

## REACTIVITY OF SOME VINYLIMIDAZOLES TOWARDS OTHER VINYL MONOMERS IN RADICAL COPOLYMERIZATION

Despite a considerable volume of patent literature on the use of imidazole-containing polymers, and despite recent interest in imidazole as a model for enzymatic reactions (1-3), there is very little data on the behavior of vinyl-imidazoles in copolymerization reactions (4). It was felt that systematic work on the elementary reactivity of 1-vinylimidazoles in free radical copolymerization was needed in order to be able to control the preparation of these copolymers to a certain degree.

1-Vinylimidazole and 2-methyl-1-vinylimidazole were copolymerized in bulk with other vinyl monomers at  $60 \pm 0.01^\circ\text{C}$  using AIBN as initiator. Further, the copolymerization kinetics of two imidazolium salts, i.e., 3-ethyl-1-vinylimidazolium iodide and 3-benzyl-1-vinylimidazolium bromide with 1-vinylimidazole were also investigated.

The copolymerization parameters  $r_1$  and  $r_2$  of each monomer pair were calculated from the average composition of the copolymers' data by use of the Fineman-Ross copolymerization equation (5). The reactivity of the vinyl-imidazoles studied was expressed in terms of the Alfrey-Price Q-e scheme (6).

### Experimental

Styrene, vinyl acetate, methyl methacrylate, 1-vinyl-pyrrolidone, 1-vinylimidazole, and 2-methyl-1-vinylimidazole were obtained commercially. The monomers were purified by fractional distillation and their purity was checked by GLC (purity >99.8%).

3-Ethyl-1-vinylimidazolium iodide was prepared by reacting 1-vinylimidazole (19 g,  $2 \times 10^{-1}$  mole) with excess ethyl iodide (64 g,  $4 \times 10^{-1}$  mole) in ethyl acetate (100 ml) at room temperature overnight. The product crystallized out from the reaction mixture to give a near quantitative yield of white, needle-like crystals. Found (%): C, 33.30; H, 4.30; N, 11.54.  $\text{C}_7\text{H}_{11}\text{IN}_2$  requires (%): C, 33.70; H, 4.43; N, 11.20.  $^1\text{H}$  NMR and IR spectra were consistent with the structure of the title compound.

3-Benzyl-1-vinylimidazolium bromide was obtained by quaternizing 1-vinylimidazole (9.4 g,  $10^{-1}$  mole) with benzyl bromide (17.1 g,  $10^{-1}$  mole) in dry acetonitrile at about  $-5^\circ\text{C}$  for a month to give a near quantitative yield of the title compound. Found (%): C, 54.01; H, 5.04; N, 10.51; Br, 29.67.  $\text{C}_{12}\text{H}_{13}\text{BrN}_2$  requires (%): C, 54.35; H, 4.95; N, 10.75; Br, 30.13. The  $^1\text{H}$  NMR and IR spectra were consistent with the expected product structure.

The bulk copolymerization experiments were performed in glass ampoules. After the conventional freeze-thaw cycle, the ampoules were sealed at a pressure  $\leq 10^{-3}$  mm. AIBN, recrystallized twice from methanol ( $10^{-1}$  mol wt %), was used as the radical initiator. The sealed ampoules were kept at  $60 \pm$

TABLE I

Copolymerization Experimental Data. 0.02 g ( $1 \times 10^{-4}$  mole) of AIBN  
Used in Each Experiment Unless Stated Otherwise;  
 $t = 60 \pm 0.01^\circ\text{C}$ ; Bulk

(1) - 1-vinylimidazole; (2) - styrene					
Monomer		time (hr)	Conv (%)	mole% 1 charged	mole% 1 in copolymer
1 (g)	2 (g)				
4.71	5.21	3½	<5	50	9.8
5.65	4.17	3½	<5	60	13.4
6.59	3.12	3½	<5	70	18.8
7.53	2.08	3½	<5	80	29.1
8.47	1.04	3½	<5	90	47.3
3.76	6.25	6	12	40	6.9
4.71	5.21	6	11	50	9.1
5.65	4.17	6	10	60	12.9
(1) - 1-vinylimidazole; (2) - vinyl acetate					
7.53	1.72	5	3.2	80	88.7
4.71	4.30	5	3.3	50	80.9
1.88	6.89	5	3.4	20	63.9
(1) - 1-vinylimidazole; (2) - methyl methacrylate					
7.53	2.00	0.83	<10	80	36.9
8.47	1.00	0.83	<10	90	43.2
8.94	0.50	0.83	<10	95	60.6
6.59	3.00	0.83	<10	70	27.9
(1) - 1-vinylimidazole; (2) - 1-vinyl-2-pyrrolidone					
4.71	5.56	3	7.3	50	63.7
5.65	4.45	3	5.0	60	68.0
3.76	6.67	3	10.5	40	55.6
6.59	3.33	3	3.5	70	75.2

$0.01^\circ\text{C}$  for a given time. The copolymers were isolated by precipitating the diluted (methanol, acetone) reaction mixtures into a nonsolvent for both corresponding homopolymers (usually ether or petroleum spirit). The copolymers were then reprecipitated twice in the same solvent/nonsolvent system, and dried to constant weight at  $40^\circ\text{C}/0.5$  mm. Water-soluble copolymers were purified by ultrafiltration (Amicon stirred cell, UM 05 membrane) and freeze-dried.

The copolymer composition was usually determined from the elemental

TABLE I

(continued from previous page)

Monomer		time (hr)	Conv (%)	mole% 1 charged	mole% 1 in copolymer
1 (g)	2 (g)				
(1) - 1-vinylimidazole; (2) - 3-ethyl-1-vinylimidazolium iodide					
5.20	2.50	3	~9	84.7	77.0
5.00	1.50	3	~9	90.1	84.8
5.02	0.70	3	~9	95.2	88.5
(0.01 g of AIBN used in each experiment)					
(1) - 2-methyl-1-vinylimidazole; (2) - styrene					
5.41	5.21	3	<5	50	10.6
6.49	4.17	3	<5	60	14.1
7.57	3.12	3	<5	70	21.5
8.65	2.08	3	<5	80	31.6
(1) - 2-methyl-1-vinylimidazole; (2) - methyl methacrylate					
8.65	2.00	0.5	<7	80	39.4
7.61	3.01	0.5	<7	70	30.5
6.49	4.01	0.5	<7	60	22.0
5.45	5.01	0.5	<7	50	18.6
(1) - 1-vinylimidazole; (2) - 3-benzyl-1-vinylimidazolium bromide					
4.23	1.33	3	11.7	90.1	77.5
7.53	3.98	3	7.0	84.0	70.0
15.02	2.65	3	4.2	94.0	83.3
(0.01 g of AIBN used in each experiment)					

analysis data. However, poly(1-vinylimidazole)-co-(1-vinylpyrrolidone) was analyzed by GC pyrolysis in a Hewlett-Packard 58/30 instrument equipped with a Packard 891 pyrolysis unit. 2  $\mu$ l of copolymer 5% solution were coated on a metal wire and pyrolyzed by the Curie point technique at 610°C. The products of pyrolysis were chromatographed on a 1 m Chromosorb 101 column, temperature programmed from 50 to 230°C at 15°C/min. The pyrolysis of mixtures of the corresponding homopolymers led mainly to depolymerization of the polymers. The copolymer composition was determined by comparing its pyrolysis result with the homopolymer mixture pyrolysis data.

A simple computer program (7) was used to calculate the copolymerization parameters from the initial monomer mixture and the final copolymer composition by the Fineman-Ross method.

The experimental conditions for the copolymerization of selected monomer pairs and the chemical composition of the resulting copolymers are given in Table I.

TABLE II

## Copolymerization Parameters

	$r_1$		$r_2$
1-vinylimidazole	$0.10 \pm 0.02^b$	styrene	$10.0 \pm 0.2$
	$1.50 \pm 0.02$	vinyl acetate	$0.2 \pm 0.02$
	$0.03 \pm 0.1$	methyl methacrylate	$4.1 \pm 0.02$
	$0.95 \pm 0.01$	1-vinylpyrrolidone	$0.17 \pm 0.01^a$
	$0.27 \pm 0.1$	3-benzyl-1-vinylimidazolium bromide	$0.63 \pm 0.01$
	$0.3 \pm 0.2$	3-ethyl-1-vinylimidazolium iodide	$1.6 \pm 0.01$
2-methyl-1-vinylimidazole	$0.06 \pm 0.03$	methyl methacrylate	$3.7 \pm 0.01$
	$0.10 \pm 0.01$	styrene	$8.66 \pm 0.02$

<sup>a</sup>Analyzed by GC pyrolysis only.

<sup>b</sup>The value of standard deviation reflects the error of calculation only.

TABLE III

## Q and e Values of 1-Vinylimidazole and 2-Methyl-1-Vinylimidazole

1-vinylimidazole	$e = -0.7$	$e = -0.9$
	$Q = 0.1$	$Q = 0.1$
2-methyl-1-vinylimidazole	$e = -0.6$	$e = -1.0$
	$Q = 0.1$	$Q = 0.1$

## Results and Discussion

The monomer reactivity ratios  $r_1$  and  $r_2$  were calculated from the experimental data by use of the Fineman-Ross linear form of the copolymerization equation. The calculated values are summarized in Table II.

From the data on the reactivity of 1-vinylimidazole and 2-methyl-1-vinylimidazole towards styrene, the Q and e parameters of the two imidazoles were estimated (cf. Table III).

Although the Q-e system is the most frequently used scheme for codifying experimental reactivity data, it fails, particularly when factors not considered in the design of the scheme have a significant effect on the reactivity of the

TABLE IV

Q-e Values Obtained Using Reference Monomers Other Than Styrene

	Reference Comonomer			1-vinylimidazole		
	Q	e	r <sub>2</sub>	r <sub>1</sub>	Q	e
1-vinylpyrrolidone	0.14 <sup>a</sup>	-1.14 <sup>a</sup>	0.169	0.942	0.175	0.214
					3.860	-2.49
vinyl acetate	0.026 <sup>a</sup>	-0.22 <sup>a</sup>	0.199	1.484	0.102	0.883
					0.166	-1.323

<sup>a</sup>The values taken from J. Brandrup, E. H. Immergut, Ed., Polymer Handbook, Interscience, New York, 1967.

monomer under investigation (8). The calculations, based on the assumption that 1-vinylimidazoles behave either as electron donors or as electron acceptors with respect to the reference comonomer (i.e., styrene,  $e = -0.80$ ), gave two sets of similar Q-e values that agree well with the data reported previously by S. Murahashi et al. (9), and by K. Matsuoka et al. (10) (the representative values of  $e$  ranging from  $-0.91$  to  $-1.73$ , and the Q values ranging from  $0.10$  to  $0.24$ ). However, when reference monomers other than styrene were employed, considerably different Q-e values were obtained (c.f. Table IV).

Recently, Kelen and Tüdös (11) devised a simple graphical method for calculating the reactivity ratios of copolymerization, which is based on solving the linear equation

$$\eta = (r_1 + \frac{r_2}{a}) \xi - \frac{r_2}{a},$$

where  $\eta = G/(a + F)$ ;  $\xi = F/(a + F)$ ;  $a > 0$  [an arbitrary constant, usually  $a = (F_{\min} F_{\max})^{1/2}$ ];  $G = x(y - 1)/y$ ;  $F = x^2/y$ ;  $x = M_1/M_2$  (initial monomer feed);  $y = dM_1/dM_2$  (initial copolymer composition). Extrapolation to  $\xi = 0$  and  $\xi = 1$  gives  $-r_2/a$  and  $r_1$  (both as intercepts). A linear plot of  $\eta$  vs.  $\xi$  is considered clear evidence that a particular copolymerization can be described by the simple two-parameter copolymerization equation. The  $\eta$  vs.  $\xi$  plots for the 1-vinylimidazole/styrene and 2-methyl-1-vinylimidazole/styrene copolymerizations from the data of Table I are shown in Figure 1.

The copolymerization parameter values obtained by the Kelen-Tüdös method (1-vinylimidazole,  $r_1 = 0.06$ ; styrene,  $r_2 = 9.8$ ; 2-methyl-1-vinylimidazole,  $r_1 = 0.1$ ; styrene,  $r_2 = 9.4$ ) do not differ significantly from the values obtained by the Fineman-Ross method.

Copolymerization kinetics of the two quaternized 1-vinylimidazoles showed an increased reactivity of the double bond with respect to 1-vinylimidazole.

To conclude, data on radical copolymerization behavior of 1-vinylimidazoles

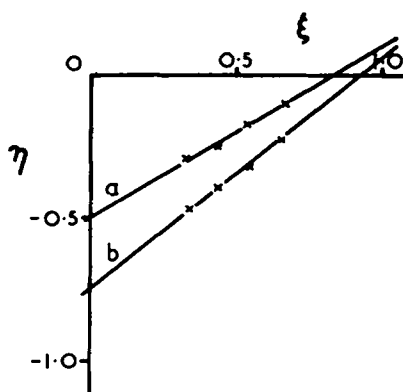


Fig. 1. Kelen-Tüdös plot for the calculation of reactivity ratios: (a) 2-methyl-1-vinylimidazole/styrene, (b) 1-vinylimidazole/styrene.

have been obtained. The data can be used only for the monomer pairs studied. An attempt to describe radical copolymerization by applying the Q-e scheme to the experimental data, failed to produce a conclusive result.

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