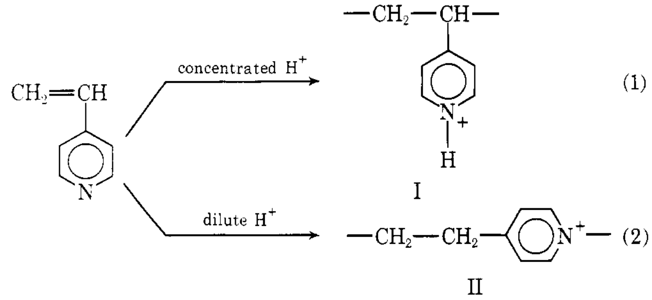
Communications to the Editor

Polymerization of Vinylpyridinium Salts. VI. Spontaneous Polymerization by Concentrated Sulfuric Acid

The utilization of strong protonic acids to effect vinyl polymerizations has been known for many years. In most instances, these cationic initiators lead to the formation of low molecular weight polymers.[1] We wish to report, however, that if either 2- or 4-vinylpyridine is treated with concentrated sulfuric acid, polymerization easily occurs giving a poly(2- or 4-vinylpyridinium salt) of high molecular weight. Furthermore, in the case of 2-vinylpyridine, it also seems likely that the products obtained are of a narrow molecular weight distribution.

Several years ago, Kabanov and Kargin and their coworkers reported that when 4-vinylpyridine is treated with a strong mineral acid, spontaneous polymerization occurred giving the corresponding poly(4-vinylpyridinium salt) (I, reaction 1).[2-4] However, it was later found that in dilute, acidic solutions the spontaneous polymerization reactions instead lead to the formation of ionene polymers of poly(1,4-pyridiniumdiylethylene salts) (II, reaction 2) in which the pyridinium units were in the polymer main chain.[5-13] This process appeared to be a step-growth hydrogen-transfer polymerization which gave low molecular weight ionene polymers.[14] On the other hand, when 4-vinylpyridine was reacted with concentrated, neat sulfuric acid or with concentrated sulfuric acid suspended in an organic solvent, a rapid polymerization occurred which gave, after neutralization, high molecular weight poly(4-vinylpyridine),[7] such as was described by Kabanov *et al.*[2-4]



It was suggested at that time that such a process was most likely a chain-growth polymerization which involved a cationic-type initiation. An initiation mechanism of this nature would contrast with the pyridylethylation initiation step which was found for ionene formation and for the spontaneous polymerization of *N*-alkyl salts of 4-vinylpyridine.[5-10]

Since 2-vinylpyridine is related to its 4-substituted isomer in its chemical reactions, this monomer was also studied by several groups for similar spontaneous polymerizations.[15-19] In reacting the neutral monomer with concentrated mineral acid solutions, it was noted that the resulting poly(2-vinylpyridinium salt) or neutralized product was of high intrinsic viscosity. We have now extend our studies of the spontaneous polymerization of 2- and 4-vinylpyridine by concentrated sulfuric acid solution to include an analysis of the molecular weights which can be obtained. For poly(2-vinylpyridine), gel permeation chromatography (GPC) was utilized to determine $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_w/\bar{M}_n$.[20] The GPC experiments were conducted on a Waters Associates Anaprep gel permeation chromatograph equipped with three Styragel columns (1.5×10^4, 1×10^5, and 1×10^6 Å) using dimethylformamide as eluent. The system was operated at 50° with an injection time of 5 min and a permanent flow rate of 1 ml/min. The elution volumes were measured in 5-ml increments. Unfortunately, the Mark–Houwink constants are not presently available for poly(4-vinylpyridine) under these conditions to allow quantitative GPC analysis, and only viscosity-average molecular weight data were determined.[20] All GPC and intrinsic viscosity measurements were performed on unfractionated, neutralized samples.

In Tables I and II are presented preliminary results on the spontaneous polymerizations of 2- and 4-vinylpyridine, respectively, in concentrated sulfuric acid (18 *M*) at 0 and 25°. These reactions were all done in the presence of air. The cooler reactions were conducted for longer periods of time, *i.e.*, 15 days at 0° as compared to 5 days at 25°, since these polymerization rates appeared somewhat slower. Each reaction employed 1.0 ml of 2- or 4-vinylpyridine (10 mmol) to 2.0 ml of 18 *M* sulfuric acid (36 mmol). The molar ratio of acid to monomer given in both tables is for the excess amount of sulfuric acid relative to 2- or 4-vinylpyridinium bisulfate, since it is assumed that the neutral monomers are instantly protonated on mixing. Polymerization is then considered to occur from the protonated, monomeric salt form. Each polymerization reaction was terminated by dissolving the product in a large quantity of water (*ca.* 500 ml) followed by neutralization with excess sodium carbonate. The resulting neutral poly(2- or 4-vinylpyridine) was filtered, washed throughly with water, and dried *in vacuo*. *Anal.* Calcd for $(C_7H_7N)_x$: C, 79.97; H, 6.71; N, 13.22. Found [for poly(2-vinylpyridine)]: C, 80.36; H, 6.48; N, 13.13. Found [for poly(4-vinylpyridine)]: C, 80.08; H, 6.62; N, 13.31. The neutralized poly-

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(1) See, for example, Robert W. Lenz, "Organic Chemistry of Synthetic High Polymers," Interscience Publishers, New York, N. Y., 1967, Chapter 14 and the references cited therein.

(2) V. A. Kabanov, K. V. Aliev, O. V. Kargina, T. Patrikeeva, and V. A. Kargin, *J. Polym. Sci., Part C*, **16**, 1079 (1967).

(3) V. A. Kabanov, *Pure Appl. Chem.*, **15**, 391 (1967).

(4) V. A. Kabanov, T. I. Patrikeeva, O. V. Kargina, and V. A. Kargin, *J. Polym. Sci., Part C*, **23**, 357 (1968).

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(6) J. C. Salamone, B. Snider, and W. L. Fitch, *Macromolecules*, **3**, 707 (1970).

(7) J. C. Salamone, B. Snider, and W. L. Fitch, *J. Polym. Sci., Part A-1*, **9**, 1493 (1971).

(8) I. Mielke and H. Ringsdorf, *J. Polym. Sci., Part C*, **31**, 107 (1970).

(9) I. Mielke and H. Ringsdorf, *J. Polym. Sci., Part B*, **9**, 1 (1971).

(10) I. Mielke and H. Ringsdorf, *Makromol. Chem.*, **142**, 319 (1971).

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(12) V. A. Kabanov, O. V. Kargina, and V. A. Petroskaya, *Vyskomol. Soedin.*, 13 (2), 348 (1971).

(13) V. A. Kabanov, *XXIIIrd Intern. Congr. Pure Appl. Chem., Boston*, **4**, 425 (1971).

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(16) J. C. Salamone, E. J. Ellis, and S. C. Israel, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 13 (1), 276 (1972).

(17) J. C. Salamone, E. J. Ellis, and S. C. Israel, *J. Polym. Sci., Part B*, **10**, 605 (1972).

(18) H. Ringsdorf and G. Walter, *Makromol. Chem.*, **149**, 295 (1971).

(19) C. Klein and H. G. Elias, *Makromol. Chem.*, **149**, 303 (1971).

(20) N. Ho-Duc, H. Daoust, and A. Gourdenne, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 12 (1), 639 (1971).

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

$[H_2SO_4]^a$/ $[2VP{\cdot}H_2SO_4]$	Temp (°C)	Time (Days)	Yield (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
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

$[H_2SO_4]^a$/ $[4VP{\cdot}H_2SO_4]$	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 appreciably 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 $C \simeq 0.30$. 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.