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The Copolymerization of 2-Methyl-5-Vinylpyridine[1]

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SUMMARY:

The bulk copolymerization reactions of 2-methyl-5-vinylpyridine(MVP) with styrene(St), methyl methacrylate(MMA), methyl acrylate(MA), and acrylonitrile(AN) at 60 °C. have been investigated. The copolymer compositions were estimated by means of electrometric titrations in a nonaqueous solvent mixture.

The monomer reactivity ratios of the following systems were determined: St/MVP $(r_1 = 0.812 \pm 0.005; r_2 = 0.91 \pm 0.02)$, MMA/MVP $(r_1 = 0.46 \pm 0.02; r_2 = 0.61 \pm 0.08)$, MA/MVP $(r_1 = 0.172 \pm 0.007; r_2 = 0.88 \pm 0.10)$, and AN/MVP $(r_1 = 0.116 \pm 0.003; r_2 = 0.27 \pm 0.04)$. Moreover the Q- and e-values were calculated for the methyl vinylpyridine and its behavior in copolymerization is discussed.

ZUSAMMENFASSUNG:

Die Copolymerisation des 2-Methyl-5-vinylpyridins mit Styrol(St), Methacrylsäuremethylester(MMA), Acrylsäuremethylester(MA) und Acrylnitril(AN) bei 60 °C wird untersucht. Zur Bestimmung der Zusammensetzungen der Copolymeren wird die elektrometrische Analyse in der Mischung von nichtwäßrigen Lösungen verwendet.

Die Copolymerisationsparameter folgender Systeme werden bestimmt: St/MVP $(r_1 = 0,812 \pm 0,005; r_2 = 0,91 \pm 0,02)$; MMA/MVP $(r_1 = 0,46 \pm 0,02; r_2 = 0,61 \pm 0,08)$; MA/MVP $(r_1 = 0,172 \pm 0,007; r_2 = 0,88 \pm 0,10)$ und AN/MVP $(r_1 = 0,116 \pm 0,003; r_2 = 0,27 \pm 0,04)$. Ferner werden die Q- und e-Werte für 2-Methyl-5-vinylpyridin berechnet und sein Verhalten bei der Copolymerisation diskutiert.

Introduction

In the previous papers[1,2] the copolymerization reactivities of 2-vinylpyridine, 5-ethyl-2-vinylpyridine, and 4-vinylpyridine with several common vinyl monomers were discussed.

The purpose of this investigation was to provide some information concerning the copolymerization of 2-methyl-5-vinylpyridine, which as a

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[1]) This is the 3rd in a series of papers concerned with the copolymerization of vinylpyridines. For the previous paper in this series, see T. TAMIKADO, J. Polymer Sci., in press.

[2]) Y. IWAKURA, T. TAMIKADO, M. YAMAGUCHI, and K. TAKEI, J. Polymer Sci. **39** (1959) 203.

vinylpyridine having a vinyl group in the β-position of the nucleus might show variations in reaction tendency in comparison with α- and γ-vinyl-pyridines examined before. Difference between 2-methyl-5-vinylpyridine and 5-ethyl-2-vinylpyridine in copolymerization behavior were also interesting since both the monomers were prepared in large scale from the same starting material, 2-methyl-5-ethylpyridine(aldehyde-collidine).

Bulk copolymerizations of 2-methyl-5-vinylpyridine with styrene, methyl methacrylate, methyl acrylate, and acrylonitrile over a wide range of initial monomer concentrations have been carried out in sealed tubes in the presence of 2,2'-azo-bis-isobutyronitrile as an initiator at 60°C.

For determining basic nitrogen in the copolymers, electrometric titration techniques have been developed. The analytical procedures are described in full detail.

The monomer reactivity ratios, r_1 and r_2 have been determined for each pair of the copolymerizations, and, further, the polarity of the double bond in the methyl vinylpyridine has been discussed in connection with the reactivity ratio products.

From the results presented herein, it is concluded that the pyridyl group of 2-methyl-5-vinylpyridine acts as an electron donor for the double bond, as do the pyridyl groups in the 2-, 4-vinylpyridines, and 5-ethyl-2-vinylpyridine investigated before; thus, the 2-methyl-5-vinylpyridine is similar in reactivity to the other vinylpyridines.

Experimental

1. Monomers

The 2-methyl-5-vinylpyridine was a sample obtained from *Takeda Pharmaceutical Industries*, Osaka; it was a commercial grade (99.5% minimum purity) product and was fractionally distilled under reduced pressure just prior to use (b.p. 44°C./4 mm., n_D^{20}-1.5440). The styrene (46°C./20 mm.), methyl methacrylate (43°C./90 mm.), methyl acrylate (80°C.), and acrylonitrile (77°C.) were commercial materials, fractionally distilled before use, and stored under refrigeration. The initiator, 2,2'-azo-bis-isobutyronitrile (m.p. 105°C.) was freshly prepared[3]).

2. Polymerization

Bulk copolymerizations were carried out at 60 ± 0.1°C. on various molar ratios of monomers in sealed tubes in absence of air. The copolymerizations were allowed to proceed to low conversions (mainly $< 5\%$) and the initial copolymers were isolated and purified, as described in previous papers in this series[1,2]). All copolymers were soluble in benzene (acetone used only for acrylonitrile copolymers) and were precipitated with petroleum ether. Results of all experiments reported here are listed in Table III.

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[3]) R. T. ARNOLD, Org. Syntheses, Wiley, New York 1952, Vol. 32, p. 17 and 51.

Analytical Procedures

1. Reagents

Perchloric acid, 0.05 N in glacial acetic acid was prepared, and standardized by titration against potassium biphthalate, essentially as described in the previous paper[1]).

2. Potentiometric titration

A BECKMAN Model H 2 pH meter was used. The electrodes were BECKMAN No. 4990-80 and No. 1170 glass and calomel electrodes. A sample of 0.1−0.2 g. was accurately weighed into a tared 200 ml. beaker and stirred with 70 ml. of a 20 : 80 (volume) mixture of glacial acetic acid and acetonitrile until a clear solution was obtained; then, the glass and calomel electrodes were introduced into the solution. The solution was titrated with standardized 0.05 N perchloric acid under mechanical stirring, the millivolt-scale of the pH meter being used. The millivolts, E were recorded every 0.1 ml. in the vicinity of the expected end-point. The exact end-point was determined by plotting a graph of $\Delta E/\Delta V$ vs. V(ml.), as shown in Figure 1. The solvent blank was negligible.
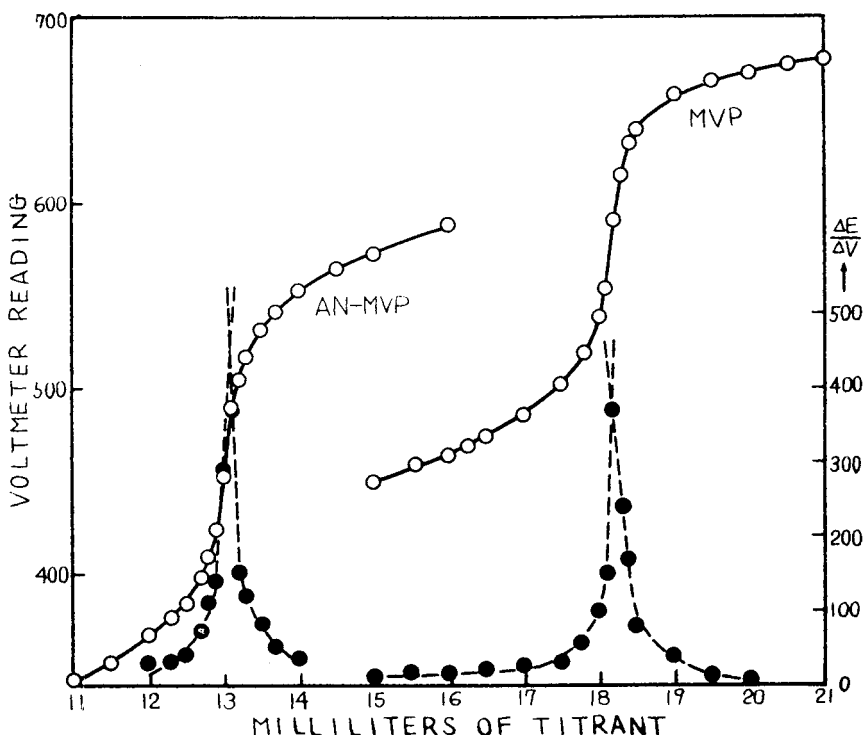

Fig. 1. Potentiometric titration curves for acrylonitrile-methyl vinylpyridine copolymer (AN-MVP) and polymethyl vinylpyridine (MVP).

3. High-frequency titration

The titrimeter was a TŌA-DENPA Model IK-I high-frequency titrimeter. A sample solution was prepared as described under the potentiometric titration.

The solution was placed in the titrimeter, continuously stirred, and titrated with standardized 0.05N perchloric acid. The end-point was easily estimated by sharp break in the titration curve, as represented in Figure 2. and 3.
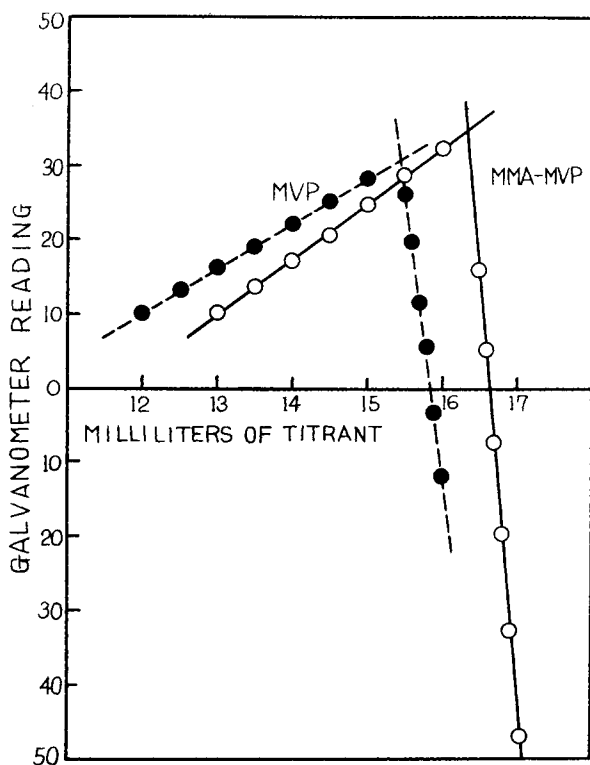

Fig. 2. High-frequency titration curves for methyl methacrylate-methyl vinylpyridine copolymer (MMA–MVP) and polymethyl vinylpyridine.

4. *Visual titration*

A sample solution was prepared as described above. The solution, being added a few drops of the solution of crystal violet indicator in glacial acetic acid, was titrated with standardized 0.05 N perchloric acid under mechanical stirring. The correct shade of the end-point should be previously determined by visual standardization against the primary standard, potassium biphthalate and the color matched in the titration of samples.

Results and Discussion

Analysis of copolymers

In the previous papers of this series[1,2]) it was demonstrated that the compositions of the copolymers composed of vinylpyridines and common vinyl compounds were accurately determined by a visual titration of the

copolymers in a properly selected non-aqueous solvent mixture, with perchloric acid in glacial acetic acid. A mixture of glacial acetic acid and acetonitrile was an excellent solvent for both the copolymers and the
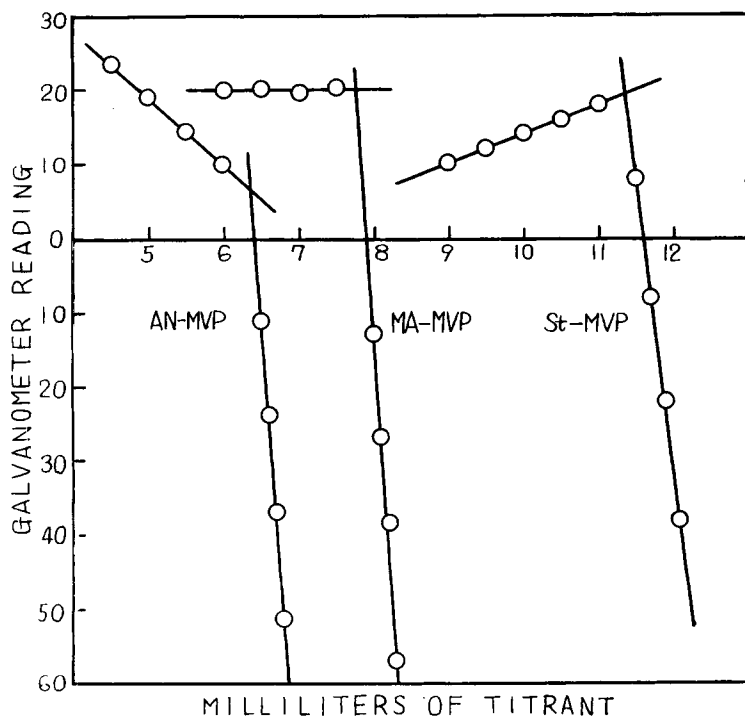

Fig. 3. High-frequency titration curves for acrylonitrile-methyl vinylpyridine (AN—MVP),methyl acrylate-methyl vinylpyridine (MA—MVP), and styrene-methyl vinylpyridine(St—MVP)copolymers.

titration products. The copolymer compositions determined by the titration were in good agreement with the compositions calculated for the nitrogen contents by the DUMAS method with the exception of the acrylonitrile copolymers.

Table I. Comparison of the three titration methods

Comonomer	Pyridine contents in weight-%		
	visual	potentiometric	high-frequency
Styrene*)	53.1	53.5	52.7
Methyl methacrylate*) . . .	46.0	46.2	46.4
Methyl acrylate	44.3	44.3	44.3
Acrylonitrile	41.5	41.6	40.7

*) For the nitrogen contents by the DUMAS analyses 51.6 and 45.9 in wt.-% were respectively calculated.

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For the present work, potentiometric and high-frequency techniques have been tried for the same non-aqueous titration system. Some preliminary estimations on pure poly-2-methyl-5-vinylpyridine by the electrometric methods gave somewhat low pyridine contents (98—99 % in weight compared with the theoretical value of 100 %). Even though the error is unavoidable in case of the copolymer analyses, this order of error will not affect significantly the reactivity ratio values. Data in Table I are shown for comparison of the results determined for the same copolymer samples by the electrometric methods and the visual method. Those agree well with one another.

Figure 1, 2, and 3 represent the typical titration curves for samples of polymethyl vinylpyridine and its copolymers.

The reproducibility of the titration analyses for the same product were satisfactory, as shown in Table II. Figure 4 shows the calibration plots of the data in Table II. The extrapolated straight lines pass accurately through the origine of the graph.

Table II. Reproducibility of titration analyses

Wt. of sample taken (mg.)	$0.05 N-HClO_4$ used (ml.)	Combined vinylpyridine	
		weight (mg.)	weight (%)
Potentiometric titration: Comonomer: Methyl acrylate			
100.7	7.41	44.16	43.9
157.8	11.75	70.04	44.4
206.4	15.30	91.18	44.2
252.7	18.76	111.8	44.2
306.5	22.70	135.3	44.1
		Mean and variance:	44.2 ± 0.2
High-frequency titration: Comonomer: Acrylonitrile			
56.9	3.88	23.15	40.7
75.2	5.08	30.28	40.3
102.1	6.94	41.37	40.5
125.7	8.49	50.58	40.2
150.2	10.14	60.44	40.2
		Mean and variance:	40.4 ± 0.2

Copolymerization reactivity of 2-methyl-5-vinylpyridine

The results of the copolymerization experiments are listed in Table III; from these data the monomer-copolymer composition curves can be drawn. In Figure 5 the curves for copolymerization of 2-methyl-5-vinylpyridine

and 5-ethyl-2-vinylpyridine with methyl methacrylate are shown. The data of 5-ethyl-2-vinylpyridine referred to the previous paper[1]). From
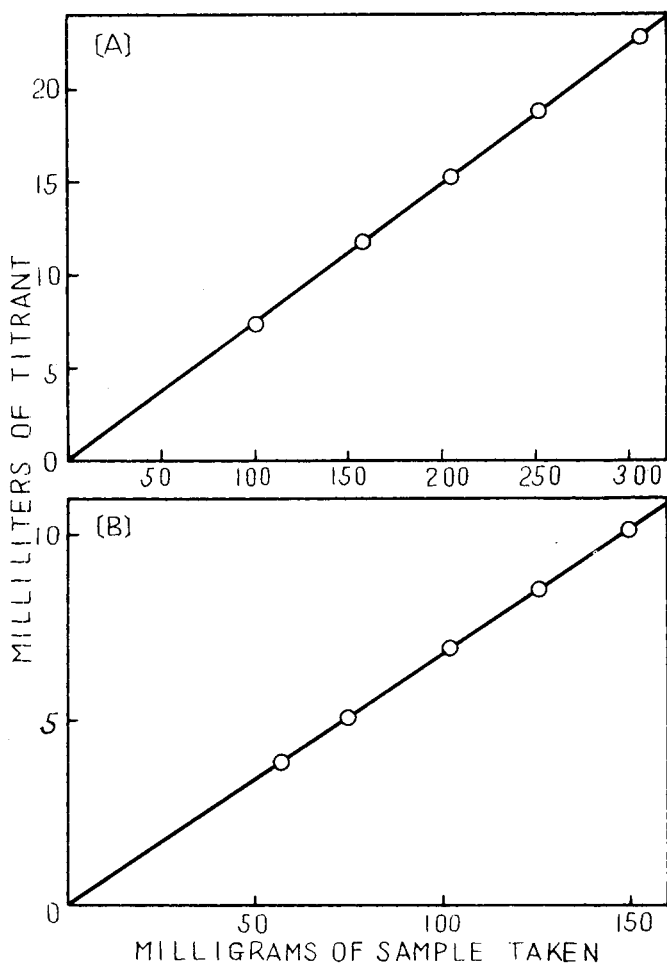

Fig. 4. Calibration plots of potentiometric titration for methyl acrylate-methyl vinylpyridine copolymer(A) and of high-frequency titration for acrylonitrile-methyl vinylpyridine copolymer(B).

the graph it is observed that the curves for methyl and ethyl vinylpyridines lie very close to each other, the same results being observed in the curves for copolymerization with other comonomers, styrene, methyl acrylate, and acrylonitrile.
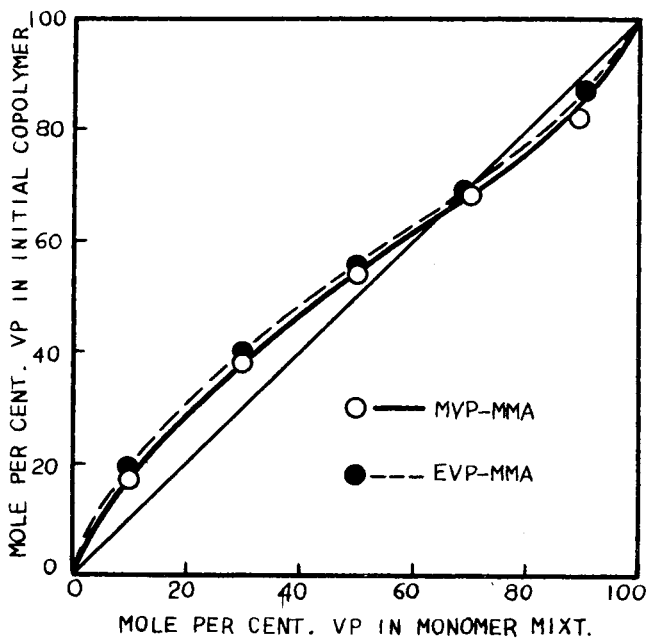
Fig. 5
Comparison of mono-
mer-copolymer compo-
sition curves for me-
thyl   vinylpyridine
(MVP) and ethyl vinyl-
pyridine (EVP)   with
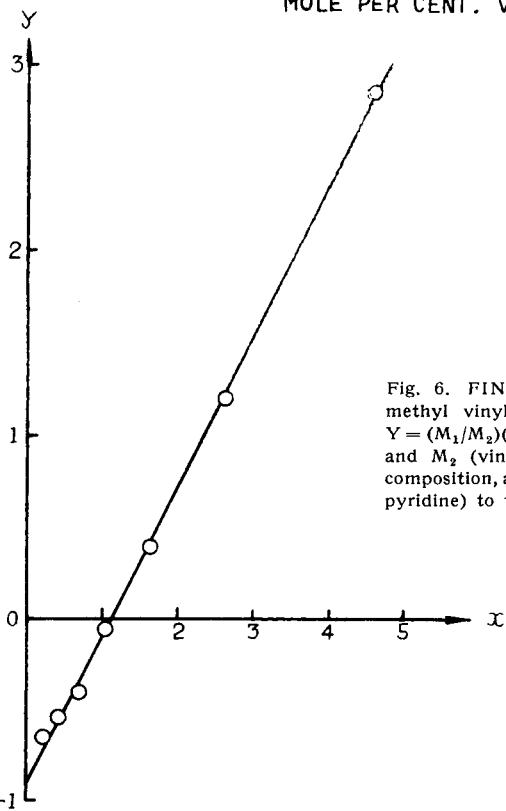methyl   methacrylate
(MMA).

Fig. 6. FINEMAN-ROSS plots for styrene-
methyl vinylpyridine: $X = (M_1/M_2)^2(m_2/m_1)$;
$Y = (M_1/M_2)(1 - m_2/m_1)$, where M_1 (comonomer)
and M_2 (vinylpyridine) refer to the monomer
composition, and m_1 (comonomer) and m_2 (vinyl-
pyridine) to the copolymer composition.

The monomer reactivity ratios, r_1 and r_2 were determined graphically by means of the FINEMAN and ROSS method[4]) as represented in Figure 6, and are given in Table IV.

Table III. Azo-bis-isobutyronitrile-initiated bulk copolymerizations of 2-methyl-5-vinylpyridine(MVP) with common vinyl compounds

MVP in monomer mixture (mole-%)	Analyses of combined MVP (wt.-%)	Calcd. contents of MVP in copolymer (mole-%)
Comonomer: Styrene		
10.01	13.13	11.7
19.98	24.89	22.4
29.98	35.23	32.7
40.01	45.76	42.4
49.93	54.70	51.3
60.24	64.75	61.6
69.18	71.42	68.6
80.13	80.33	78.1
89.97*)	87.64*)	86.1*)
Methyl methacrylate		
10.11	19.97	17.3
29.91	42.27	38.1
50.00	57.83	53.5
70.03	71.83	68.2
89.12	84.27	81.8
Methyl acrylate		
10.04	37.45	30.2
30.22	57.00	48.9
50.14	71.31	64.2
69.86	80.56	75.0
89.57	90.23	87.0
Acrylonitrile		
10.02	53.06	33.5
19.92	62.93	43.0
30.01	65.03	45.3
40.61	68.77	49.5
50.02	71.79	53.1
60.26	74.61	56.7
70.04	79.44	63.2
80.17	83.08	68.6
90.04	88.66	77.7

*) Data omitted in calculating r_1 and r_2 because of large deviation.

4) M. FINEMAN and F. D. ROSS, J. Polymer Sci. 5 (1950) 259.

Assuming $Q = 1.0$ and $e = -0.8$ for styrene, $Q = 0.74$ and $e = 0.4$ for methyl methacrylate, $Q = 0.42$ and $e = 0.6$ for methyl acrylate, and $Q = 0.44$ and $e = 1.2$ for acrylonitrile[5]), the $Q-e$ values for the 2-methyl-5-vinylpyridine in each copolymerization system were calculated; these are given in Table IV.

Table IV. Monomer reactivity ratios and $Q-e$ values in copolymerization of 2-methyl-5-vinylpyridine with common vinyl compounds*)

Comonomer	r_1 Comonomer	r_2 Vinylpyridine	Q	e
Styrene	0.812 ± 0.005	0.91 ± 0.02	0.76	-0.2
Methyl methacrylate	$0.46 \ \pm 0.02$	0.61 ± 0.08	1.04	-0.7
Methyl acrylate . .	0.172 ± 0.007	0.88 ± 0.10	1.05	-0.8
Acrylonitrile . . .	0.116 ± 0.003	0.27 ± 0.04	0.38	-0.7

*) The estimates of variances were calculated according to BENNETT and FRANKLIN[6]).

MAYO, LEWIS, and WALLING[7]) arranged common vinyl compounds in order of their increasing tendency to alternate with styrene, as measured by the decreasing products of monomer reactivity ratios; the vinyl compounds were then seen to be arranged approximately in order of the polarity of the double bonds. In Table V, all the vinylpyridines concerned with the author's papers[1,2]) are listed after the manner of MAYO et al.

Table V. Monomer reactivity ratio products for copolymerization of vinylpyridines

Styrene						
0.95	5-Ethyl-2-vinylpyridine					
0.74		2-Methyl-5-vinylpyridine				
0.50			2-Vinylpyridine			
0.38				4-Vinylpyridine		
0.24*)	0.27	0.28	0.34	0.45	Methyl methacrylate	
0.14*)	0.21	0.15	0.27	0.37		Methyl acrylate
0.02*)	0.01	0.03	0.05	0.05	0.24*)	1.3**) Acrylonitrile

*) Data of LEWIS et al.[8,9]).   **) Data of the author[10]).

[5]) C. C. PRICE, J. Polymer Sci. 3 (1948) 772.
[6]) C. A. BENNETT and N. L. FRANKLIN, Statistical Analysis in Chemistry and the Chemical Industry, Wiley, New York 1954, p. 227 and 230.
[7]) F. R. MAYO, F. M. LEWIS, and C. WALLING, J. Amer. chem. Soc. 70 (1948) 1529.
[8]) F. M. LEWIS, F. R. MAYO, and W. F. HULSE, J. Amer. chem. Soc. 67 (1945) 1701.
[9]) F. M. LEWIS, C. WALLING, W. CUMMINGS, E. R. BRIGGS, and F. R. MAYO, J. Amer. chem. Soc. 70 (1948) 1519.
[10]) T. TAMIKADO and Y. IWAKURA, J. Polymer Sci. 36 (1959) 529.

The double bond of 5-ethyl-2-vinylpyridine seems to be the most negative, followed in turn by those of 2-methyl-5-vinylpyridine, 2-vinylpyridine, and 4-vinylpyridine.

In the pyridine molecule, it is believed that the carbon atoms in the 2- and 4-position of the nucleus are positively charged by a contribution of resonance structures(I)[11]).

(I)   (II)
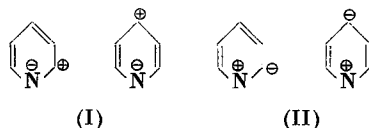
The experimental results for the copolymerization of vinylpyridines, however, have been somewhat anomalous: in the previous papers negative polarization of the double bond in the 2- or 4-position was demonstrated; the present results described herein before are also inconsistent with the resonance structures(I).

From these considerations it seems reasonable to assume that an appreciable contribution by the structures(II) is submitted for the molecules of vinylpyridines. The negative polarization of the double bond in the 3-position of the methyl vinylpyridine may be interpreted as being due to the electron-donating effect of the negative charges on the carbon atoms in the 2- and 4-positions, and the presence of methyl group at the para position to the double bond.

[11]) L. F. Fieser and M. Fieser, Textbook of Org. Chemistry, Japanese ed., Maruzen, Tokyo 1952, p. 604.