

Copolymerization of Acrylonitrile and Vinyl Pyridine

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INTRODUCTION

The copolymerization reactions of vinyl pyridine have been studied by several groups of workers in recent years,¹⁻⁶ but reliable values of reactivity ratios for the system vinyl pyridine-acrylonitrile have not yet been reported. The present investigation has been directed primarily toward determining reactivity ratios in copolymerization reactions for 2-vinyl pyridine, 4-vinyl pyridine, and 5-ethyl-2-vinyl pyridine with acrylonitrile. Since elementary analyses of nitrogen for the copolymers of acrylonitrile and vinyl pyridine (by both the Kjeldahl and the Dumas methods) did not prove consistently successful, it was thought advisable to find a precise method determining the composition of the copolymers, as the first step of the investigation. The titration method was found satisfactory for the copolymer in nonaqueous solvents, with perchloric acid in glacial acetic acid. Reactivity ratios for the vinyl pyridine copolymerizations with acrylonitrile are presented here. The $Q-e$ values have been calculated for the individual monomers from the reactivity ratios obtained. The data reported herein has indicated that the three kinds of vinyl pyridine have reactivity similar to that of styrene in copolymerization reactions with acrylonitrile.

EXPERIMENTAL

Materials

The 2-vinylpyridine, 4-vinylpyridine, and 5-ethyl-2-vinyl pyridine were samples obtained from Yuki-Gōsei Kōgyo Co.; they were a commercial grade of about 97% purity which were fractionally distilled under reduced pressure just prior to use. The fractions used were: 2-vinyl pyridine, b. p. 71°C. at 30 mm., n_D^{20} 1.5509, d_{20}^{20} 0.9746; 4-vinyl pyridine, b. p. 65°C. at 15 mm., n_D^{20} 1.5499, d_{20}^{20} 0.9880; 5-ethyl-2-vinyl pyridine, b. p. 97°C. at 18 mm., n_D^{20} 1.5380, d_{20}^{20} 0.9449. The acrylonitrile was commercial material, fractionally distilled before use and stored in a refrigerator (b. p. 77°C., n_D^{25} 1.3888). The initiator, α,α' -azobisisobutyronitrile was prepared according to the manner of Overberger et al.⁷

Copolymerization Technique

Copolymerization was carried out in bulk with α, α' -azobisisobutyronitrile as an initiator at 60 °C. The conversion was kept below 10% and a wide range of monomer mixture was used in order to minimize the errors arising from changes in the monomer composition. The monomer mixtures, comprising a total of 20 g. were prepared by adding appropriate weights of acrylonitrile, vinyl pyridine, and 0.05 g. of α, α' -azobisisobutyronitrile to 50-ml. Pyrex glass tubes. The compositions employed are given in Table II. Air above the monomers was swept out with oxygen-free nitrogen under cooling at -60°C . prior to sealing the tubes. The tubes were allowed to come to room temperature and placed in a thermostat held to $60 \pm 0.1^{\circ}\text{C}$. After about one hour, the slightly viscous reaction mixture was poured into 300 ml. of stirred nonsolvent at room temperature. The precipitated polymer was purified at least three times by reprecipitations from a solvent system into a nonsolvent system. The solvents and nonsolvent used are given in Table II. After the polymer was dried in an vacuum oven held to 60°C . at 1 mm. for seventy-two hours, the amount of combined vinylpyridine in the initial copolymer was determined by duplicate titrations.

ANALYSIS

The method of analysis used for determining the combined vinylpyridine in the copolymers was the same in principles as Fritz' method of titration for organic bases in nonaqueous solvents⁸ however, it had to be modified for application to the copolymer system investigated.

Apparatus used for titrations consisted of a 25-ml. buret, a 1-l stock bottle for the standardized solution, and a 300-ml. Erlenmeyer flask as a titration vessel provided with a mechanical stirrer sealed with mercury; the parts were connected to each other by glass joints in such a way that contamination by humidity could be eliminated. In our experiment, a ready-made apparatus for the Karl Fischer method of aquametry could be conveniently used.

Roughly an hour's stirring was required to dissolve a sample of 0.1–0.2 g. in 100 ml. of the solvent (20:80 glacial acetic acid–acetonitrile mixture). A few drops of methyl violet (in glacial acetic acid) indicator were added, and the solution was very slowly titrated, with 0.1 *N* perchloric acid in acetic acid under stirring, to a green color. Rapid titration brought about the precipitation of the partly neutralized polymer on the wall of the titration vessel and the stirrer—a result opposite to what was desired. The perchloric acid solution was prepared by dissolving 9 ml. of 70% perchloric acid in 1 l. of glacial acetic acid. The water was removed by adding about 18 ml./l. of acetic anhydride and allowing the solution to stand overnight. This solution was then standardized against sodium carbonate in glacial acetic acid, with methyl violet as indicator. The presence of small amounts of water in the solvents used caused a very poor

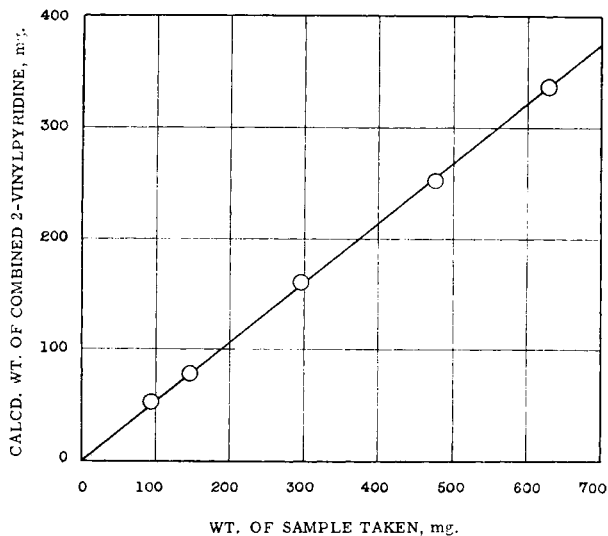


Fig. 1. Calibration plot of titration analysis for acrylonitrile-2-vinyl pyridine copolymer.

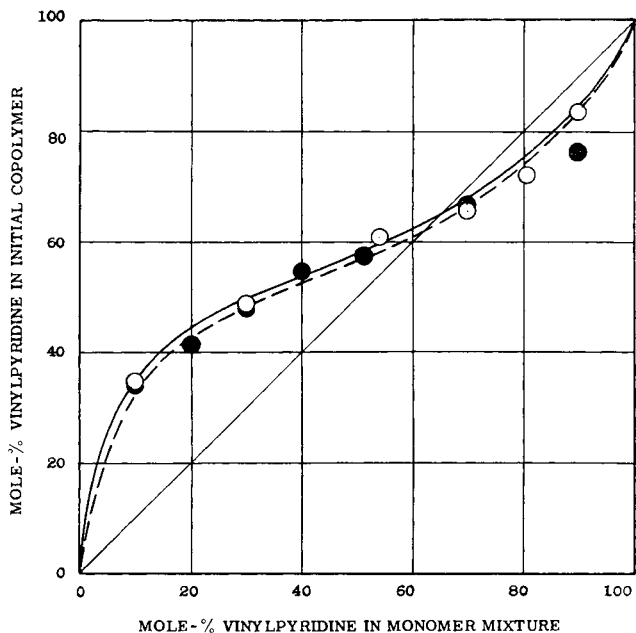


Fig. 2. Monomer-copolymer composition curves for acrylonitrile-2-vinyl pyridine (O, —) and acrylonitrile-4-vinyl pyridine (●, - -).

end point. Appropriate amounts of acetic anhydride and potassium permanganate were added to the glacial acetic acid and refluxed prior to fractional distillation. The acetonitrile was dehydrated with anhydrous phosphoric acid prior to fractional distillation. The concentration range of 0.1–0.6 g. of the copolymers in 100 ml. of the mixed solvents was found

TABLE I
Titration of Vinyl Pyridine Homopolymer and Copolymer in
Nonaqueous Solvent with Perchloric Acid in Glacial Acetic Acid

Wt. of sample taken, mg.	N/10 HClO ₄ used, ml.	Wt. of combined vinyl pyridine, mg.	Wt.-% of combined vinyl pyridine
2-Vinylpyridine homopolymer ^a			
83.2	7.85	82.5	99.2
4-Vinyl pyridine			
203.6	19.40	203.9	100.1
5-Ethyl-2-Vinyl pyridine			
123.5	9.27	123.4	99.9
2-Vinyl pyridine copolymer with acrylonitrile			
93.6	4.84	50.9	54.38 ^b
145.0	7.27	76.4	52.69
296.4	15.12	158.9	53.61
476.8	23.91	251.3	52.71
629.9	32.06	336.9	53.48

^a N % by Dumas method: 2-VP, found 13.0, calcd. 13.3; 4-VP, found 13.0, calcd. 13.3; 5-ethyl-2,-VP, found 10.8, calcd. 10.5.

^b The estimate of variance is ± 0.70 .

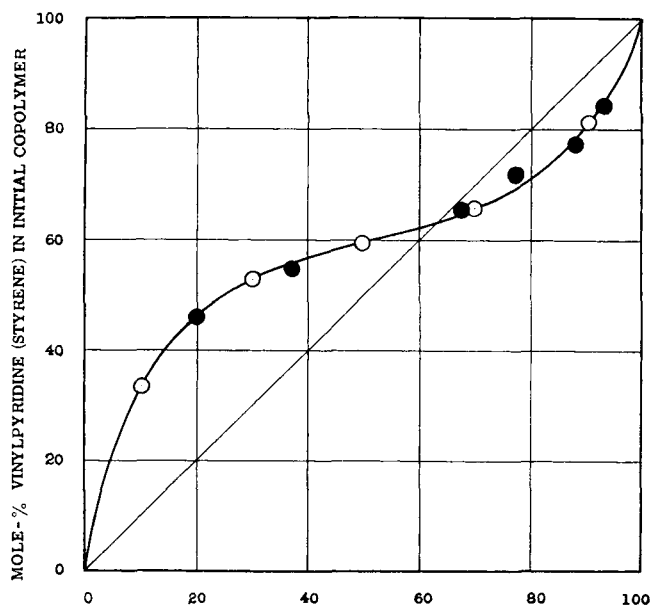


Fig. 3. Monomer-copolymer composition curve for acrylonitrile-5-ethyl-2-vinyl pyridine (O, —) and acrylonitrile-styrene (●). Abscissa: Mole-% vinyl pyridine (styrene) in monomer mixture.

suitable for analyses. Figure 1 shows the calibration curve for the copolymer of acrylonitrile and 2-vinyl pyridine in this region. The curve in Figure 1 was drawn from the data in Table 1, which also contains the results for the homopolymers of 2-, 4-vinyl pyridine, and 5-ethyl-2-vinyl pyridine.

RESULTS

The results of the investigation are summarized in Table II from which the monomer-copolymer composition curves, Figure 2 and Figure 3, for the three series of experiments, were drawn. In determining the monomer reactivity ratios for acrylonitrile and vinyl pyridines, the Fineman and Ross method⁹ was used, since only products obtained at low conversions

TABLE II
Azobisnitrile-Catalyzed Copolymerization of Vinyl Pyridines
with Acrylonitrile at 60°C.^c

Mole-% of vinylpyridines in monomer mixt.	Analyses of combined vinyl pyridine wt.-%		Calcd. mole-% of vinyl pyridine in copolymer ^a
2-Vinyl pyridine			
10.46	51.89	50.94	34.9
29.88	65.40	65.37	48.8
54.04	75.43	75.31	60.7
69.76	78.79	78.91	65.3
80.64	83.72	83.58	72.1
90.02	90.80	90.77	83.3
4-Vinyl pyridine			
9.98	50.15	51.50	34.3
19.96	57.83	58.84	41.4
30.09	64.79	64.03	47.8
40.07	69.93	70.54	54.4
51.33	73.06	72.16	57.2
70.07	79.92	79.01	66.2
90.10 ^b	86.58	85.93	76.0
5-Ethyl-2-vinyl pyridine			
10.00 ^b	55.52	56.18	33.5
30.04	73.22	74.26	52.8
49.86	78.84	78.94	59.8
69.95	82.84	83.67	66.5
90.29	91.41	91.96	81.5

^a The estimates of variances in the mole-% determination were calculated in the systems 2-vinyl pyridine copolymers (± 0.3 based on 6 degrees of freedom), 4-vinyl pyridine (± 0.7 based on 7 degrees of freedom), and 5-ethyl-2-vinyl pyridine (± 0.7 based on 5 degrees of freedom).¹²

^b Data omitted in calculating r_1 and r_2 for its large deviation.

^c The reprecipitation solvent was benzene except that the 4-vinyl pyridine copolymers were dissolved in chloroform and petroleum ether was used as nonsolvent throughout the three series.

were analyzed. From Figure 2 it will be seen that the monomer-copolymer composition curves for the two series of 2-vinyl pyridine and 4-vinyl pyridine are identical within the error of analysis. From Figure 3 it will be also observed that the monomer-copolymer composition curve for 5-ethyl-2-vinyl pyridine lies close to those for 2- and 4-vinyl pyridine. The copolymerization data for styrene-acrylonitrile has been given by R. G. Fordyce and E. C. Chapin.¹⁰ Their result has been also plotted for comparison in Figure 3, in which the experimental points for vinyl pyridine copolymerization and those for styrene fall on almost exactly the same curve. The reactivity ratios obtained are given in Table III. Assuming

TABLE III
Monomer Reactivity Ratios and Q - e Values in Copolymerizations
of Vinyl Pyridines with Acrylonitrile

	r_1 (nitrile)	r_2 (pyridine)	Q	e
2-Vinyl pyridine	0.113 \pm 0.002	0.47 \pm 0.03	0.50	-0.5
4-Vinyl pyridine	0.113 \pm 0.005	0.41 \pm 0.09	0.49	-0.6
5-Ethyl-2-vinyl pyridine	0.02 \pm 0.02	0.43 \pm 0.05	1.6	-1.0

$e = 1.2$ and $Q = 0.44$ ¹¹ for acrylonitrile, we have calculated the Q - e values for the individual vinyl pyridine. These are also given in Table III. For 2-vinylpyridine, Price¹¹ has quoted $Q = 1.07$ and $e = -0.1$ from copolymerization with styrene, and $Q = 1.09$ and $e = -0.6$ from methyl methacrylate copolymerization. The variation in Q - e values with the kinds of co-monomer is quite great, but the values may be used in the present instance as a basis for comparison with these experimental results.

On the basis of these data on copolymerization with acrylonitrile, it seems reasonable to conclude that no evidence has been found to emphasize the different reactivities between 2- and 4-vinyl pyridine. The reactivity of 5-ethyl-2-vinyl pyridine is quite identical with that of styrene and similar to those of above two pyridines, but some difference caused by the presence of ethyl group has been detected.

We are indebted to Assistant Professor K. Kojima of the Tokyo Medical and Dental University for a grant of the use of the analytical apparatus, and to Yūki-Gōsei Kōgyō Co., Tokyo, for the vinylpyridine monomers.

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Synopsis

The copolymerization of acrylonitrile with 5-ethyl-2-vinyl pyridine, 2-vinyl pyridine, and 4-vinyl pyridine has been investigated. The copolymer compositions have been determined by the titration of the copolymers in nonaqueous solvents with perchloric acid in glacial acetic acid, using methyl violet as an indicator. The reactivity ratios r_1 and r_2 , respectively, have been determined in the three systems: AN/5-ethyl-2-VP, (0.02 ± 0.02 and 0.43 ± 0.05); AN/2-VP, (0.113 ± 0.002 and 0.47 ± 0.03); and AN/4-VP, (0.113 ± 0.005 and 0.41 ± 0.09). The $Q-e$ values for individual monomers have been calculated and compared with each other. The data obtained present no evidence for different reactivities of 2- and 4-VP. The data shows that 5-ethyl-2-VP has reactivity similar to those of above two monomers, but some difference caused by its ethyl group has been found. It has been also shown that the reactivity of 5-ethyl-2-VP is quite identical with that of styrene.

Résumé

La copolymérisation du nitrile acrylique avec les 5-éthyl-2-vinyl et 4-vinylpyridines a été étudiée. La composition des copolymères a été déterminée par titration en milieu non-aqueux au moyen d'acide perchlorique dissous dans l'acide acétique anhydre, en présence de violet de méthyle comme indicateur. Les rapports de réactivité ont été déterminés pour les nitrile acrylique/5-éthyl-2-vinylpyridine ($r_1 = 0.02 \pm 0.02$ et $r_2 = 0.43 \pm 0.05$), et nitrile acrylique/2-vinylpyridine ($r_1 = 0.113 \pm 0.002$ et $r_2 = 0.47 \pm 0.03$) et la nitrile acrylique/4-vinylpyridine ($r_1 = 0.113 \pm 0.005$ et $r_2 = 0.41 \pm 0.09$). Les valeurs de $Q-e$ pour les monomères individuels ont été calculées et comparées entre eux. On a trouvé qu'il n'y a aucune preuve d'une différence de réactivité entre les 2- et 4-vinylpyridines, et que la 5-éthyl-2-vinylpyridine possède une réactivité similaire à celles des deux monomères, bien que la groupe éthylique entraîne quelque différence. La réactivité de la 5-éthyl-2-vinylpyridine est identique avec celle du styrène.

Zusammenfassung

Die Copolymerisation von Acrylnitril sowohl mit 5-Äthyl-2-Vinylpyridin als auch mit 2- und 4-Vinylpyridin wurde untersucht. Zur Bestimmung der Copolymer-Zusammensetzungen wurden die Copolymeren in nicht-wässriger Lösung mit n/10-Lösung von Überchlorsäure in Eisessig unter Verwendung von Methylviolett als Indikator titriert. Folgende Werte für die Reaktivitätsverhältnisse bei der Copolymerisation mit Acrylnitril wurden erhalten: 5-Äthyl-2-Vinylpyridin $r_1 = 0,02 \pm 0,02$ und $r_2 = 0,43 \pm 0,05$; 2-Vinylpyridin $r_1 = 0,113 \pm 0,002$ und $r_2 = 0,47 \pm 0,03$; 4-Vinylpyridin $r_1 = 0,113 \pm 0,005$ und $r_2 = 0,41 \pm 0,09$. Die Q - und e -Werte für die Monomeren wurden berechnet und mit einander verglichen. Die experimentellen Resultate zeigten, dass 2-Vinylpyridin und 4-Vinylpyridin ganz gleiche Reaktivitäten für Copolymerisation mit Acrylnitril hatten, und dass die Reaktivität von 5-Äthyl-2-Vinylpyridin der des 2- und 4-Vinylpyridins zwar ähnlich war, aber doch ein von der Äthylgruppe herestammender Unterschied auftrat. Weiters wurde gefunden, dass auch 5-Äthyl-2-Vinylpyridin und Styrol ganz gleiche Reaktivitäten hatten.

Received October 24, 1958