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Preparation, Polymerization, and Copolymerization of *N*-Vinyl Phthalimidine[1]

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The preparation, polymerization, and copolymerization of *N*-vinyl phthalimidine were investigated. The monomer was prepared by the dehydrochlorination of *N*-(β-chloroethyl) phthalimidine. Polymerization was carried out in the presence of radical or cationic initiators in bulk and in solution. It was found that polymerizability with cationic initiators was larger than that with radical ones. The resulting polymers had a softening point in the range of 160—180 °C, the reduced viscosities being small. Copolymerization with acrylonitrile and styrene was carried out in dimethylformamide and benzene by radical initiators. The monomer reactivity ratios and Alfrey-Price Q and e values calculated from the copolymerization data of the monomer (M_1) and styrene (M_2) were $r_1=0.05$, $r_2=7.4$, $Q_1=0.30$, and $e_1=-1.80$. Values for *N*-vinyl pyrrolidone (M_1) were likewise determined for the sake of comparison, and found to be $r_1=0.02$, $r_2=12.0$, $Q_1=0.22$, and $e_1=-1.99$.

The polymerization and copolymerization of *N*-vinyl imides such as *N*-vinyl phthalimide and *N*-vinyl succinimide by radical process have been reported by many workers. In previous papers,[2–4] the author reported on the polymerization and graft-copolymerization by γ-ray radiation, and the copolymerization by radical initiators.

N-Vinyl phthalimidine has been synthesized by Ooki,[5] and Kato and Yoshida,[6] but its polymerization and copolymerization have hardly been discussed at all.

In this paper the author reports a new preparative method of *N*-vinyl phthalimidine, and its polymerization and copolymerization.

Experimental

N-*Vinyl Phthalimidine.* The monomer was prepared *via* the dehydrochlorination of *N*-(β-chloroethyl) phthalimidine obtained after the condensation of monoethanolamine with phthalide and the following chlorination.

N-*(β-Hydroxyethyl) Phthalimidine*: To 16.0 g (0.26 mol) of monoethanolamine was added 35.0 g (0.26 mol) of phthalide, and the mixture was heated at 190—200 °C for about 6 hr to remove the water formed by condensation reaction. The amount of water removed was approximately 4 ml. The reaction product crystallized completely at room temperature. Recrystallization from benzene yielded 41.4 g (90%) of *N*-(β-hydroxyethyl) phthalimidine as colorless plates with a melting point of 119—120 °C (lit. mp 113—114 °C[6]).

Found: C, 67.48; H, 6.06; N, 7.81%; mol wt (Rast), 181. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.91%; mol wt, 177.2.

N-*(β-Chloroethyl) Phthalimidine*: To a solution containing 23.0 g (0.13 mol) of *N*-(β-hydroxyethyl) phthalimidine in 100 ml of benzene was added, drop by drop, 18.0 g (0.15 mol) of thionyl chloride with stirring at 5—10 °C for 30 min. After addition was completed, stirring was continued for 6 hr at room temperature. The solvent and volatile parts were removed as much as possible under reduced pressure, and the remaining part then began to crystallize. The crude crystals were also dissolved in a small amount of fresh benzene and the solution was poured into a large amount of petroleum benzine (bp 50—90 °C) to obtain 24.2 g (95%) of the crystals with a melting point of 78—82 °C. Recrystallization from petroleum benzine gave *N*-(β-chloroethyl) phthalimidine as colorless plates, mp 81—82 °C.

Found: C, 61.89; H, 5.06; N, 7.29%; mol wt (Rast), 199. Calcd for $C_{10}H_{10}NOCl$: C, 61.39; H, 5.15; N, 7.16%; mol wt, 195.7.

N-*Vinyl Phthalimidine*: To a solution containing 19.6 g (0.10 mol) of *N*-(β-chloroethyl) phthalimidine in 150 ml of benzene was added 10 g (0.18 mol) of potassium hydroxide pellets. The mixture was refluxed for 15 hr, while the liberated water was collected in a receiver. The reaction product was filtered to remove potassium chloride. The filtrate was concentrated under reduced pressure, and the remaining part then began to crystallize. Recrystallization from petroleum benzine gave 11.0 g (69%) of *N*-vinyl phthalimidine as colorless needles with a melting point of 66—67 °C (lit. mp 66—67 °C,[5] mp 66.5 °C[6]); its infrared absorption bands were at 1680 (phthalimidine carbonyl), 1610 (benzene ring), 1630, 1420, 975, 935 (vinyl), and 730 cm^{-1} (*o*-disubstituted benzene) (Fig. 1).

The ultraviolet absorption maxima in ethanol were: 228.5 (ε, 10900), 236 (8390), 276 (10000), and 280 nm (9860).

Found: C, 75.52; H, 5.52; N, 8.83%; mol wt (Rast), 164. Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80%; mol wt, 159.2.

Other Materials. Commercial vinyl monomers such as acrylonitrile, styrene, and *N*-vinyl pyrrolidone were purified in the usual manners prior to use. Commercial initiators, azobisisobutylonitrile, benzoyl peroxide, boron trifluoride etherate, and stannic chloride were purified by reprecipitation, recrystallization, and distillation. Solvents, benzene and dimethylformamide were also purified according to the usual methods.

Polymerization Procedure. For polymerization and copolymerization in the presence of initiator, the required amounts of monomers, initiator, and solvent were weighed into a glass ampule, sealed under nitrogen atmosphere except for the cationic polymerization. In the radiation-induced polymerization, the ampule was irradiated by a cobalt-60 source for a given time.

After polymerization, the contents in the ampule were poured into a large amount of diethylether and methanol to precipitate the homopolymer and copolymer, respectively. The resulting polymers were filtered, washed with diethylether or methanol, dried under reduced pressure and weighed.

Elemental Analyses. The copolymers were purified by repeated precipitations. The copolymer compositions were determined by carbon and nitrogen analyses with a Yanagimoto C. H. N. Corder, Model MT-1.

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1) Paper presented at the 20th Annual Meeting of the Society of Polymer Science, Japan, Tokyo, May 25, 1971.

2) K. Murata, *J. Polym. Sci., A*-1, **5**, 2942 (1967).

3) K. Murata, This Bulletin, **40**, 2187 (1967).

4) K. Murata and A. Terada, This Bulletin, **39**, 2494 (1966).

5) S. Ooki, *Yakugaku Zasshi*, **70**, 102 (1950).

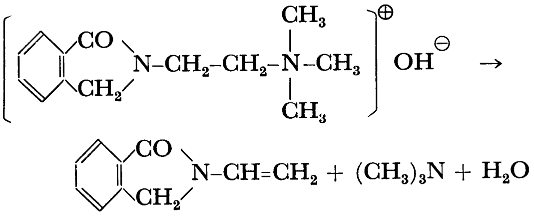
6) K. Kato and M. Yoshida, *Nippon Kagaku Zasshi*, **87**, 1100 (1966).

Viscosity Measurement. The reduced viscosity of the resulting polymer was determined at 30±0.01 °C as a 0.50% solution in dimethylformamide with an Ostwald viscometer.

Infrared Absorption Spectra. The infrared absorption spectra were obtained with a JASCO Infrared spectrophotometer, Model IR–G.

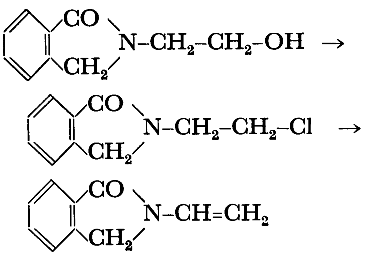
Results and Discussion

Preparation of N-*Vinyl Phthalimidine.* *N*-Vinyl phthalimidine was prepared by the olefin decomposition of the corresponding quaternary ammonium hydroxide by Ooki[5] for the first time with only a 43% yield. Kato and Yoshida[6] obtained the same monomer by the pyrolysis of *N*-(*β*-acetoxyethyl) phthalimidine, but the method when traced by the author gave a very poor yield.



A new method was worked out to improve the yield. The monomer was prepared by the dehydrochlorination of *N*-(*β*-chloroethyl) phthalimidine.

The chlorination reaction of *N*-(*β*-hydroxyethyl) phthalimidine with thionyl chloride in benzene afforded *N*-(*β*-chloroethyl) phthalimidine as colorless plates with a 119—120 °C melting point in a good yield. The dehydrochlorination reaction of the chloride was carried out by the use of potassium hydroxide pellets in benzene to give *N*-vinyl phthalimidine as colorless needles with a melting point of 66—67 °C in a 69% yield. The infrared absorption spectrum was shown in Fig. 1.



Polymerization of N-*Vinyl Phthalimidine.* This was carried out in bulk or solution state. Initiators such as azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), boron trifluoride etherate, and stannic chloride, and also *γ*-rays from a cobalt-60 source were used. The results are shown in Table 1. We see that the polymerizability by AIBN is larger than that by BPO, the tendency being observed also in the polymerization of *N*-vinyl pyrrolidone. The *N*-vinyl phthalimidine was similarly polymerized by irradiation of *γ*-rays. Polymerization in the presence of cationic initiators was carried out more effectively compared with that in the presence of radical ones. This is because Alfrey-Price *e* value for *N*-vinyl phthalimidine is large and negative (Table 4).

The resulting polymer is a transparent resin having a 160—180 °C softening point, and soluble in benzene and insoluble in water in contrast to *N*-vinyl pyrrolidone polymer. The reduced viscosities of all the polymers were small, particularly in the polymers obtained by cationic polymerization.

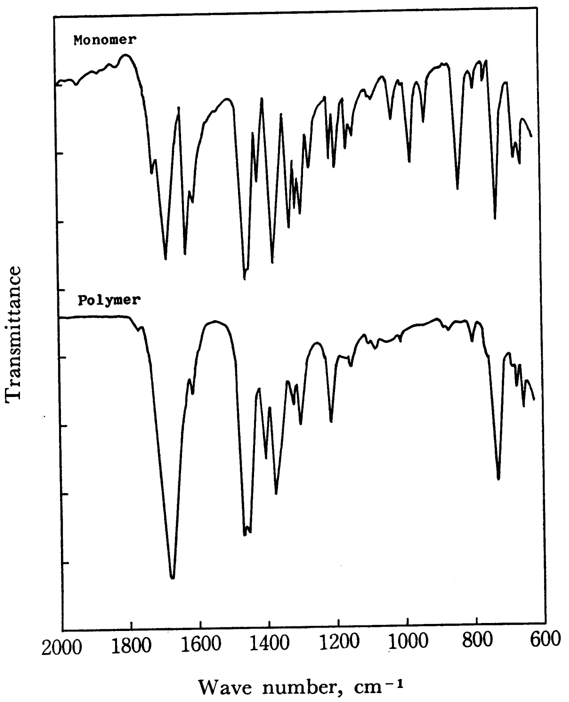


Fig. 1. Infrared absorption spectra of *N*-vinyl phthalimidine and its polymer in Nujol paste.

The infrared absorption spectrum of this *N*-vinyl phthalimidine polymer is shown in Fig. 1, no absorption bands (1630, 975, and 933 cm^{-1}) due to vinyl group in the original monomer being found.

Copolymerization of N-*Vinyl Phthalimidine.* The results of the copolymerization of *N*-vinyl phthalimidine with acrylonitrile and styrene by the use of BPO in dimethylformamide at 60 °C are shown in Table 2, together with those of *N*-vinyl pyrrolidone for comparison. The analytical data show that the *N*-vinyl phthalimidine can polymerize with the vinyl monomers, but *N*-vinyl phthalimidine is less reactive to enter the copolymer with styrene than that with acrylonitrile. The tendency was also observed in the copolymerization of *N*-vinyl pyrrolidone.

In an attempt to determine the monomer reactivity ratios for the system of *N*-vinyl phthalimidine and styrene, copolymerizations in dimethylformamide and in benzene were carried out statically at 60 °C. The monomer ratio in the initial stage was varied, while BPO or AIBN was used as the radical source at a concentration of 1.0 mol% in each case. All the procedures were carried out in less than 10% conversion to determine the initial stage of each copolymerization.

The results of copolymerization by BPO in dimethylformamide are given in Table 3. M_1 and M_2 denote the molar concentrations of *N*-vinyl phthalimidine and styrene, respectively, at the initial feeding, and m_1 and m_2 the molar fractions of the monomers

TABLE 1. POLYMERIZATION OF *N*-VINYL PHTHALIMIDINE[a)]

Initiator	mol%	Benzene ml	Temperature °C	Time hr	Yield %	Reduced viscosity dl/g
AIBN	1.0	0	70	1.0	28.2	—
AIBN	1.0	0	70	3.0	60.3	0.14
AIBN	1.0	1.00	60	24.0	23.8	—
BPO	0.66	0	70	24.0	6.5	—
BPO	3.0	1.00	70	45.0	16.1	0.05
γ-Ray	2.5×10^5 R/hr	1.00	25	42.0	29.7	0.07
γ-Ray	2.5×10^5 R/hr	1.00	25	96.0	63.4	—
BF_3Et_2O	2.0	1.00	20	0.33	74.0	0.03
BF_3Et_2O	8.0	1.00	20	0.17	87.1	0.03
$SnCl_4$	2.0	1.00	20	0.17	36.1	0.03

a) Cationic polymerization was carried out in air.

TABLE 2. COPOLYMERIZATIONS OF *N*-VINYL PHTHALIMIDINE (VPH) AND *N*-VINYL PYRROLIDONE (VPY) WITH ACRYLONITRILE (AN) AND STYRENE (St) BY BENZOYL PEROXIDE[a)]

Monomer (M_1)	10^{-4} mol	Comonomer	10^{-4} mol	BPO mg	Time hr	Yield %	Nitrogen %	m_1 in copolymer mol%
VPH	25	AN	75	5	1.3	6.8	14.75 14.75	40
VPH	22	AN	66	10	3.0	28.2	14.81 14.86	39
VPH	22	St	34	10	26.0	19.3	1.28 1.37	10
VPY	32	AN	66	5	1.0	22.0	18.13 18.20	42
VPY	32	St	34	10	26.0	17.3	1.23 1.22	9

a) Solvent, dimethylformamide 1.00 ml; temperature, 60 °C.

TABLE 3. COPOLYMERIZATION OF *N*-VINYL PHTHALIMIDINE (M_1) WITH STYRENE (M_2) BY BENZOYL PEROXIDE[a)]

Monomers M_1	10^{-4} mol M_2	Polymn. rate %/hr	Carbon %	Nitrogen %	Mol% from C% m_1	Mol% from C% m_2	mol% from N% m_1	mol% from N% m_2
5	45	3.1_0	92.13 92.05	0.27 0.30	0.5	99.5	2.6	97.4
10	40	2.3_8	91.68 91.55	0.59 0.58	2.3	97.7	4.5	95.5
15	35	1.8_2	91.25 90.98	0.84 0.84	4.3	95.7	6.5	93.5
20	30	1.6_7	90.38 90.37	1.10 1.13	7.4	92.6	8.7	91.3
25	25	1.1_9	89.01 89.03	1.41 1.45	13.3	86.7	11.3	88.7
30	20	0.7_7	87.92 88.19	1.76 1.87	17.7	82.3	14.6	85.4
35	15	0.4_2	86.19 87.11	2.27 2.29	24.5	75.5	18.6	81.4

a) Initiator, BPO 1.0 mol%; solvent, dimethylformamide 0.50 ml; temperature, 60 °C.

in the resulting copolymers calculated from the carbon and nitrogen analyses. According to the curve fitting method with use of all the average values of respective m_1 and m_2, the following was obtained.

$$r_1=0.05$$

$$\text{and}\quad r_2=7.4.$$

The results of copolymerization by AIBN in benzene were close to those obtained above.

The copolymerization of *N*-vinyl pyrrolidone–styrene system was similarly carried out in the presence of BPO in dimethylformamide. The monomer reactivity ratios were calculated in the same way and found to be

$$r_1=0.02$$

$$\text{and}\quad r_2=12.0.$$

Bork and Coleman[7)] have dealt with the copoly-

[7)] J. F. Bork and L. E. Coleman, *J. Polym. Sci.*, **43**, 413 (1960).

TABLE 4. ALFREY-PRICE *Q* AND *e* VALUES OF *N*-VINYL LACTAMS AND *N*-VINYL IMIDES

Monomer	*Q*	*e*
N-Vinyl phthalimidine	0.30	−1.80
N-Vinyl pyrrolidone	0.22	−1.99
N-Vinyl phthalimide	0.09	−0.13
N-Vinyl succinimide	0.06	−0.17

merization of the same system by AIBN in benzene at 50 °C, their results being $r_1=0.045$ and $r_2=15.7$. These are close to the values obtained herewith.

In the copolymerizations of *N*-vinyl phthalimidine and *N*-vinyl pyrrolidone with styrene, it was also found that the rates of copolymerization decreased in proportion to the increase in the initial feedings of *N*-vinyl phthalimidine and *N*-vinyl pyrrolidone.

The Q and e Parameters. The *Q* and *e* parameters for these monomers were calculated according to the Alfrey-Price scheme[8] by using the values, r_1 and r_2, and $Q=1.0$ and $e=-0.8$ for styrene. The calculated *Q* and *e* values and those of *N*-vinyl imides[3] of related type are shown in Table 4. The respective pairs of the *Q* and *e* parameters of *N*-vinyl phthalimidine and *N*-vinyl pyrrolidone are very similar to each other. This indicates that the effects of the two substituents on the radical polymerization of such monomers closely resemble each other.

The *e* values of *N*-vinyl phthalimidine and *N*-vinyl pyrrolidone are much more negative than those of *N*-vinyl phthalimide and *N*-vinyl succinimide. This may be explained by the electron-attractive power (mesomeric effect) of carbonyl group in these monomers.

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[8] T. Alfrey and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1974).