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Copolymerizations of 1-Phthalimido-1, 3-butadiene and 1-Succinimido-1, 3-butadiene[1]

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1-Phthalimido-1, 3-butadiene (1-PB) and 1-succinimido-1, 3-butadiene (1-SB) were copolymerized readily with acrylonitrile, methyl methacrylate and styrene, but somewhat less readily with vinyl acetate. The monomer reactivity ratios for the system with styrene were calculated by the Fineman-Ross method and found to be r_1(1-PB)$=1.48$, r_2(St)$=0.32$ for the 1-phthalimido-1, 3-butadiene-styrene system, and r_1(1-SB)$=1.62$, r_2(St)$=0.28$ for the 1-succinimido-1, 3-butadiene - styrene system. The Q, e-values for these systems were successively evaluated and obtained as Q(1-PB)$=1.57$, e(1-PB)$=+0.06$, Q(1-SB)$=1.76$ and e(1-SB)$=+0.09$, when Q(St)$=1.0$ and e(St)$=-0.8$. Likewise, such values for *N*-vinyl phthalimide (VPI) and *N*-vinyl succinimide (VSI) were investigated in order to compare them with the values obtained above for the imidobutadienes; they were shown to be r_1(VPI)$=0.09$ and r_2(St)$=6.3$ for the *N*-vinyl phthalimide - styrene system, and r_1(VSI)$=0.07$ and r_2(St)$=9.6$ for the *N*-vinyl succinimide - styrene system. Subsequently, the following Q and e values were determined: Q(VPI)$=0.09$, e(VPI)$=-0.13$, Q(VSI)$=0.06$, and e(VSI)$=-0.17$.

As part of the investigation of aminobutadienes and related compounds, experiments have presented some results of the syntheses of several imidobutadiene monomers,[3-6] and of attempts to improve the dyeability of polypropylene fiber[7] and to make high-equivalent anion exchange resins.[8] Since it became desirable to determine some of the reactivity parameters of the imidobutadienes toward polymerization and copolymerization, a previous paper has dealt with the polymerization and copolymerization of 2-phthalimido-1, 3-butadiene and the determination of the Q, e-parameters.[9]

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1) Paper VII on Aminobutadienes: Abstracts of the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

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3) A. Terada, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **81**, 1773 (1960).

4) A. Terada and S. Takahashi, ibid., **83**, 485 (1962).

5) A. Terada and K. Murata, ibid., **83**, 490 (1962).

6) A. Terada and K. Murata, Abstracts of the Meeting on Olefin Chemistry of the Society of Organic Synthetic Chemistry, Japan, Tokyo, November, 1964.

7) A. Terada, Abstracts of the Ōita Meeting of the Chemical Society of Japan, Ōita, December, 1965.

8) A. Terada and K. Murata, Japanese Pat. 468683 (1966).

9) K. Murata and A. Terada, Paper VI on Aminobutadienes, *J. Polymer Sci.*, **A**, Nov., (1966), in press.

Likewise, data presented in one of the previous reports[10] have demonstrated that 1-phthalimido- and 1-succinimido-1, 3-butadienes easily polymerize, using a free radical source, to give high polymers, and that the polymerizations take place smoothly even by a cationic process. The purpose of the present investigation is to extend these data to copolymerization systems with various vinyl monomers, and to supply some of the basic data for the above-mentioned utilizations. The copolymerizations of each of these imidobutadiene monomers with acrylonitrile (AN), methyl methacrylate (MMA), styrene (St) and vinyl acetate (VAc), and, in addition, the copolymerizations of *N*-vinyl phthalimide and *N*-vinyl succinimide with such vinyl monomers will also be described. The monomer reactivity ratios for the copolymerization systems of these imidobutadienes and of vinyl imides with styrene will be determined, and the evaluation of the Q, e-parameters will also be attempted according to the Alfrey-Price scheme.[11]

Experimental

Materials.—1-Phthalimido-1, 3-butadiene (1-PB) and 1-succinimido-1, 3-butadiene (1-SB) were prepared as previously reported,[5] and obtained as yellow needles with a m. p. of 114.5—116°C, and as white crystals with a m. p. of 75—76°C respectively. *N*-Vinyl phthalimide (VPI) was prepared via the pyrolysis of the *N*-β-acetoxyethylphthalimide obtained after the condensation of monoethanolamine with phthalic acid and following acetylation; it was obtained as pale yellow needles (from methanol), 85—86°C (lit., 86,[12,13] 85.5—86°C[14,15]). *N*-Vinyl succinimide (VSI) was prepared by a similar manner, using succinic acid and monoethanolamine as the starting meterials; it was obtained as white crystals, m. p. 48—48.5°C (lit., m. p. 48,[16] 48.5,[17] 48—49°C)[18]. The other vinyl monomers, acrylonitrile (b. p. 76—77°C), methyl methacrylate (b. p. 44.5—46°C/118 mmHg), styrene (b. p. 46.5—47°C/24 mmHg) and vinyl acetate (b. p. 71—71.5°C), were obtained commercially as reagent grade materials, just prior to use they were purified to the above state according to the usual manner.[19] Benzoyl peroxide (analytical-grade reagent) was purified by repeated precipitations into methanol from a chloroform solution and then dried under a vacuum, m. p. 104°C. Purified dimethylformamide was prepared by repeated fractional distillations through a 30 cm. fractionating-distillation column after dehydration over anhydrous sodium sulfate; the middle fraction was used as a solvent for the polymerization, b. p. 65—66°C/40 mmHg.

Polymerization Procedure.—This was carried out as usual.[9,10]

Results and Discussion

The Copolymerization of 1-Phthalimido-1, 3-butadiene.—Table I shows the results of the radical copolymerization of this monomer with various comonomers in the bulk state or in solution. The infrared spectra of the resulting copolymers are illustrated in Fig. 1.[20] In each of the spectra, there is a strong absorption band, showing a *trans* di-substituted ethylenic bond internal in the polymer chain, as has been shown previously in the case of the homopolymer.[10] This obviously indicates

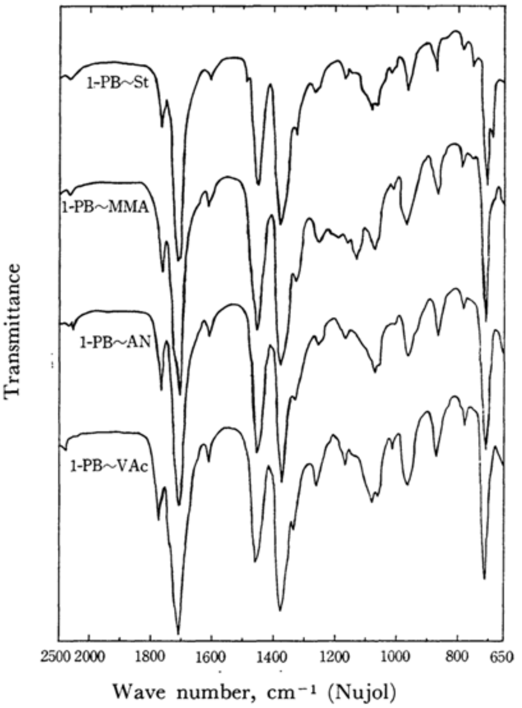

Fig. 1. Infrared spectra of copolymers of 1-phthalimido-1, 3-butadiene with various vinyl monomers.

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10) A. Terada and K. Murata, Paper V on Aminobutadienes: Abstracts of the Tokuyama Meeting of the Chemical Society of Japan, Tokuyama, May, 1961.

11) T. Alfrey and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947).

12) M. Bachstez, *Chem. Ber.*, **46**, 3087 (1913).

13) U. S. Pat. 2276840.

14) T. Yoshida and H. Hirakawa, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zassi)*, **55**, 83 (1952).

15) S. Akiyoshi, K. Yanagi and T. Matsuda, ibid., **59**, 658 (1956).

16) U. S. Pat. 2231905.

17) A. F. Nikolaev and S. N. Ushakov, *Izvest. Akad. Nauk. S. S. S. R., Otdel. Khim. Nauk.*, **1957**, 1235; *Chem. Abstr.*, **52**, 6283 (1958).

18) J. Furukawa, A. Ōnishi and T. Tsuruta, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zassi)*, **60**, 350 (1957).

19) The Society of Polymer Science, Japan, "Synthetic Methods of Monomers," in "Lectures on High Polymer Experiments (Kobunshi Zikken Koza)," Vol. 9, Ed. by S. Kambara, Kyoritsu Publ. Co., Tokyo (1957).

20) Taken in Nujol Paste by a Hitachi Infrared Spectrophotometer, Model EPI-2.

TABLE I. THE COPOLYMERIZATIONS OF 1-PHTHALIMIDO-1, 3-BUTADIENE (M_1) WITH VARIOUS VINYL MONOMERS (M_2) IN THE PRESENCE OF 1.0 mole-% OF BENZOYL PEROXIDE AT 60°C

M_1	10^{-4}mole	M_2	DMF[a] ml.	Time hr.	Yield wt.-%	N[b] wt.-%	m_1 mole-%	m_2[c] mole-%
10	St	90	—	24	40.8	2.19 2.08	18.6	81.4[d]
10	MMA	90	—	20	83	1.34 1.38	19.3	80.7[d]
10	AN	90	—	20	90	—	—	—
10	VAc	90	—	24	8.5	5.71 5.76	65.8	34.2
15	St	35	1.50	20	16.2	4.96	55.6	44.4
15	MMA	35	2.00	20	19.3	5.00	55.2	44.8
15	AN	35	2.00	20	26.9	8.88	72.4	27.6
15	VAc	35	1.50	24	13.0	6.45	82.7	17.3

a) Dimethylformamide.
b) Determined by the Micro-Dumas method.
c) Calculated by means of the nitrogen content.
d) Calculated by means of the average value of the nitrogen content.

that the monomer arrangement in the copolymerization is mainly of the 1, 4-type, also. The absorption peaks at 1710 and 1770 cm^{-1} in these spectra are assigned to the phthalimido-carbonyl; another striking band, at 710 cm^{-1}, is that of the *o*-di-substituted benzene of phthalimido. 1-Phthalimido-1, 3-butadiene easily copolymerizes with these monomers, whereas vinyl acetate enters into the copolymer somewhat less readily.

In an attempt to determine the relative reactivity ratios for the 1-phthalimido-1, 3-butadiene - styrene system, the copolymerization in a dimethylformamide solution was carried out at 60°C; the monomer ratio in the initial charge was varied, while benzoyl peroxide was used as the free radical source at a concentration of 2.0 mol.-% in each case (Table II).

TABLE II. THE COPOLYMERIZATION OF 1-PHTHALIMIDO-1, 3-BUTADIENE (M_1) AND STYRENE (M_2) AT 60°C

M_1 10^{-4}mole	M_2 10^{-4}mole	DMF ml.	Time hr.	Yield wt.-%	N, % wt.-%	m_1[a] mole-%	m_2[a] mole-%
10	90	0.30	6.0	11.4	2.30 2.41	20.9	79.1
10	45	1.00	5.0	8.0	3.85 3.78	38.1	61.9
10	30	1.00	6.0	8.3	4.37 4.25	45.4	54.6
20	30	1.50	6.0	9.1	4.86 5.14	56.2	43.8
15	10	1.00	5.0	8.1	5.84 5.98	73.3	26.7

a) Calculated by means of the average value of the nitrogen content.

The M_1 and M_2 in Table II represent the molar concentrations of 1-phthalimido-1, 3-butadiene and styrene respectively at the initial feeding, while m_1 and m_2 are the molar fractions of them in the resulting copolymers as determined by the Micro-Dumas method. According to the Fineman-Ross plot,[21] we obtain:

$$r_1(\text{1-PB}) = 1.48$$

$$r_2(\text{St}) = 0.32$$

The copolymer composition curve for this system, calculated from these r_1 and r_2 values, is shown in

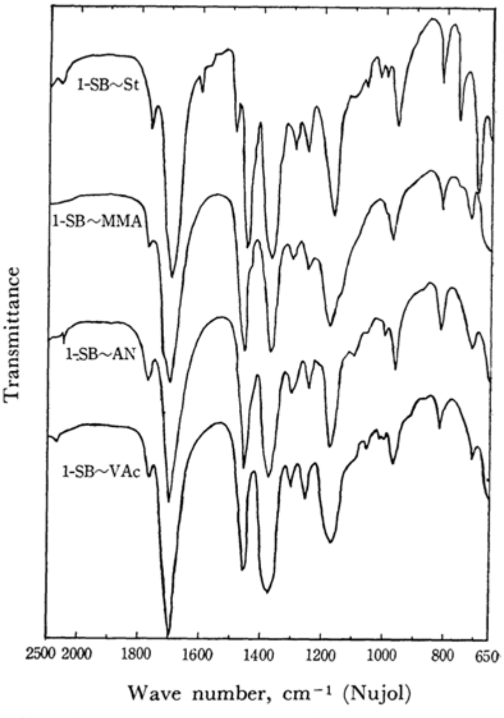

Fig. 2. Infrared spectra of copolymers of 1-succinimido-1, 3-butadiene with various vinyl monomers.

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[21] M. Fineman and S. D. Ross, *J. Polymer Sci.*, **5**, 269 (1950).

TABLE III. THE COPOLYMERIZATIONS OF 1-SUCCINIMIDO-1, 3-BUTADIENE (M_1) WITH VARIOUS VINYL MONOMERS (M_2) IN THE PRESENCE OF 1.0 mole-% OF BENZOYL PEROXIDE AT 60°C

M_1	10^{-4}mole	M_2	DMF ml.	Time hr.	Yield wt.-%	N wt.-%	m_1 mole-%	m_2 mole-%
15	St	35	0.50	20	31.6	4.98 4.88	43.7	56.3
30	MMA	70	1.00	20	25.9	5.87	53.4	46.6
30	AN	70	1.00	20	53.5	12.28	62.2	37.8
15	VAc	35	0.50	20	11.8	7.78 7.74	74.6	25.4
8	VAc	61	—	24	3.5	8.22	81.8	18.2

Fig. 3; it gives the best fit to the experimental data.

The Copolymerization of 1-Succinimido-1, 3-butadiene.—The results of the radical copolymerizations with various vinyl monomers are presented in Table III, while the infrared spectra of the resulting copolymers are illustrated in Fig. 2.

The strong absorption bands at 1700 and 1770 cm^{-1}, assignable to succinimido-carbonyl, are found in all of the polymer spectra; this fact and the data in Table III clearly show that this monomer could copolymerize preferentially with all of such comonomers as well as in the above case of 1-phthalimido-1, 3-butadiene. However, only vinyl acetate was less reactive to enter into the copolymer.

TABLE IV. THE COPOLYMERIZATION OF 1-SUCCINIMIDO-1, 3-BUTADIENE (M_1) AND STYRENE (M_2) IN THE PRESENCE OF 1.0 mole-% OF BENZOYL PEROXIDE AT 60°C

M_1 10^{-4}mole	M_2 10^{-4}mole	DMF ml.	Time hr.	Yield wt.-%	N wt.-%	m_1 mole-%	m_2 mole-%
10	90	0.50	3.0	6.8	2.85 2.89	23.6	76.4
15	35	0.50	3.0	5.3	5.64 5.57	51.4	48.6
22.5	27.5	0.50	2.5	4.2	6.69 6.53	63.3	36.7
20	20	0.50	2.5	5.4	6.81 7.05	67.2	32.8
30	20	0.50	2.0	4.1	7.36 7.59	74.2	25.8

By the usual treatment, we obtain Table IV and;

$$r_1(\text{1-SB}) = 1.62$$

$$r_2(\text{St}) = 0.28$$

The copolymer composition curve calculated for this system agrees exactly with the experimental results (Fig. 4).

The Copolymerizations of *N*-Vinyl Phthalimide and *N*-Vinyl Succinimide.—Tables V and VI show the results of the copolymerizations of *N*-vinyl phthalimide and of *N*-vinyl succinimide respectively with styrene. Similar calculations of the monomer reactivity ratios give the following values:

$$r_1(\text{VPI}) = 0.09$$ [22]

$$r_2(\text{St}) = 6.3$$

and;

$$r_1(\text{VSI}) = 0.07$$ [24]

$$r_2(\text{St}) = 9.6$$

TABLE V. THE COPOLYMERIZATION OF *N*-VINYL PHTHALIMIDE (M_1) AND STYRENE (M_2) IN THE PRESENCE OF 1.0 mole-% of BENZOYL PEROXIDE AT 60°C

M_1 10^{-4}mole	M_2 10^{-4}mole	DMF ml.	Time hr.	Yield wt.-%	N wt.-%	m_1 mole-%	m_2 mole-%
10	90	0.50	2.5	6.9	0	0	100
15	35	0.50	2.0	2.4	0.81	6.3	93.7
20	20	0.50	2.5	3.2	1.57	12.7	87.3
35	15	1.00	5.0	5.6	3.08	27.0	73.0
40	10	1.00	5.0	3.3	3.60	32.6	67.4

TABLE VI. THE COPOLYMERIZATION OF *N*-VINYL SUCCINIMIDE (M_1) AND STYRENE (M_2) IN THE PRESENCE OF 1.0 mole-% OF BENZOYL PEROXIDE AT 60°C

M_1 10^{-4}mole	M_2 10^{-4}mole	DMF ml.	Time hr.	Yield wt.-%	N wt.-%	m_1 mole-%	m_2 mole-%
10	40	0.50	4.0	10.4	0.42	3.1	96.9
15	35	0.50	4.0	9.0	0.58 0.61	4.5	95.5
20	30	0.50	4.0	8.6	0.77	5.8	94.2
25	25	0.50	4.0	7.6	1.21 1.23	9.2	90.8
30	20	0.50	4.0	6.9	1.73	13.2	86.8
35	15	0.50	4.0	5.8	2.36 2.40	18.4	81.6
40	10	0.70	4.0	4.8	3.48	27.3	72.7

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22) Recently, Nikolaev et al.[23] have dealt with the copolymerization system of vinyl phthalimide with styrene; their results are $r_1(\text{VPI}) = 0.075 \pm 0.03$ and $r_2(\text{St}) = 8.3 \pm 0.3$. These results are very close to the results obtained here.

23) A. F. Nikolaev and M. N. Tereshchenko, *Vysokomolekul Siedin*, **6**, 379 (1964); *Chem. Abstr.*, **61**, 5771 (1964).

24) Furukawa et al.[25] and, independently, Hopff and Schlumbon[26] have also investigated this copolymerization system, *N*-vinyl succinimide and styrene, and their results were $r_1 = 0.09$ and $r_2 = 7.0$, and $r_1 = 0.07$ and $r_2 = 10.5$ respectively.

25) J. Furukawa, T. Tsuruta, H. Fukatani and N. Yamamoto, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zassi)*, **60**, 1085 (1957).

26) H. Hopff and P. Schlumbon, *Makromol. Chem.*, **43**, 173 (1961).

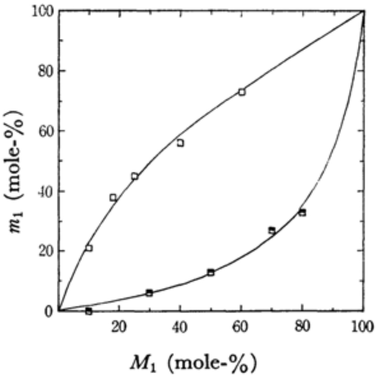

Fig. 3. Copolymerization curves. The solid lines were calculated for the monomer reactivity ratios of each copolymerization system.

□: 1-PB∼St
■: VPI∼St

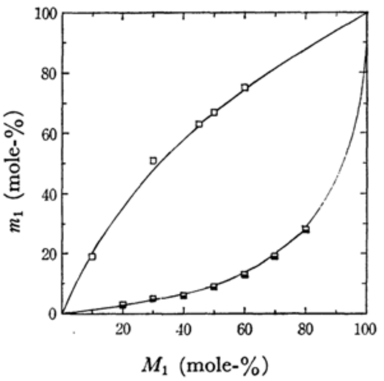

Fig. 4. Copolymerization curves. The solid lines were calculated for the monomer reactivity ratios of each copolymerization system.

□: 1-SB∼St
⬓: VSI∼St

TABLE VII. Q, e-PARAMETERS AND ULTRAVIOLET ABSORPTION MAXIMA OF IMIDO-MONOMERS

Monomer	Q	e	UV, mμ	
			λ_{max}	ε_{max}
1-Phthalimido-1, 3-butadiene	1.57	+0.06	278.5	35400[3]
1-Succinimido-1, 3-butadiene	1.76	+0.09	248	26000[5]
2-Phthalimido-1, 3-butadiene	5.0	−0.05[9]	219	55000[4]
2-Succinimido-1, 3-butadiene	—	—	219.5	18500[4]
1, 3-Butadiene	1.33	−0.8[27]	217	21000
N-Vinyl phthalimide	0.09	−0.13	234.5	26200[3]
	0.41	−1.63[29]		
	0.21	−1.14[23]		
N-Vinyl succinimide	0.06	−0.17	212	17900[5]
	0.10	−0.12[25]		
	0.15	−0.27		
	0.15	−0.25[26]		
	0.13	−0.23[34]		
Ethylene	0.03	−0.43[32]	175	10000
N-Vinyl pyrrolidone	0.087	−1.22[31]	235	14700
N-Vinyl ethylurea	0.14	−1.6[33]		
N-Vinyl ethylcarbamate	0.12	−1.9[33]		
N-Vinyloxazolidone	0.07	−0.8[33]		

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27) T. Alfrey, J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, New York (1952), p. 91.

28) Nikolaev et al. have obtained the Q and e-values of *N*-vinyl phthalimide as Q=0.41 and e=−1.63 from the copolymerization with vinyl acetate,[29] they also obtained them as Q=0.21 and e=−1.14 from the system with styrene.[23] While there are large differnces between these values and the values we present here, the discrepancy can be explained as follows: In general, when the Q and e values are calculated, two values for the e are usually given. Nikolaev et al. have chosen the more negative e value of the two in each case; however, we have taken the less negative e value (−0.05) between −0.8+0.75 and −0.8−0.75, with regard to the values for *N*-vinyl acetamide (e=−1.39 and −1.44)[30] and for *N*-vinyl pyrrolidone (e=−1.22)[31] and also to those of such other related *N*-vinyl compounds as *N*-vinyl succinimide reported on hitherto.

29) A. F. Nikolaev, S. N. Ushakov, L. P. Vishnevetskaya, N. A. Voronova and E. I. Rodina, *Vysokomolekul Soedin*, **4**, 1053 (1962); *Chem. Abstr.*, **59**, 10243 (1963).

30) Yu-Wu Hsu, S. S. Skorokhodov and A. A. Vansheidt, ibid., **6**, 1291 (1964); *Chem. Abstr.*, **61**, 14790 (1964).

31) J. F. Bork and L. E. Coleman, *J. Polymer Sci.*, **43**, 413 (1960).

32) R. D. Burkhart and N. L. Zutty, ibid., **A1**, 1137 (1963).

33) From the report by R. Hart and D. Timmerman, *Makromol. Chem.*, **31**, 223 (1959).

34) L. J. Young, *J. Polymer Sci.*, **54**, 411 (1961).

The Q, e-Parameters.—The calculated copolymer composition curves of these imido-monomers are figured as in Fig. 3 and in Fig. 4 respectively from the above-obtained monomer reactivity ratios.

From these curves the following considerations are possible. These two imidobutadienes preferentially enter into the copolymers, while the two vinyl imides do so less readily. The curves of the two imidobutadienes are so similar that they are virtually superimposable; those of the vinyl imides are very similar to each other also. Therefore, it may be concluded that the natures and the effects of these two imido groups on the monomer reactivity are very similar and that, therefore, the reactivity differences between the imidobutadienes and vinyl imides on copolymerization are due to the differences between butadienyl and vinyl.

To investigate the structural features of these imido-monomers, the Q and e-parameters were evaluated from the above-indicated monomer reactivity ratios according to the Alfrey-Price scheme,[11] using the values of $Q=1.0$ and $e=-0.8$ for styrene. The calculated Q and e-values, and those of the other monomers of related type which have appeared in the literature, are shown in Table VII, along with their ultraviolet spectral data for the sake of comparison. The respective pairs of the Q and e-parameters of 1-phthalimido- and 1-succinimido-1, 3-butadienes, and of *N*-vinyl phthalimide and *N*-vinyl succinimide are very similar to each other. This fact indicates that the effects of the two substituents on the radical copolymerizations of such monomers closely resemble each other, as has already been established.

The Q values of 1-phthalimido- and 1-succinimido-1, 3-butadienes are much larger than those of *N*-vinyl phthalimide and *N*-vinyl succinimide. This means that, by the substituting butadienyl group for vinyl, the conjugated systems in the former two are more extended and more resonance-stabilized than in the latter two. A clear proof for this is the conclusion to be drawn from their ultraviolet spectroscopic data (Table VII), in which such imidobutadienes exhibit a more bathochromic displacement of their K bands and a much greater increase in intensity than do *N*-vinyl imides.[3,5] Similar relationships also hold in comparison with the Q value of 1, 3-butadiene.[27] Those of 1-imido-1, 3-butadienes indicate somewhat larger values; this means a similar extension of the butadienyl conjugation to the imido-nitrogen.

When the e value of 1, 3-butadiene (-0.8) is compared, those of such 1-imido-1, 3-butadienes exhibit a decrease and become near to zero. This fact may be explained by the M-effect of carbonyls in both the imido rings serving, in the opposite direction, to reduce the electron-donating power of the imido-nitrogen extending over the butadiene chain, because there is a so-called Branch-Calvin cross conjugation in these structures. Similar relationships and explanations should also hold between ethylene and *N*-vinyl imides. The e values for *N*-vinyl pyrrolidone and other *N*-vinyl acylamide are remarkably more negative than that of *N*-vinyl succinimide (Table VII); this fact may give support to our theory here.

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