

Reactivity Ratios of Some Monomer Pairs*

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The copolymerization behavior of eight monomer pairs has been investigated. The systems which have been studied and the monomer reactivity ratios (r_1 and r_2) are listed in Table I.

TABLE I

System No.	M_1	M_2	r_1	r_2
1	Vinyl acetate	Methyl vinyl ketone	0.05	7.0
2	Vinyl acetate	1-Acetoxy-1,3-butadiene	0.0	*
3	Acrylonitrile	1-Acetoxy-1,3-butadiene	0.0	0.7
4	Methylacrolein	Acrylonitrile	2.0	0.06
5	Vinylsulfonic acid	Methyl methacrylate	0.0	*
6	2,5-Dichlorostyrene	2,5-Dimethylstyrene	1.55	0.27
7	Vinyl acetate	Fumaryl chloride	^b	0.0
8	Styrene	Fumaryl chloride	0.04	0.0

* Very large. ^b See discussion.

EXPERIMENTAL

The preparation and purification of the monomers are described below.

Methyl vinyl ketone azeotrope (du Pont, 85% methyl vinyl ketone) has been purified¹ by fractionation from an acetic anhydride solution at atmospheric pressure. The pure monomer boiled at 81.2°C.

Vinyl acetate (Niacet) was distilled and collected at 71–2°C./760 mm. leaving the nonvolatile inhibitor behind.

1-Acetoxy-1,3-butadiene was prepared by reaction of crotonaldehyde with isopropenyl acetate.² The product distilled at 35°C./35 mm., and n_D^{25} was 1.4640.

Acrylonitrile (American Cyanamid) and methylacrolein (Eastman Kodak) were purified by distillation; b.p. 78 and 68°C., respectively.

Vinylsulfonic acid was prepared by the hydrolysis of ethane disulfonyl chloride; ^{3,4} b.p. 128°/1 mm., $n_D^{25} = 1.4505$.

The inhibitor was removed from du Pont methyl methacrylate by several washings with aqueous sodium carbonate followed by water washings. The monomer was then dried over Drierite, fractionated and collected at 100°C.

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2,5-Dichlorostyrene (Dow) was purified from contaminating polymer.⁵ 2,5-Dimethylstyrene was synthesized by acetylation of *p*-xylene, reduction, and dehydration,⁶ b.p. 75°C./14 mm.

Fumaryl chloride (Eastman Kodak) was employed as received. Styrene (Dow) was washed with dilute alkali, water, dried, and fractionated under vacuum.

All copolymerizations except System 8 (see below) were carried out in sealed Pyrex test tubes at $70 \pm 1^\circ\text{C}$. using benzoyl peroxide, 0.1% by weight of the monomers, as the catalyst. Initial copolymers were isolated, purified, and dried for analysis at 50°C. under vacuum. The experimental data are tabulated below. M_2 is the mole fraction of monomer 2 in the monomer mixture; m_2 the mole fraction of monomer 2 in the copolymer. The monomer reactivity ratios were calculated by fitting the best theoretical curves to the data.

SYSTEM 1

Vinyl Acetate (M_1)-Methyl Vinyl Ketone (M_2)

Tube No.	M_2	% C ⁷	m_2	Conversion (%)
1	0.133	62.42	0.568	<5% for all tubes
2	0.233	66.41	0.856	
3	0.497	67.06	0.900	
4	0.688	67.20	0.908	
5	0.835	67.74	0.945	

The copolymers were isolated by precipitation into hexane and purified by several reprecipitations from acetone into hexane.

SYSTEM 2

Vinyl Acetate (M_1)-1-Acetoxy-1,3-butadiene (M_2)

Tubes were prepared containing various monomer mixtures. Initial copolymers were isolated by precipitation into hexane and purified by reprecipitation from acetone into hexane. Carbon analyses⁷ for all five polymers fell between 63.5 and 63.8% C. Since pure polyacetoxybutadiene contains 63.4% C, it is apparent that these two monomers do not copolymerize. Pure polyacetoxybutadiene is obtained from all monomer mixtures.

SYSTEM 3

Acrylonitrile (M_1)-1-Acetoxy-1,3-butadiene (M_2)

Tube No.	M_2	% N ⁷	m_2	Conversion (%)
1	0.054	7.66	0.532	6.81
2	0.193	7.23	0.556	8.79
3	0.425	4.84	0.676	8.37
4	0.593	5.32	0.652	7.30
5	0.784	3.29	0.768	Low

These polymers were precipitated into hexane and reprecipitated from acetone into hexane.

SYSTEM 4

 Methylacrolein (M_1)-Acrylonitrile (M_2)

Tube No.	M_2	% N [†]	m_2	Conversion (%)
1	0.116	1.48	0.073	0.5
2	0.303	3.15	0.157	4.9
3	0.503	3.88	0.185	5.0
4	0.702	8.09	0.369	4.6
5	0.890	13.73	0.548	3.7

The copolymers were insoluble in the monomer mixtures and were purified by repeated washings with hexane.

SYSTEM 5

 Vinylsulfonic Acid (M_1)-Methyl Methacrylate (M_2)

Tube No.	M_2	% S	M_2	Conversion (%)
1	0.903	0	1.0	<5
2	0.794	0	1.0	<5
3	0.527	0	1.0	<5
4	0.333	0	1.0	<5
5	0.136	—	—	—

Tubes were sealed off under a carbon dioxide atmosphere. Polymers from tubes 1-3 inclusive were precipitated in methanol, reprecipitated from acetone into hexane, extracted with water and dried. Tube 4 was precipitated in water, reprecipitated from methanol into water and dried. No polymer was obtained from tube 5 after five days at 70°C. All polymers were insoluble in alkali. Polymer from tube 4, unlike polymers from tubes 1-3, was soluble in methanol.

SYSTEM 6

 2,5-Dichlorostyrene (M_1)-2,5-Dimethylstyrene (M_2)

Tube No.	M_2	% Cl [†]	m_2	Conversion (%)
1	0.935	9.5	0.813	0.78
2	0.861	15.5	0.684	1.23
3	0.695	23.8	0.484	2.10
4	0.475	30.4	0.312	2.70
5	0.319	33.9	0.213	2.10

The copolymers were precipitated into methanol and purified by reprecipitation from benzene into methanol.

SYSTEM 7

 Vinyl Acetate (M_1)-Fumaryl Chloride (M_2)

Tube No.	M_2	% Cl	m_2	Conversion (%)
1	0.880	26.8	0.435	2.12
2	0.597	23.3	0.362	3.21
3	0.294	22.9	0.356	2.56
4	0.150	19.6	0.292	4.59
5	0.062	17.6	0.256	0.39

Copolymers were precipitated into hexane (distilled from and dried over sodium), reprecipitated from dioxane (purified and dried over sodium) into hexane, and washed with hexane until free of fumaryl chloride. The polymers were dried for three hours at 50°C. under high vacuum and analyzed immediately after drying as follows: samples for analysis were weighed out and dissolved in 10 ml. of dry dioxane; 50 ml. of distilled water containing 0.2 g. of sodium carbonate was added and the solutions boiled until all polymer dissolved. The solutions were then acidified with 6 ml. of 6 *N* nitric acid and the chloride determined by the Volhard method. These copolymers have been found to be unstable and to lose hydrogen chloride on standing although completely dry. Fumaryl chloride shows no tendency to polymerize by itself in the presence of benzoyl peroxide at 70°C.

SYSTEM 8

Styrene (M_1)-Fumaryl Chloride (M_2)

Tube No.	M_1	% Cl	m_2	Conversion (%)
1	0.043	21.90	0.378	1.30
2	0.054	21.45	0.370	0.59
3	0.109	19.75	0.337	1.42
4	0.153	24.80	0.440	1.37
5	0.500	24.95	0.465	1.25
6	0.893	24.95	0.465	1.35

Because of the rapid rates of copolymerization for this system, copolymerizations were carried out at 27°C. without peroxide, in rubber stoppered tubes. The free radical nature of this reaction was verified by the use of hydroquinone which was found to inhibit the polymerization. The copolymers were isolated by precipitation into dry hexane, reprecipitated from sodium distilled benzene into hexane and washed with hexane. The analyses were carried out immediately after 3 hours of drying in the same manner employed for system 7.

DISCUSSION

The study of vinyl acetate with methyl vinyl ketone has shown, as one would expect, that the latter is considerably more reactive in copolymerization. Our experimentally determined values of 0.05 and 7 for r_1 and r_2 do not compare too well with the values of 0.01 and 23 estimated by Mayo and Walling.⁹

1-Acetoxy-1,3-butadiene is so much more reactive than vinyl acetate that the two monomers do not copolymerize, all monomer mixtures yielding pure polyacetoxybutadiene.

1-Acetoxybutadiene adds to acrylonitrile radical at a much greater rate than does acrylonitrile monomer but self propagation is only 0.7 times as fast as the addition of acrylonitrile to acetoxybutadiene radical. Like the butadiene-acrylonitrile system,¹⁰ the alternation tendency is large. 1-Acetoxy-1,3-butadiene appears slightly more reactive than butadiene toward acrylonitrile radical.

Methylacrolein adds both to its own radical and to an acrylonitrile radical at a faster rate than does acrylonitrile monomer. Comparison with data for acrylonitrile-methyl methacrylate¹¹ shows that methylacrolein is approximately three times as reactive as methyl methacrylate toward

acrylonitrile radical. Since methacrylic acid¹² has also been found to be more reactive than the ester, it seems that both aldehyde and carboxyl substituents result in somewhat greater reactivity of the double bond than the carbomethoxyl group.

Contrary to statements made by Alderman, Arden, and Hanford,⁴ we have found that methyl methacrylate and vinylsulfonic acid do not copolymerize to any appreciable extent. As pointed out by Price and Gilbert,¹³ there is no evidence for conjugation between free radical or double bond in methyl vinyl sulfone or sulfoxide. Since resonance stabilization of the radical is probably also absent in vinylsulfonic acid, one would expect this monomer to have a relatively low reactivity in copolymerization. It appears that vinylsulfonic acid is actually less reactive than methyl vinyl sulfone which copolymerizes with methyl methacrylate to only a small extent.¹⁴

2,5-Dichlorostyrene is more reactive than 2,5-dimethylstyrene monomer toward its own radical and toward the radical of 2,5-dimethylstyrene. Data collected by Marvel and co-workers¹⁵ also indicate that the 2,5-dichloro derivative is the more reactive, the relative reactivities of the two monomers toward butadiene being 1.6 and 1.2, respectively, for 2,5-dichloro and the 2,5-dimethylstyrenes.

The deep color of styrene-fumaryl chloride solutions suggests molecular complex formation of the type discussed by Walling *et al.*¹⁶ The alternation tendency in this system is very large, fumaryl chloride adding to styrene radical twenty-five times more rapidly than styrene monomer adds to styrene radical.

Data obtained from copolymerization of vinyl acetate and fumaryl chloride (System 7) do not appear to follow a theoretical copolymerization curve. This may be similar to the anomalous behavior observed by Fordyce and Ham¹⁷ during a study of the styrene-fumaronitrile system, where it has been found that fumaronitrile reactivity diminishes at higher concentrations. However, because of the instability of these copolymers and possible associated error, we do not wish to make a definite statement to this effect at present. If the initial slope is taken as a measure of fumaryl chloride reactivity, an r_1 value of approximately 0.14 is obtained.

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Synopsis

To continue the study of the effect of structure on reactivity, an experimental investigation of the free radical copolymerization behavior of eight monomer pairs has been made. The monomer pairs include: vinyl acetate-methyl vinyl ketone; vinyl acetate-1,3-acetoxybutadiene; acrylonitrile-1,3-acetoxybutadiene; methylacrolein-acrylonitrile; vinylsulfonic acid-methyl methacrylate; 2,5-dichlorostyrene-2,5-dimethylstyrene; vinyl acetate-fumaryl chloride; and styrene-fumaryl chloride.

Résumé

En vue de continuer l'étude de l'effet qu'exerce la structure des monomères sur leur réactivité, une recherche expérimentale a été menée au moyen de la copolymérisation, initiée par des radicaux, au dépens de huit paires de monomères. Les couples suivants de monomères ont été envisagés: acétate de vinyle-méthylvinyle cétone; acétate de vinyle-1,3-acétoxybutadiène; acrylonitrile-1,3-acétoxybutadiène; méthylacroléine-acrylonitrile; acide vinylsulfoniqueméthacrylate de méthyle; 2,5-dichlorostyrène-2,5-diméthylstyrène; acétate de vinyle-chlorure de fumaroyle; et styrène-chlorure de fumaroyle.

Zusammenfassung

Im Laufe der Untersuchung über die Wirkung von Struktur auf die Reaktivität wurde eine experimentelle Untersuchung des Frei-Radikal Copolymerisationsverhaltens von acht Monomerpaairen unternommen. Die Monomerpaaire sind: Vinylacetat-Methylvinylketon; Vinylacetat-1,3-Acetoxybutadien; Acrylnitril-1,3-Acetoxybutadien; Methylacrolein-Acrylnitril; Vinylsulfonsäure-Methylmethacrylat; 2,5-Dichlorstyrol-2,5-Dimethylstyrol; Vinylacetat-Fumarylchlorid; und Styrol-Fumarylchlorid.

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