for β carbons). This rule is fairly general[8,9] but is not infallible (see below).

Consider, for example, the methine carbon. In going from **2a** to **2b** the conformation of the left-hand formyl group with respect to the central methine changes from β-syn to β-anti so that a downfield shift of 1–2 ppm is expected; the observed shift is 58.30–57.26 = 1.04 ppm. In going from **2a** to **2c** the conformation of the right-hand formyl group with respect to the central methine changes from α-anti to α-syn so that an upfield shift of about 5 ppm is expected; the observed shift is 57.26–51.80 = 5.46 ppm. We may arrive at **2d** either by rotating the right-hand formyl group in **2b,** in which case an upfield shift of ~5 ppm is to be expected (to 53.3 ppm), or by rotating the left-hand formyl group in **2c** in which case a downfield shift of 1–2 ppm is to be expected (to 52.8–53.8 ppm). In fact this peak is so weak that it is lost in the noise of the shoulder of the 51.80-ppm peak.

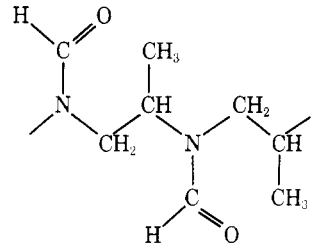
The argument for the methylene carbon is similar to that for the methine carbon and the predicted positions of the four peaks bear a mirror image relationship to those for the methine carbon. The expected peak positions are indicated against the formulae and in Figure 1b. It will be observed that the peak labeled 51.80 ppm in Figure 1a is in fact a composite of two medium peaks from **2b** and **2c** respectively and two very weak peaks, both from **2d.**

For the methyl carbon, in going from **2a** to **2c** the conformation of the right-hand formyl group with respect to the methyl changes from β-anti to β-syn so that an upfield shift of 1–2 ppm is to be expected; the observed shift is 19.37–18.00 = 1.37 ppm. The other formyl group is γ to the methyl and is too far away for its conformation to have much influence.

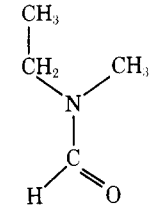
The coupling constants derived from Figure 1b are as follows: J_{CHO} = 197.1, J_{CH} = 138.3, J_{CH_2} ~ 127, J_{CH_3} = 126.5 Hz. These are as expected.[8]

^{13}C-{^1H} NMR Spectrum of Atactic Poly(*N*-formylpropylenimine). Some variations in the appearance of the spectrum of the atactic polymer, compared with that of the isotactic polymer, were noted in the methine/methylene region but the spectrum was too complicated for detailed analysis. The requisite information on tacticity is much more easily obtained from the spectrum of the hydrolysis product[2] (see the introductory section).

^{13}C-{^1H} NMR Spectra of Model Compounds. Two compounds were prepared in order to check the expected shift differences for α and β carbons in the syn and anti conformations. These were *N*-ethyl-*N*-methylformamide (**4**) and *N*-isopropyl-*N*-*n*-propylformamide (**5**). Their relationship to the polymer is indicated below. The spectra are shown in Figures 2 and 3, the assignments



2a



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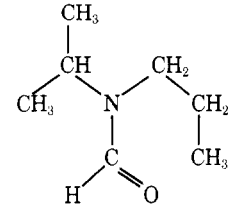

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being made from off-resonance experiments. The shifts and their differences are listed in Table I. The differences in α shifts, expressed as the anti shift minus the syn shift, are as follows. For compound **4**, NCH_2 5.53, NCH_3 −5.13; for compound **5**, NCH 5.20, NCH_2 4.03 ppm. The outward visible sign that the rule for the α

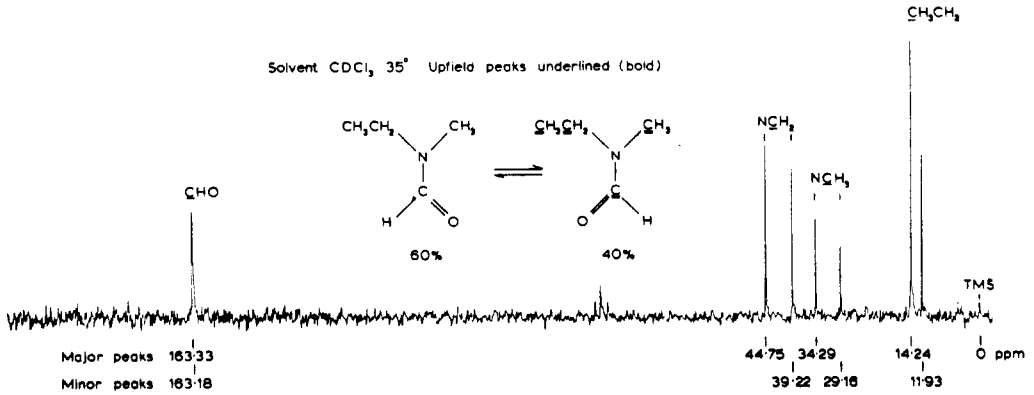


Figure 2. ^{13}C-{^{1}H} NMR spectrum (25.14 MHz) of *N*-ethyl-*N*-methylformamide, 15% solution in $CDCl_3$, 5000 pulses, pulse width 35 μsec, acquisition time 0.8 sec, 8192 points, 35°C.

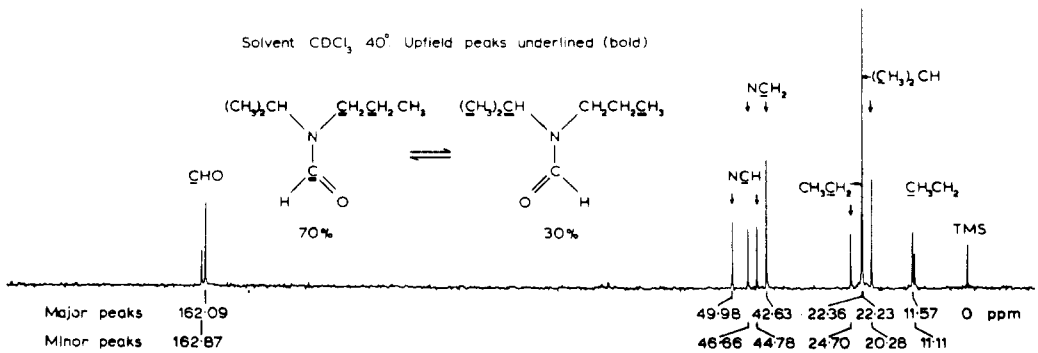
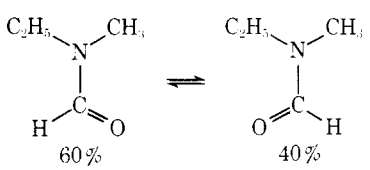
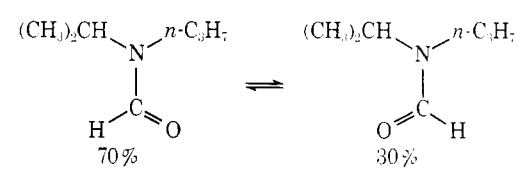


Figure 3. ^{13}C-{^{1}H} NMR spectrum (22.63 MHz) of *N*-isopropyl-*N*-*n*-propylformamide, 15% solution in $CDCl_3$, 1900 pulses, pulse width 11 μsec, dwell time 143 μsec, acquisition time 0.7 sec, 4096 points, 40°C.

Table I
^{13}C Shifts for Two Unsymmetrically Substituted Formamides[a]



C atom	δ_1	δ_2	$\delta_1 - \delta_2$
CH_3CH_2	14.24	11.93	2.31
NCH_3	34.29	29.16	5.13
NCH_2	44.75	39.22	5.53
*C*HO	163.33	163.18	0.15



C atom	δ_1	δ_2	$\delta_1 - \delta_2$
CH_3CH_2	11.57	11.11	0.46
$(CH_3)_2CH$	22.23	20.28	1.95
CH_3CH_2	22.36	24.70	−2.34
NCH_2	42.63	46.66	−4.03
NCH	49.98	44.78	5.20
CHO	162.09	162.87	−0.78

[a] Solvent $CDCl_3$; ppm downfield from TMS. δ_1 and δ_2 refer to the more abundant and less abundant conformers, respectively. Reasons have been given[5] for believing that the more abundant conformer is that in which the more heavily substituted side of the nitrogen is anti (trans) to the carbonyl group.

shifts breaks down for NCH_3 in compound **4** is that the intensity pattern for the four N–*C* lines is not of the "back-to-back" type.[8] Compound **5** is clearly a better model for the polymer in this case. The differences in β shifts, expressed as the anti shift minus the syn shift, are as follows. For compound **4**, CH_3CH_2 2.31; for compound **5**, $(CH_3)_2CH$ 1.95, CH_3CH_2 2.34 ppm. These are somewhat bigger than the values observed in the polymer (1.04, 0.88, 1.37 ppm).

The ^{1}H chemical shifts for these compounds are recorded in the Experimental Section. The shift differences for the protons in the two conformers sometimes have the same sign and sometimes the opposite sign compared with the ^{13}C shifts of the nuclei to which they are attached. The interpretation of such shift differences in terms of magnetic anisotropy of the C=O group and the C=O electric dipole effect is complex and will not be discussed here.

Mutarotation of Isotactic Poly(*N*-formylpropylenimine) and Associated Changes. When polymer **2** is dissolved in water (2.7 g $l.^{-1}$) and quickly transferred to a polarimeter cell at 15°C the optical rotation increases by about 10% over a period of 6 hr. Increasing the temperature speeds up the process and also increases the final specific rotation as shown in Figure 4. The change follows a strictly first-order law, the half-life being 62.1, 29.4, and 15.3 min at 15.0, 20.05, and 25.2°C, respectively, corresponding to an activation energy of 98 kJ mol^{-1} and a frequency factor of 1.3×10^{14} sec^{-1}. The final specific rotation increases continuously as the wavelength is reduced from 589 nm ($[\alpha]^{25}D$ +107°) to 365 nm.

The mutarotation effect is reversible. If the solvent is evaporated in a stream of air and the polymer dried in a vacuum desiccator and then redissolved in water, the optical rotation follows essentially the same path as before. Evidently the relative proportions of formyl groups in the two possible orientations at equilibrium are different in solution from those in the solid and it might

Table II
^{13}C Chemical Shifts for $+X-CH_2-C(CH_3)H+_n$

X	Solvent	Ref compd	CH[a]	CH_2	CH_3	Ref
O	$CCl_4-C_6D_6$ (9:1), 60°	TMS	75.4 *mm* 75.3 *mr/rm* 75.2 *rr*	73.5 *m* 73.1 *r*	17.6	11
S	$CCl_4-C_6D_6$ (9:1), 60°	TMS	41.3 *r* 41.1 *m*	38.35	20.75	12
SO_2	DMSO, 60°	TMS	52.84	48.55 *m* 47.90 *r*	14.04 *m* 13.06 *r*	13
NH	D_2O, 60°	TSP	55.11 *m* 54.9 *r*	53.75	20.08	2
NH_2^+	D_2O, 60°	TSP	55.75 *r* 55.62 *m*	49.82 *rr* 49.65 *mr/rm* 49.45 *mm*	17.39 *m* 17.11 *r*	2
NCHO	D_2O, 60°	TSP	58.30 *aa* 57.26 *sa* ~53 *as* 51.80 *ss*	~52.4 *aa* ~51 *as* 47.96 *sa* 47.08 *ss*	19.37 *a* 18.00 *s*	This paper

[a] Configurational effects: *m* isotactic dyad, *r* syndiotactic dyad. Conformational effects: *a* anti, *s* = syn; *as*, etc., refer to nearest neighbors.

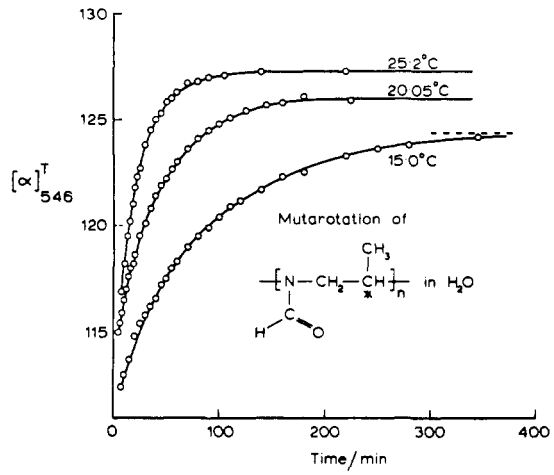


Figure 4. Specific rotation of isotactic poly(*N*-formylpropylenimine) in water (2.7 g $l.^{-1}$) as a function of time at three temperatures. The final value of $[\alpha]$ showed a smooth variation from 0 to 60°C, with no indication of any helix–coil transition in this range.

have been thought therefore that the polymer, being isotactic, would have crystallized on evaporation of the solvent. However, the x-ray diffraction pattern of the polymer prepared in this way indicated that it is completely amorphous. A small amount of crystallinity could be induced by annealing at 100° overnight (x-ray diffraction peak at $2\theta = 21.4°$) but this reached a limit when the polymer was estimated to be less than 10% crystalline. Surprisingly the atactic polymer showed similar behavior. The isotactic polymer also did not give a good fibre pattern when drawn from the melt.

From this evidence one cannot say whether the increase in optical rotation on dissolution in water is associated with an increase or a decrease in the proportion of formyl groups having the direction shown in **2a**, nor can we say whether there is any contribution from changing helicity of the chain. However, assuming that the optical rotation is a linear function of the proportion of formyl groups having a given direction, we can say that the activation energy of 98 kJ mol^{-1} represents the average barrier to rotation of the formyl group between two positions differing only slightly in energy and this is of the right order compared with values for small molecules.

From the fact that there was no change in the ^1H or ^{13}C spectrum of the isotactic polymer with time or temperature it would appear that the optical rotation is in fact a rather sensitive function of the proportion of formyl groups pointing in a given direction. A small rise (0.3%) in specific viscosity was observed over the first 60 min after dissolution of the polymer in water at 25° indicating that the mutarotation is accompanied by a slight expansion of the coiled molecule.

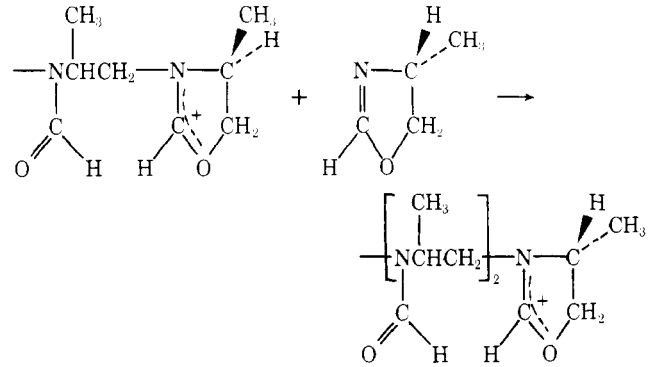
Poly(*N*-benzoylpropylenimine). Preliminary experiments[10] on the optically active and racemic polymers made from 2-phenyl-4-methyl-2-oxazoline show that the $^{13}C-\{^1H\}$ spectra are not noticeably different from each other. However, the main chain carbons give very broad peaks in comparison with poly(*N*-formylpropylenimine), perhaps because of hindrance to rotation in the main chain by the bulkier side groups.

Summary of Chemical Shifts of Analogous Polymers. These are shown in Table II. Two observations may be made. First, the shifts are always in the same order, namely CH > CH_2 > CH_3. The reason for the order CH > CH_2 lies in the fact that whereas the methine carbons can suffer a single gauche interaction with other methine carbons, the methylene carbons can suffer gauche interactions not only with each other but also with the methyl groups. The net effect is that there is a greater upfield (gauche) shift for the methylene than there is for the methine carbons. The second observation is that tacticity effects cause the shifts to vary by up to 0.7 ppm, but there is no consistent line order.

Discussion

Although hindered rotation about the N–CHO bond is well known in small molecules this is the first time that it has been demonstrated in a polymer molecule. Related observations have been made in other polymers, for example in poly(*N*-acetylethylenimine),[14] where there is restricted rotation about the side chain N–$COCH_3$, and in polyproline and its derivatives[15] where there is restricted rotation about the main chain peptide link. However, unlike polyproline it appears that poly(*N*-formylpropylenimine) cannot easily be brought into a single conformation with respect to the peptide linkage, even for isotactic polymer.

It has been postulated[16] that the propagating species in the cationic polymerization of oxazolines is an oxazolinium ion. The propagation step is then written as follows for the addition of an L ion to a D monomer.



To facilitate the transfer of charge in the transition state

and to minimize steric interaction of the methyl groups one may imagine the incoming monomer molecule to approach the oxazolinium ion from above the plane of the five-membered oxazolinium ring, with the plane of the monomer ring roughly parallel to it but twisted slightly clockwise to facilitate the formation of the new CH_2–N bond. However, from the fact that racemic monomer gives atactic polymer it is evident that there is an equally efficient pathway for the addition of L monomer to L ions. In this case we may imagine the same sort of approach of monomer to the ion but with the monomer ring turned over so as to avoid the methyl–methyl interactions. The polymerization of 4-methyl-2-oxazoline initiated by methyl iodide is thought to proceed via a covalent intermediate[17] and it will be interesting to see whether this results in any degree of stereoelectivity, unlike initiation by dimethyl sulfate.

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^{13}C Nuclear Spin–Lattice Relaxation and Nuclear Overhauser Enhancement in Aqueous Solutions of Poly(methacrylic acid)

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ABSTRACT: ^{13}C spin–lattice relaxation times (T_1) and nuclear Overhauser enhancement (NOE) factors have been measured for aqueous solutions of poly(methacrylic acid) (PMA). The T_1's are independent of pH, but the NOE's exhibit a definite pH dependence. Comparison of these data indicates that dipolar relaxation mechanisms dominate, and correlation times are calculated. The correlation times indicate that (1) the extended conformation of the polymer (high pH) is more motionally free than the random coil conformation (low pH); (2) the backbone motions are not in the high-temperature limit for either conformation; (3) segmental motions dominate the relaxation of backbone carbons in the extended conformation, but slower overall molecular tumbling may play a role in the relaxation of these carbons in the random coil conformation; (4) methyl reorientation is rapid enough in either conformation to increase the observed NOE. Linewidth and integrated intensities of ^2H NMR spectra have also been measured for aqueous solutions of perdeuterio-PMA. These results support and contribute to our interpretation of the ^{13}C data. Considerations for ^{13}C relaxation studies of biopolymers are discussed.

The application of ^{13}C NMR to macromolecular systems of biophysical interest is occurring at an accelerating rate. In particular relaxation studies involving Fourier transformed spectra are providing data which are useful in characterizing motional phenomena. To provide some assessment of the problems encountered in such studies a model system is useful as illustrated by Allerhand and Oldfield.[1]

Aqueous solutions of poly(methacrylic acid) (PMA) have several properties which make them attractive as model systems for ^{13}C relaxation studies of biopolymers. Many small proteins or enzymes of current biophysical interest have molecular weights of approximately 15000, and PMA can be easily polymerized from the monomer in this molecular weight range. In addition one of the important properties of biopolymers is the ability to undergo conformational changes. Aqueous PMA solutions are known to exhibit a conformational transition from what is evidently a spherical mass distribution (i.e., random coil) at low pH to an elongated form at high pH.[2] The solution properties of PMA are also favorable with respect to high solubility and availability of an aqueous theta solvent.[3] From the NMR standpoint the ^{13}C spectrum of PMA is known to be considerably simpler than that of biopolymers in the same molecular weight range, and complications arising from stereochemical effects have been analyzed.[4] Furthermore, the methyl groups attached to the PMA backbone provide an analogy to the side groups attached to the backbone of biopolymers. Such side groups may possess independent motional degrees of freedom quite different from those of the backbone. Finally the presence of both methylene and quaternary carbons on the backbone is useful in judging the extent to which nondipolar relaxation mechanisms are significant.

Acrylic polymers have figured prominently in the NMR literature on macromolecular systems with ^{13}C studies receiving considerable recent emphasis in stereochemical

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