

Copolymerization. VII. Relative Rates of Addition of Various Monomers in Copolymerization

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INTRODUCTION

Within the last four years the theory of vinyl copolymerization has progressed to the point at which quantitative predictions concerning monomer reactivity in copolymerizations can be made. Alfrey and Price (1) proposed that monomer reactivity in copolymerization is related to two constants Q and e which are unique for each monomer. The validity of this relationship is now well established and has been checked by these laboratories (2) and by Price (3) using the published data of numerous authors. Copolymerization data have been obtained in great quantity, a partial list of which is given (4).

The prior literature, however, with the exception of data on itaconic acid (5) is devoid of copolymerization studies on unsaturated acids. The purpose of this paper is to present data we have obtained on copolymerizations involving acrylic acid, methacrylic acid, and crotonic acid as well as other monomers. The systems studied include styrene-methacrylic acid, styrene-acrylic acid, vinylidene chloride-crotonic acid, and vinyl acetate-crotonic acid. The reactivity ratios, r_1 and r_2 , for these copolymerizations were obtained in the conventional way by allowing polymerizations to proceed to conversions of less than 4%, isolating and purifying the initial copolymer formed, and analyzing for carbon and hydrogen in the case of styrene-methacrylic acid and styrene-acrylic acid copolymerizations, for chlorine in the case of vinylidene chloride-crotonic acid copolymerization, and for acid numbers in the case of vinyl acetate-crotonic acid copolymerization. Other copolymer systems studied are acrylonitrile-vinyl 2-ethyl hexoate, acrylonitrile-vinyl formate, acrylonitrile-vinyl benzoate, acrylonitrile- α -acetoxystyrene, acrylonitrile-allyl chloride, vinylidene chloride-vinyl benzoate, vinylidene chloride-methyl isopropenyl ketone, vinyl chloride-vinyl isobutyl ether, and styrene-citraconic anhydride.

RESULTS AND DISCUSSION

All of the experimental data obtained are consistent with and lend further support to the general scheme of monomer reactivity in copolymerization as proposed by Alfrey and Price. The experimental results and analytical data are summarized in Table I-XIII.

The r_1 and r_2 monomer reactivity ratios for these systems were determined by choosing values which gave the best curve fit on

TABLE I. Styrene-Methacrylic Acid Copolymerizations. Mass Polymerization at 60°, 0.1% Bz₂O₂

Monomer, mole % styrene	Conversion, wt. %	Analyses				Copolymer, mole % styrene
		Carbon		Hydrogen		
		I	II	I	II	
95.0	< 3	85.67	85.53	7.44	7.54	78.4
75.0	< 3	76.97	77.01	7.76	7.69	54.2
50.0	< 3	72.23	72.33	7.66	7.73	39.7
25.0	< 3	66.60	66.35	7.30	7.29	25.6
5.0	< 3	59.24	59.03	7.28	7.05	8.4

TABLE II. Styrene-Acrylic Acid Copolymerizations. Mass Polymerization at 60°, 0.1% Bz₂O₂

Monomer, polymer- mole % styrene	Time at polymer- ization temp., hrs.	Conversion wt. %	Analyses				Copolymer, mole % styrene
			Carbon		Hydrogen		
			I	II	I	II	
93.0	Very short	< 3	86.40	86.44	7.54	7.56	81.6
50.5	Very short	< 3	75.68	75.72	7.06	7.11	52.3
27.1	24 hrs. at 23°	< 3	72.52	72.82	7.36	7.16	45.4
7.7	Same as above		63.60	63.60	6.71	6.58	26.5

TABLE III. Vinylidene Chloride - Crotonic Acid Copolymerizations. Dioxane Solution Polymerization at 60°, 0.1% Bz₂O₂

Monomer, mole % vinylidene chloride	Time at polymer- ization temp., hrs.	Conversion wt. %	Chlorine		Copolymer, mole % vinylidene chloride
			I	II	
88.9	--	< 3	72.65	72.66	99.3
42.2	3.0	< 3	70.81	71.17	96.5
18.25	2.0	< 3	67.62	67.75	91.6

TABLE IV. Vinyl Acetate - Crotonic Acid Copolymerizations. Mass Polymerization at 68°, 0.05% Bz₂O₂

Monomer, Mole % vinyl acetate	Time at polymer- ization temp., hrs.	Conversion, wt. %	Acid No. ^a		Copolymer, mole % vinyl acetate
			I	II	
90	16.5	5.0	134.9	136.3	79.2
80	16.5	1.6	188.9	196.9	70.4
60	16.5	1.6	276.5	274.5	57.8
40	16.5	2.0	297.9	300.9	54.0

^aMilligrams of KOH to neutralize 1 gram of sample. Titrations were carried out in alcohol-water solution using phenolphthalein as indicator.

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TABLE V. Acrylonitrile - Vinyl 2-Ethylhexoate Copolymerizations
Mass Polymerization at 30°C.

Monomer, mole % acrylo- nitrile	Time at polymer- ization temp., months	Conversion, wt. %	Nitrogen analysis	Copolymer, mole % acrylonitrile
88.4	2	3	24.64, 24.39	97.8
69.5	2	3	22.98, 23.10	95.5
47.5	2	3	20.03, 19.88	91.0
23.4	2	5.4	15.32	81.5
18.8	2	3.2	13.25	76.5

TABLE VI. Acrylonitrile - Vinyl Formate Copolymerizations.
Mass Polymerization at 60°, 0.05% Bz₂O₂

Monomer, mole % acrylo- nitrile	Time at polymer- ization temp.	Conversion, wt. %	Nitrogen		Copolymer, mole % acrylonitrile
			I	II	
66.7	6 days	0.1	21.06	--	84.3
47.6	6 days	0.18	19.88	19.70	80.3
25.4	72 hrs.	0.1	14.72	14.29	63.3
13.12	24 hrs.	0.2	13.24	13.26	57.8

TABLE VII. Acrylonitrile - Vinyl Benzoate Copolymerizations.
Mass Polymerization at 75°, 0.05% Bz₂O₂

Monomer, mole % acrylonitrile	Conversion, wt. %	Nitrogen		Copolymer, mole % acrylonitrile
		I	II	
86.8	0.2	22.88	22.94	95.0
71.3	5.0	21.67	21.42	92.5
53.6	1.6	19.07	18.73	87.5
23.3	2.2	12.08	12.18	70.8
13.2	2.0	8.75	8.70	58.0

TABLE VIII. Acrylonitrile - Acetoxystyrene Copolymerizations.
Mass Polymerization at 75°, 0.05% Bz₂O₂

Monomer, mole % acrylonitrile	Conversion, wt. %	Nitrogen		Copolymer, mole % acrylonitrile
		I	II	
96.6	0.4	12.29	12.55	73.7
77.5	2.4	7.01	7.06	52.5
53.8	4.6	5.80	5.47	45.5
20.8	1.6	2.99	2.99	28.0
17.6	4.0	2.59	2.79	25.8

TABLE IX. Acrylonitrile - Allyl Chloride Copolymerizations. Mass Polymerization at 60°, 0.1% Bz₂O₂

Monomer, mole % acrylo- nitrile	Time at polymer- ization temp., hrs.	Conversion, wt. %	Nitrogen		Copolymer, mole % acrylon- itrile
			I	II	
68.4	8.0	2.2	22.15	22.28	88.2
59.0	8.0	2.0	21.30	21.64	86.0
38.2	144.0	0.6	17.10	17.49	73.3
13.84	144.0	0.2	10.57	10.65	49.0
7.08	68.0	0.4	8.15	8.30	39.4

TABLE X. Vinylidene Chloride - Vinyl Benzoate Copolymerizations. Mass Polymerization Using No Catalyst

Monomer, mole % vinyl- idene chloride	Time at polymer- ization temp., hrs.	Conversion, wt. %	Polymer- ization Temp., °C.	Chlorine analysis	Copolymer, mole % vinyl- idene chloride
93.2	3.75	< 3	24	69.90	96.95
82.1	5.0	< 3	24	68.82	95.94
69.6	72.5	< 3	24	66.31	93.60
21.2	216.0	< 3	50	40.43	65.28
7.4	483.0	< 3	50	23.90	42.60

TABLE XI. Vinylidene Chloride - Methyl Isopropenyl Ketone Copolymerizations. Mass Polymerization Using No Catalyst at 60° C.

Monomer, mole % vinylidene chloride	Conversion, wt. %	Chlorine analysis	Copolymer, mole % vinylidene chloride
95	< 3	59.20	75.5
75	< 3	34.67	39.4
50	< 3	16.46	17.2
25	< 3	7.68	7.8
5	< 3	2.92	2.9

TABLE XII. Vinyl Chloride - Vinyl Isobutyl Ether Copolymerizations. Mass Polymerization at 50° C. Using 1.0% Bz₂O₂

Monomer, mole % vinyl chloride	Time at polymer- ization temp., hrs.	Conversion, wt. %	Chlorine analyses		Copolymer, mole % vinyl chloride
			I	II	
96.82	1.25	1.0	55.70	56.06	99.0
93.51	1.25	1.0	55.96	55.62	98.9
87.44	16.0	2.7	49.20	49.69	91.5
71.47	16.0	3.0	43.58	43.91	84.3
51.19	16.0	3.7	37.37	37.25	75.1
7.78	16.0	1.0	21.16	21.47	49.0

TABLE XIII. Styrene - Citraconic Anhydride Copolymerizations.
Mass Polymerization at 60°C. Using No Catalyst

Monomer, mole % styrene	Conversion, wt. %	Analyses				Copolymer, mole % styrene
		Carbon		Hydrogen		
		I	II	I	II	
95	< 3	81.38	81.18	6.62	6.58	73.3
75	< 3	77.41	77.29	6.44	6.22	63.8
50	< 3	73.17	72.81	6.25	6.08	53.2
25	< 3	70.98	70.67	6.43	5.98	48.3
5	< 3	69.81	69.49	5.67	5.43	44.1

substitution in the differential copolymer equation (6,7). This method gives more weight to the individual contributions of all experimental points than the intersecting method of Mayo and Lewis. The reactivity ratios for these systems and azeotropic compositions where they exist are given in Table XIV.

It is of interest that the azeotrope of the system styrene-methacrylic acid (74%) occurs at a much higher acid concentration than that of styrene-acrylic acid (48%). This difference is reflected in *Q* and *e* values of methacrylic acid as calculated from the Price and Alfrey relationship (1):

$$r_1 = \frac{Q_1}{e_1} e^{-e_1(e_1-e_2)}$$

$$r_2 = \frac{Q_2}{e_1} e^{e_2(e_1-e_2)} = \frac{Q_2}{Q_1} e^{-e_2(e_2-e_1)}$$

	$\frac{Q_1}{e_1}$	$\frac{e_1}{e_2}$
Acrylic acid*:	1.58 ± 0.05	1.0 ± 0.05
Methacrylic acid*:	2.0 ± 0.1	0.7 ± 0.05

These values may be interpreted as evidence of higher resonance stability of the radical adduct formed from methacrylic acid than from acrylic acid, and lower polarity of methacrylic acid than acrylic acid.

It will be noted that an azeotrope occurs in the system vinyl acetate-crotonic acid, but not in vinylidene chloride-crotonic acid. The cause for this is probably due to the higher resonance stability of radical adducts from vinylidene chloride than from vinyl acetate.

The data on acrylonitrile copolymerization with vinyl formate and vinyl 2-ethylhexoate supplements the vinyl acetate-acrylonitrile copolymerization data ($r_1 = 0.02 \pm 0.02$, $r_2 = 6 \pm 2$) reported previously (2). It will be noted that vinyl ester reactivity in copolymerization diminishes as the chain length increases. The comparatively high r_1 value (0.05 ± 0.005) of the vinyl benzoate-acrylonitrile system indicates a contribution of the aromatic nucleus to radical adduct stability even though no conjugation of the vinyl group exists.

*Based on styrene values of $Q = 1$; $e = -0.8$.

The system α -acetoxystyrene-acrylonitrile shows that the polar and steric effects of an α -acetoxy group in styrene are of little importance in copolymerization with acrylonitrile (2). Conjugation of the vinyl group with the phenyl nucleus is the major factor in copolymerization of styrene derivatives.

Allyl chloride exhibits an expectedly low tendency to copolymerize with acrylonitrile. The copolymerization of vinylidene chloride and vinyl benzoate shows a lower resonance stabilization of vinyl benzoate than vinylidene chloride.

The copolymerization of methyl isopropenyl ketone and vinylidene chloride shows the considerable effect of vinyl ketone conjugation on resonance stabilization.

TABLE XIV.

	r_1		r_2		Composition (8.) of azeotrope in % M_2	
Styrene-methacrylic acid	0.15 \pm	.01	0.7 \pm	0.05	74	
Styrene-acrylic acid	0.15 \pm	.01	0.25 \pm	0.02	48	
Crotonic acid-vinylidene chloride	0.065 \pm	.005	35 \pm	5	--	
Vinyl acetate-crotonic acid	0.3 \pm	.05	0.01 \pm	0.01	44	
Vinyl 2-ethylhexoate- acrylonitrile	0.01 \pm	.01	12 \pm	2	--	
Vinyl formate-acrylo- nitrile	0.04 \pm	.005	3.0 \pm	0.05	--	
Vinyl benzoate-acrylo- nitrile	0.05 \pm	.005	5.0 \pm	0.05	--	
- Acetoxystyrene-acrylo- nitrile	0.4 \pm	.05	.08 \pm	0.01	40	
Allyl chloride-acrylo- nitrile	0.05 \pm	.01	3.0 \pm	0.2	--	
Vinyl benzoate-vinyl- idene chloride	0.1 \pm	.02	7.0 \pm	1	--	
Methyl isopropenyl ketone- vinylidene chloride	4.5 \pm	.1	0.15 \pm	0.02	--	
Vinyl chloride-vinyl iso- butyl ether	2.0 \pm	.2	0.02 \pm	0.01	--	
Styrene-citraconic anhyd- ride	0.15 \pm	.02	0.01 \pm	0.01	44	

The copolymerization of vinyl chloride and vinyl isobutyl ether indicates that vinyl isobutyl ether has an even lower resonance stabilization of its adduct than vinyl chloride. The ready formation of this copolymer is interesting in view of the fact that, according to our own observations vinyl isobutyl ether will not polymerize alone by free radical catalysis.

The copolymerization of styrene and citraconic anhydride was found to yield a copolymerization curve similar to that of styrene-maleic anhydride previously reported by Alfrey (8). It appears that citraconic anhydride is slightly less reactive toward a styrene free radical than maleic anhydride.

EXPERIMENTAL

Styrene monomer. Redistilled Monsanto Chemical Co. material was used

Acrylonitrile was the redistilled product of American Cyanamid Co.

Methacrylic acid was the redistilled Rohm and Haas product.

Acrylic acid was the redistilled Rohm and Haas product.

Vinylidene chloride was the redistilled Dow Chemical Co. product.

Vinyl isobutyl ether was the redistilled General Aniline Corp. product.

Crotonic acid was obtained from Shawinigan Chemical Corp. and used as received.

Allyl chloride was the redistilled Shell Chemical Corp. product.

Benzoyl peroxide. The Lucidol Corp. product was used as received.

Copolymerization Method

Essentially the same experimental procedure was used for determining all monomer-copolymer relationships. A total of 100 g. of mixed monomers was placed in 4 oz. French square bottles with the desired quantity of benzoyl peroxide. The concentrations used are shown in Tables I-XIII. The air above the reaction mixture was swept out with nitrogen and the bottle was closed with a metal cap. Polymerization times and temperatures are described in Tables I-XIII. An air oven regulated to $\pm 1^\circ$ was used, and polymerization was interrupted at the point of slight viscosity increase or appearance of insoluble polymer (as in the case of copolymers containing above 60% acrylonitrile). The copolymer formed was isolated by pouring the reaction mixture into 3000 ml. of denatured ethanol (2B) at room temperature or into hexane in case of acrylic acid, methacrylic acid, or crotonic acid copolymers. Bottle rinsings were added to the precipitated mixture. The mixture was then boiled to render filtration easier and filtered. After triturating the copolymer with two successive quantities of 1500 ml. portions of ethanol, it was dried in an evaporating dish for two days in a circulating air oven at 60°C . and analyzed for nitrogen by the micro-Dumas method in the case of acrylonitrile copolymers, for carbon and hydrogen by combustion in the case of acrylic acid, methacrylic acid or citraconic anhydride copolymers, for chlorine by the Parr bomb method in the case of vinyl chloride or vinylidene chloride copolymers, or by acid number in the case of vinyl acetate-crotonic acid copolymers. Copolymerizations of vinyl chloride-vinyl isobutyl ether, vinylidene chloride-vinyl benzoate, and vinylidene chloride-crotonic acid were carried out in capped soda pop bottles under pressure. After the desired conversion was attained, pressure was released by puncturing the cap with an ice pick. Conversions and analyses for all copolymerizations are given in Table I-XIII.

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Synopsis

Information concerning monomer reactivity in copolymerization has been obtained for thirteen copolymerization systems. The influence of substituents and chain length in vinyl polymerization is discussed in the light of this and preceding data. Unsaturated acid behavior in copolymerizations is discussed for the first time.

Résumé

Des renseignements concernant la réactivité des monomères au cours des copolymérisations ont été obtenus pour treize systèmes de copolymérisation. L'influence des substituants et de la longueur de chaîne au cours des polymérisations vinyliques est discutée à la lumière de ces résultats précédents. Le comportement d'acides non-saturés dans les copolymérisations est discutée pour la première fois.

Zusammenfassung

Die Reaktivität von Monomeren in Mischpolymerisationen wurden fuer dreizehn Mischpolymerisationssysteme untersucht. Der Einfluss von Ersatzgruppen und Kettenlaenge auf Vinylpolymerisationen wird auf Grund der neu erhaltenen und vorhergehenden Daten erörtert. Das Verhalten ungesättigter Säuren in Mischpolymerisationen wird zum ersten Mal besprochen.

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