

Table I
Spontaneous Polymerization of 2-Vinylpyridine by Concentrated Sulfuric Acid

| $\frac{[\text{H}_2\text{SO}_4]^a}{[2\text{VP}\cdot\text{H}_2\text{SO}_4]}$ | Temp (°C) | Time (Days) | Yield (%) | \bar{M}_n | \bar{M}_w | $\frac{\bar{M}_w}{\bar{M}_n}$ |
|--|--------------|----------------|--------------|-------------|-------------|-------------------------------|
| 2.6 | 0 | 15 | 57 | 1,890,000 | 2,220,000 | 1.16 |
| 2.6 | 25 | 5 | 86 | 1,230,000 | 1,640,000 | 1.33 |

^a Molar ratio of sulfuric acid to 2-vinylpyridinium bisulfate.

Table II
Spontaneous Polymerization of 4-Vinylpyridine by Concentrated Sulfuric Acid

| $\frac{[\text{H}_2\text{SO}_4]^a}{[4\text{VP}\cdot\text{H}_2\text{SO}_4]}$ | Temp (°C) | Time (Days) | Yield (%) | $[\eta]^b$ | \bar{M}_v^c |
|--|--------------|----------------|--------------|------------|---------------|
| 2.6 | 0 | 15 | 71 | 2.28 | 667,000 |
| 2.6 | 25 | 5 | 79 | 1.57 | 384,000 |

^a Molar ratio of sulfuric acid to 4-vinylpyridinium bisulfate.

^b Intrinsic viscosities obtained in ethanol at 25°. ^c J. B. Berkowitz, M. Yamin, and R. M. Fuoss, *J. Polym. Sci.*, **28**, 69 (1958).

mers were also characterized by infrared spectroscopy. It was found that the infrared spectra of the poly(2- and 4-vinylpyridine) samples prepared by spontaneous polymerization in sulfuric acid solution were virtually superimposable with the corresponding polymers prepared by free-radical polymerization. A similar comparison has previously been demonstrated for poly(4-vinylpyridine).¹¹

From the data presented in Tables I and II, it is quite apparent that both monomers are easily polymerized by concentrated sulfuric acid and that high molecular weight products are obtained. For poly(2-vinylpyridine) (Table I), it is noted that the 0° reaction produced a polymer of higher \bar{M}_n and \bar{M}_w than which occurred at 25°. This effect also seems likely for poly(4-vinylpyridine) (Table II) which had a higher \bar{M}_v for the polymer produced at lower

temperatures than that produced at higher temperatures. In addition to these results, it was found that the molecular weight distributions which were obtained for poly(2-vinylpyridine) were relatively narrow. For reactions done with a cationic-type initiator by a simple mixing of reagents in the presence of air, these results are highly unusual.

In the near future we hope to report on further studies of the spontaneous polymerization of 2- and 4-vinylpyridine and their corresponding salts with regard to the effect of acid concentration and acid strength of various strong mineral acids. In addition, the effect of strong acids on the spontaneous polymerization of 2-methyl-5-vinylpyridine, a monomer which previously has been reported to polymerize spontaneously only in the monomeric salt form in aqueous solution, will also be described.

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CORRECTION

"The Poly(hydroxy-L-proline) Ring Conformation Determined by Proton Magnetic Resonance," by D. A. Torchia, Volume 5, Number 5, September-October 1972, page 566.

The last sentence in footnote 22, page 569, should read, "It may be noted that in the two-bonded model of the native collagen molecule. . ."

"Monte Carlo of Long Lattice Chains. Variation of the Excluded Volume," by Z. Alexandrowicz and Y. Accad, Volume 6, Number 2, March-April, page 251.

In this article the authors have overlooked the fact that the first-order perturbation coefficient C becomes apprecia-

bly smaller for very short chain lengths (see, e.g., A. K. Kron and O. B. Ptitsyn, *Vysokomol. Soedin.*, **6** (5), 862 (1964)). Our value $C = 0.23$ fits the relatively short chain lengths N which constitute the main body of the data presented in Figure 1. This value however cannot be applied to very long lattice chains for which $C \rightarrow 0.33$, and the argument of eq 24-25 is incorrect. For the range N from 512 to 4096 described in Figure 2 the proper value would be $C \approx 0.30$. The theoretical lines described in the figure should be therefore displaced to the left, parallel to the $\beta N^{1/2}$ axis, by $\log(0.30/0.23)$. This would improve somewhat the agreement with the experimental data of the slow rising YT and F lines, with a corresponding change to the worse for lines A-K and A.