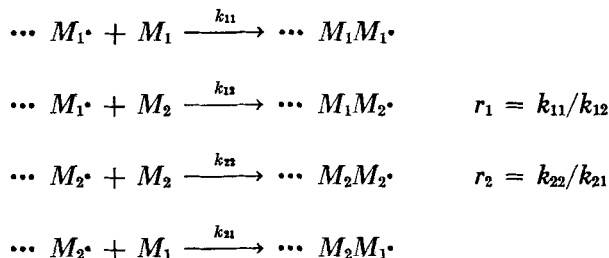# Experimental Study of Copolymerization.   II

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INTRODUCTION

Recent experimental work on free radical copolymerization has led to certain conclusions concerning the effects of structure upon monomer reactivities.[1,2] It has been generally agreed that the competition among different monomers for a given free radical can be influenced by the amount of resonance stabilization, by electrical polarities, and by steric effects.

A number of copolymer systems have been studied in this laboratory in order to test the validity of these conjectures.   The present paper presents experimental results on twelve systems.   The nomenclature used will be that agreed upon by Alfrey, Mayo, and Wall.[3]   In the copolymerization of two monomers, M_1 and M_2, the respective monomer reactivity ratios, r_1 and r_2, will be defined from the equations:

$$\cdots M_1\cdot + M_1 \xrightarrow{\;k_{11}\;} \cdots M_1M_1\cdot$$

$$\cdots M_1\cdot + M_2 \xrightarrow{\;k_{12}\;} \cdots M_1M_2\cdot \qquad r_1 = k_{11}/k_{12}$$

$$\cdots M_2\cdot + M_2 \xrightarrow{\;k_{22}\;} \cdots M_2M_2\cdot \qquad r_2 = k_{22}/k_{21}$$

$$\cdots M_2\cdot + M_1 \xrightarrow{\;k_{21}\;} \cdots M_2M_1\cdot$$

The differential equation for copolymerization then becomes:

$$\frac{d(M_1)}{d(M_2)} = \frac{(M_1)}{(M_2)} \times \frac{r_1(M_1) + (M_2)}{r_2(M_2) + (M_1)}$$

The ratios, r_1 and r_2, thus correspond to the $1/\alpha$ and β of Alfrey and Goldfinger,[4] and σ and μ of Mayo and Lewis,[5] and the σ and ρ of Wall.[6]

[1] T. Alfrey, Jr., E. Merz, and H. Mark, *J. Polymer Research*, 1, 37–43 (1946).

[2] F. M. Lewis, F. R. Mayo, and W. F. Hulse, *J. Am. Chem. Soc.*, 67, 1701 (1945).   C. C. Price, *J. Polymer Sci.*, 1, 83 (1946).   K. Nozaki, *ibid.*, 1, 455 (1946).   T. Alfrey, Jr., and C. C. Price, *ibid.*, 2, 101–106 (1947).

[3] T. Alfrey, Jr., F. R. Mayo, and F. T. Wall, *J. Polymer Sci.*, 1, 581 (1946).

[4] T. Alfrey, Jr., and G. Goldfinger, *J. Chem. Phys.*, 12, 205 (1944).

[5] F. R. Mayo and M. Lewis, *J. Am. Chem. Soc.*, 66, 1594 (1944).

[6] F. T. Wall, *J. Am. Chem. Soc.*, 66, 2050 (1944).

PURIFICATION OF MONOMERS

The inhibitors were removed from methyl, ethyl, and butyl methacrylates (du Pont), and vinylidene chloride (Dow) by repeated washings with sodium carbonate solutions, followed by water washings. They were then dried over Drierite. The monomers were then distilled at reduced pressures through a short packed column.

A continuous purification train was set up for vinyl chloride monomer. Vinyl chloride (Monsanto) was bubbled slowly through two wash bottles of 10% sodium hydroxide solution and passed over Drierite. The gas was then condensed in a 500-ml. Florence flask at Dry Ice temperature. The liquid was collected at a rate of approximately 30 g. per hour. The liquid monomer was then dispensed out of the same condenser with a controlled positive air pressure into tared heavy-walled glass tubes (in Dry Ice) which already contained known quantities of the second monomer and catalyst. Exact weights of vinyl chloride were determined by weighing the tubes on an analytical balance after sealing.

Vinyl acetate (Niacet) was purified by distillation at reduced pressure, leaving the inhibitor, copper sulfate, in the residue.

1-Pentene was used as received from Phillips Petroleum Company. It was stated to be 95 mole per cent minimum purity. The reported impurities were 2-pentene, pentane, and isomers of these compounds.

The allyl chloride, as received from Shell Chemical Corporation, was 99% pure. The reported impurities were 1-chloro-1-propene (*cis* form boils at 32°C., *trans* form boils at 36.7°) and isopropyl chloride (b.p. = 36.5°). This monomer was purified by fractional distillation.

2,5-Dichlorostyrene polymerizes slowly in the solid state in the icebox. To separate the polymer from the monomer, the mixture was brought to room temperature and added to several volumes of methyl alcohol. This precipitated the polymer; the monomer is soluble in methyl alcohol. The solution was then shaken in a separatory funnel with a 2% aqueous sodium hydroxide solution. Several such washings removed the inhibitor from the dichlorostyrene, and also the major part of the methyl alcohol. The dichlorostyrene layer was separated, washed several times with water, and dried over calcium chloride. To prevent premature polymerization, the 2,5-dichlorostyrene was used immediately after purification.

Dioctyl maleate (2-ethylhexyl maleate) was obtained from the Capital Paint and Varnish Works. Principal impurities were maleic anhydride and 2-ethylhexanol. Maleic anhydride was washed out with a sodium chloride solution. The dioctyl maleate layer was dried over calcium chloride, and 2-ethylhexanol was removed by distillation at 1 mm. pressure. The purified dioctyl maleate had a saponification equivalent which was 103% of theoretical.

COPOLYMERIZATION PROCEDURE

Pairs of monomer mixtures were made up over the entire range of compositions, sealed in glass tubes, and placed in a constant temperature bath at 68°C. Benzoyl peroxide was used as catalyst in all cases. Polymerizations were continued until it was estimated that about 5% of the monomers had reacted.

All tubes (System I) contained 0.2% of Bz_2O_2. The copolymers were precipitated in methanol, then dissolved in methyl ethyl ketone and reprecipitated. Samples 1-1 and 1-2 required the benzene freezing technique.[5] The other copolymers came down in the form of bulky fibrous materials and were then removed

from the precipitant as formed, to avoid the formation of gels.   The variation of the composition of the copolymer with mole fraction of M_2 in the monomer mixtures led to the following values for r_1 and r_2: $r_1 = 0.3$; $r_2 = 2.1$.   These values indicate that vinyl chloride enters the copolymer faster than vinyl acetate over the whole range of composition.

SYSTEM I
VINYL ACETATE (M_1)–VINYL CHLORIDE (M_2)

Tube No.	Time, min.	M_2^a	Per cent chlorine in polymer	m_2^b	Conversion, %	M_2^* (corr.)
1-1	105	0.109	10.7	0.252	10.4	0.102
1-2	110	0.415	30.3	0.611	14.7	0.401
1-3	160	0.511	35.5	0.697	$(10.7)^d$	(0.50)
1-4	190	0.520	39.5_5	0.760	$(15.5)^d$	(0.50)
1-5	60	0.863	46.8	0.866	1.3	
1-6	75	0.062	7.61	0.174	1.0	
1-7	75	0.368	28.6	0.577	1.0	
1-8	75	0.519	35.4_5	0.697	2.4	
1-9	65	0.741	45.7	0.850	5.2	
1-10	65	0.870	51.6_5	0.934	4.9	
1-11	65	0.928	53.6	0.958	5.8	

^{a} Mole fraction of vinyl chloride in monomer mixture.
^{b} Mole fraction of vinyl chloride in copolymer.
^{c} Average mole fraction of vinyl chloride in monomer mixture (corrected for conversion).
^{d} Incomplete recovery of polymer.
Note.   For yields greater than 6%, a correction was applied to M_2; M , the *average* value of M_2 during the polymerization, was used instead of the *initial* value.

Marvel and co-workers[7] have studied this system.   Most of their runs were carried to high conversion.   Three runs, however, were stopped at 3.4, 5.6, and 11% conversion, respectively.   Results reported for these three runs agree well with our composition data.

SYSTEM II
ETHYL METHACRYLATE (M_1)–VINYLIDENE CHLORIDE (M_2)

Tube No.	Time, min.	M_2	Per cent chlorine in polymer	m_2	Conversion, %	M_2^*
2-1	100	0.112	3.8	0.061	10.5	0.115
2-2	100	0.266	9.2	0.144	12.0	0.273
2-3	100	0.413	15.5	0.241	11.3	0.422
2-4	100	0.610	26.5	0.400	10.4	0.621
2-5	100	0.790	40.7	0.610	8.7	0.798
2-6	120	0.922	57.0	0.805	6.0	0.926

Tubes contained 0.2% of benzoyl peroxide.   The copolymers were precipitated twice in methanol from dilute acetone solutions.

[7] C. S. Marvel, G. D. Jones, T. W. Mastin, and G. L. Schertz, *J. Am. Chem. Soc.*, **64**, 2356 (1942).

SYSTEM III

BUTYL METHACRYLATE (M_1)–VINYLIDENE CHLORIDE (M_2)

Tube No.	Time, min.	M_1	Per cent chlorine in polymer	m_1	Conversion, %	M_1^*
3-1	90	0.092	2.44	0.048	10.2	0.094
3-2	90	0.433	14.1	0.260	8.2	0.440
3-3	90	0.400	12.4	0.230	9.2	0.408
3-4	90	0.598	22.3	0.392	8.9	0.607
3-5	120	0.763	37.1	0.601	10.6	0.772
3-6	120	0.920	54.2	0.806	4.9	0.923

All tubes contained 0.2% of benzoyl peroxide. The copolymers were precipitated twice in methanol from acetone solutions. Samples 3-5 and 3-6 required the addition of methyl ethyl ketone to the acetone to effect solution of the copolymer.

Ethyl and butyl methacrylate polymerizations with vinylidene chloride monomer give points that fall on the same curve (Fig. 1). Values of $r_1 = 2.2$ and $r_2 =$
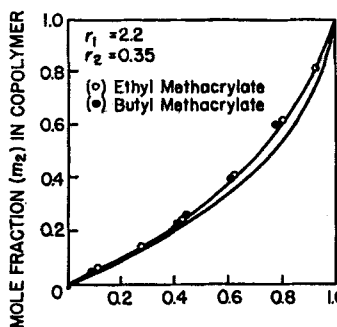

Fig. 1. Copolymer composition curves for the system ethyl methacrylate–vinylidene chloride and butyl methacrylate – vinylidene chloride (M_2) at 68°C. (upper curve), and for methyl methacrylate – vinylidene chloride (M_2) at 40° (lower curve).
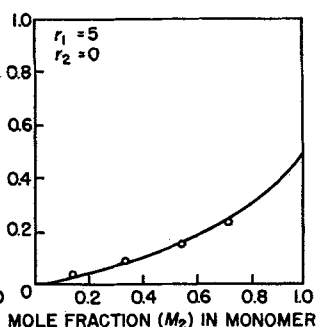
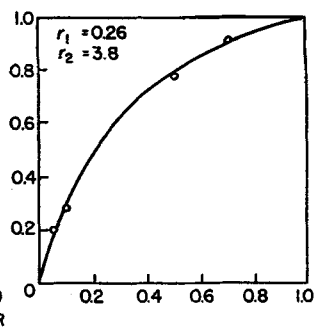Fig. 2. Copolymer composition curve for the system vinyl acetate (M_1)–tetrachloroethylene (M_2).

Fig. 3. Copolymer composition curve for the system allyl chloride (M_1)–vinylidene chloride (M_2).

0.35 indicate that the methacrylates are more reactive than vinylidene chloride over the entire composition range. Furthermore, this investigation shows that the length of the ester group has little influence on the copolymerization. The data of Lewis, Mayo, and Hulse[2] give for the system, methyl methacrylate–vinylidene chloride at 40°C., values that are not very much different, namely, $r_1 = 2.5$ and $r_2 = 0.24$. Results for all three systems are shown together in Figure 1. The lower curve represents the values reported by Lewis, Mayo, and Hulse.[2]

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System IV
Vinyl Acetate (M_1)–Tetrachloroethylene (M_2)

Tube No.	Time, min.	M_2	Per cent chlorine in polymer	m_2	Conversion, %	M_2^*
4-1	80	0.126	6.79	0.043	30	0.138
4-2	185	0.308	14.2	0.093	22	0.332
4-3	335	0.528	22.9	0.159	8.0	0.543
4-4	12 hr.	0.716	31.6	0.234	1.0	0.716
4-5	52 hr.	0.93	—[a]			

[a] Yield was too small for analysis.

All tubes contained 0.33% of benzoyl peroxides. The copolymers were dissolved in benzene and precipitated as a granular precipitate in hexane. The data are plotted in Figure 2. The reactivity ratios were: $r_1 = 5$; $r_2 = 0$.

System V
Allyl Chloride (M_1)–Vinylidene Chloride (M_2)

Tube No.	Time	M_2	Per cent chlorine in polymer	m_2	Conversion, %
5-1	1 hr.	0.709	71.0	0.921	1.1
5-2	2³/₄ hrs.	0.499	67.2	0.779	5.2
5-3	18 hr.	0.297	59.4	0.485	10[a]
5-4	20 hr.	0.099	54.0	0.282	5[a]
5-5	7 days	0.053	51.9	0.201	3[a]

[a] Estimated.

All tubes contained 0.3% benzoyl peroxide. Samples 5-1 and 5-2 were dissolved in benzene (not a very good solvent) and were precipitated in methanol. The polymers obtained in this manner were fine powders. By this method, samples 5-3, 5-4, and 5-5 precipitated as gums. The benzene freezing technique was attempted, but even this gave polymers of unsatisfactory form.

The best values for r_1 and r_2 obtained for the system vinylidene chloride–allyl chloride are: $r_1 = 0.26$; $r_2 = 3.8$. See Figure 3.

System VI
Vinyl Acetate (M_1)–Vinylidene Chloride (M_2)

Tube No.	Time	M_2	Per cent chlorine in polymer	m_2	Conversion, %
6-1	40 min.	0.922	72.6	0.989	1.2
6-2	40 min.	0.775	69.2	0.942	1.3
6-3	1¹/₂ hrs.	0.586	65.6	0.888	6.5
6-4	3 hrs.	0.214	50.3	0.662	4.0
6-5	3¹/₂ hrs.	0.120	40.7	0.527	2.9

All tubes contained 0.1 g. of benzoyl peroxide as catalyst (about 0.3% by weight). Samples 6-1, 6-2, and 6-3 were soluble in benzene, and were precipitated as fine powders in methanol. Samples 6-4 and 6-5 were prepared as powders by the benzene freezing technique.
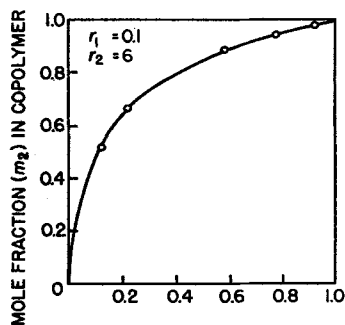

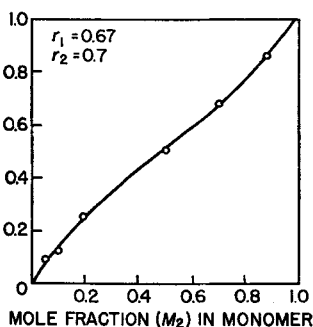Fig. 4. Copolymer composition curve for the system vinyl acetate (M_1)–vinylidene chloride (M_2).

Fig. 5. Copolymer composition curve for the system allyl chloride (M_1)–vinyl acetate (M_2).
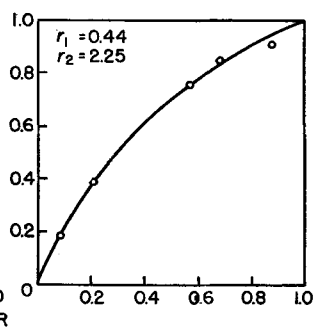
Fig. 6. Copolymer composition curve for the system methyl methacrylate (M_1)–2,5-dichlorostyrene (M_2).

The best values for r_1 and r_2 obtained for the system vinylidene chloride–vinyl acetate are: $r_1 = 0.1$; $r_2 = 6$. See Figure 4.

SYSTEM VII
METHYL METHACRYLATE (M_1)–VINYL CHLORIDE (M_2)

Tube No.	Time, hours	M_2	Per cent chlorine in polymer	m_2	Conversion, %
7-1	10	0.220	1.4	0.038	11.1
7-2	10	0.378	2.1	0.057	6.0
7-3	10	0.659	5.3	0.159	18.9
7-4	10	0.766	13.7	0.336	29.6
7-5	10	0.929	28.3	0.613	14.9
7-6	10	0.939	33.7	0.703	7.8

All samples contained approximately 0.30% by weight of benzoyl peroxide. Samples were dissolved in methyl ethyl ketone and precipitated in hexane. The yields for this system are somewhat high. One can correct for these yields as indi-

SYSTEM VIII
·PENTENE-1 (M_1)–VINYL CHLORIDE (M_2)

Tube No.	Time, hours	M_2	Per cent chlorine in polymer	m_1	Conversion, %
8-1	5¹/₂	0.909	52.9	0.955	8
8-2	22	0.807	51.4	0.945	5
8-3	72	0.520	42.3	0.840	1.2

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cated under System I. The corrected data lead to $r_1 = 10$ and $r_2 = 0.1$, indicating that methyl methacrylate is about ten times more reactive than vinyl chloride.

All samples contained 0.1 gram of benzoyl peroxide. These samples all dissolved in methyl ethyl ketone with difficulty, and precipitated in methanol to give powdered polymer. In this system only three points have been obtained. When plotted, the points do not appear to extrapolate to 100% vinyl chloride. However, it has been found that the analysis of pure polyvinyl chloride is always slightly low. If one roughly corrects the chlorine analyses of the vinyl chloride–pentene copolymers by adding 1.0% to each analysis, the composition curve comes in at the 100% line. Since the data are not complete, it is impossible to calculate definite values for r_1 and r_2, but an estimate of r_2 would be about 5. No quantitative estimate of r_1 can be made, but this ratio is almost certainly less than 0.2.

SYSTEM IX
ALLYL CHLORIDE (M_1)–VINYL ACETATE (M_2)

Tube No.	Time, hours	M_2	Per cent chlorine in copolymer	m_2	Conversion, %
9-1	342	0.052	41.7	0.090	
9-2	342	0.100	40.1	0.121	
9-3	76	0.200	33.4	0.257	Estimated
9-4	76	0.504	21.8	0.500	below 7%
9-5	30	0.708	13.8	0.677	
9-6	8	0.883	6.3	0.851	

0.4% benzoyl peroxide was used as catalyst. Samples 9-3 through 9-6, inclusive, were purified by dissolving in benzene and precipitating with hexane. The copolymers precipitated as sticky transparent gums which were not markedly improved by the benzene freezing technique. Samples 9-1 and 9-2 showed little increase in viscosity after 342 hours, at which time they were removed from the bath and allowed to evaporate. Oily residues remained which were purified by stirring with hexane (in which they were insoluble) and decanting. These two samples were obviously of low molecular weight.

Because of the nature of the copolymer, exact conversion values could not be obtained. Applying the copolymerization equation and fitting the best curve to the data gave the following values for r_1 and r_2: $r_1 = 0.67$; $r_2 = 0.7$. See Figure 5. The data indicate that both monomers have about equal reactivity.

SYSTEM X
METHYL METHACRYLATE (M_1)–2,5-DICHLOROSTYRENE (M_2)

Tube No.	Time, hours	M_2	Per cent chlorine in polymer	m_2	Conversion (approx.), %
10-1	1.5	0.091	11.5	0.184	6.5
10-2	1.5	0.208	21.4	0.388	6
10-3	6	0.57	34.5	0.755	6.8
10-4	9.5	0.68	37.1	0.846	15.7
10-5	9	0.878	38.5	0.899	6.2

The polymers were precipitated from benzene, using methanol as precipitant. They came out as white, fluffy masses which were filtered and dried to constant weight. Best values of r_1 and r_2 were found to be: $r_1 = 0.44$; $r_2 = 2.25$. See Figure 6.

SYSTEM XI
VINYL CHLORIDE (M_1)–VINYLIDENE CHLORIDE (M_2)

Tube No.	Time, min.	M_2	Per cent chlorine in polymer	m_2	Conversion (approx.), %
11-1	30	0.793	73.5	1.01	5.2
11-2	35	0.852	73.3	1.008	3.1
11-3	135	0.265	68.2	0.701	4.6
11-4	135	0.101	62.9	0.363	4.8
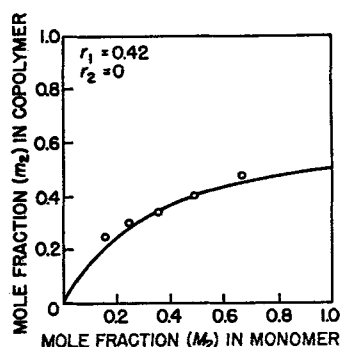
Fig. 7. Copolymer composition curve for the system vinyl chloride (M_1)–dioctyl maleate (M_2).

The copolymers at the high vinyl chloride end of the series could be dissolved in methyl ethyl ketone and precipitated with methanol. At the high vinylidene chloride end, however, because of the low solubility in methyl ethyl ketone, the purification consisted of repeated washing with methanol. Fine, white powders were obtained which could be dried to constant weight without difficulty.

The high chlorine content of the samples and the relative closeness of the chlorine contents of vinylidene chloride and vinyl chloride monomers lead to larger uncertainties than usual. Further experiments are planned with this system. The provisional values of r_1 and r_2 as obtained from the above data are as follows: $r_1 = 0.14$; r_2 is very large.

SYSTEM XII
VINYL CHLORIDE (M_1)–DIOCTYL MALEATE (M_2)

Tube No.	Time, hours	M_2	Per cent chlorine in polymer	m_2	Conversion (approx.), %
12-1	6.2	0.842	20.4	0.755	6.2
12-2	8.2	0.755	20.2	0.750	33
12-3	8.2	0.646	14.6	0.66	2.3
12-4	15.2	0.51	12.0	0.60	10.3
12-5	50	0.333	9.5	0.528	3.8

The polymers were glassy soft masses, their softness increasing with higher dioctyl maleate content. They were dissolved in methyl ethyl ketone and precipitated with methanol. Sample 12-5 was precipitated with methanol containing 10–15% water; this mixture dissolves monomeric dioctyl maleate. The results, plotted in Figure 7, lead to the following values for r_1 and r_2: $r_1 = 0.42$; $r_2 = 0$.

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DISCUSSION

The detailed analysis of these results in terms of the semiquantitative scheme[8] referred to in the introduction will be deferred until a number of additional monomer pairs have been studied. The following observations, however, can be made:

(1) In those cases where a 1,2 disubstituted ethylene was taken as monomer M_2, the ratio r_2 was observed to be equal to zero, within experimental error. This indicates a very low rate constant for self-propagation with such monomers. The conclusion, previously made,[9,10] that such monomers exhibit a specific reluctance to add to themselves in a growing chain, is thus confirmed here.

(2) In every case involving vinyl or vinylidene monomers (monosubstituted or 1,1-disubstituted ethylenes), the more reactive monomer is the one with greater amount of resonance stabilization. (This statement requires us to postulate a certain amount of double bond character in the bond between a chlorine atom and a carbon atom possessing an odd electron.) Striking examples are provided by Systems II, III, V, VI, VII, VIII, X, and XI.

(3) It should be noted that allyl chloride, vinyl acetate, and vinyl chloride all possess roughly the same reactivity with free radicals, even though allyl chloride exhibits a far lower *over-all rate* of polymerization by itself than do vinyl acetate and vinyl chloride. This presumably is an (indirect) indication of the importance of "degradative" chain transfer reactions[11] in the polymerization of allyl chloride. For example:

$$R\cdot + CH_2{=}CH{-}CH_2Cl \longrightarrow RCl + CH_2{=}CH{-}\overset{\centerdot}{C}H_2$$
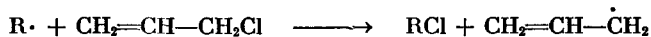
Such a reaction would act essentially as a termination step because of the low reactivity of the allylic radical.

(4) The reactivity of 1-pentene with at least one free radical is found to be less than the reactivity of vinyl chloride, vinyl acetate, etc.—but not less by a very great factor. We believe that the reluctance of olefins to polymerize by a free radical mechanism may be due to competing chain transfer reactions rather than to a low reactivity of the double bond with free radicals.

Synopsis

In order to study further the effect of structure on monomer reactivities in copolymerization the copolymer composition as a function of initial monomer mixture composition has been determined for the following monomer pairs: vinyl acetate–vinyl chloride, ethyl methacrylate–vinylidene chloride, butyl methacrylate–vinylidene chloride, vinyl acetate–tetrachloroethylene, allyl chloride–vinylidene chloride, vinyl acetate–vinylidenechloride, methyl methacrylate–vinyl chloride, pentene-1–vinyl chloride, allyl chloride–vinyl acetate, methyl methacrylate–2,5-dichlorostyrene, vinyl chloride–vinylidene chloride, and vinyl chloride–dioctyl maleate.

[8] F. M. Lewis, F. R. Mayo, and W. F. Hulse, *J. Am. Chem. Soc.*, 67, 1701 (1945). C. C. Price, *J. Polymer Sci.*, 1, 83 (1946). K. Nozaki, *ibid.*, 1, 455 (1946). T. Alfrey, Jr., and C. C. Price, *ibid.*, 2, 101–106 (1947).

[9] T. Alfrey, Jr., E. Merz, and H. Mark, *J. Polymer Research*, 1, 37–43 (1946).

[10] T. Alfrey, Jr., and E. Lavin, *J. Am. Chem. Soc.*, 67, 2044 (1945).

[11] P. D. Bartlett and R. Altschul, *J. Am. Chem. Soc.*, 67, 816 (1945).

Résumé

En continuant les études de l'effect de la structure sur les activités des monomères au cours de la polymérisation, la composition en fonction de la composition du mélange du monomère a été déterminée pour les pairs de monomère suivant: acétate de vinyle – chlorure de vinyle, méthacrylate d'éthyle – chlorure de vinylidène, méthacrylate de butyle – chlorure de vinylidène, acétate de vinyle – tetrachlorure d'éthylène, chlorure d'allyle – chlorure de vinylidène, acétate de vinyle – chlorure de vinylidène, méthacrylate de méthyle – chlorure de vinyle, pentèn-1-chlorure de vinyle, chlorure d'allyle – acétate de vinyle, méthacrylate de méthyle – 2,5-bichlorure de styrène, chlorure de vinyle – chlorure de vinylidène et chlorure de vinyle – maléate de bioctyle.

Zusammenfassung

Um das Studium des Einflusses der Struktur auf die Reaktionsfähigkeit von Monomeren bei Mischpolymerisation weiter zu verfolgen, wird die Zusammensetzung als Funktion der Anfangszusammensetzung der Mischung für die folgenden Monomerpaare von Mischpolymerisaten bestimmt: Vinylacetat – Vinylchlorid, Äthylmethacrylsäure–Vinylidenchlorid, Butylmethacrylsäure – Vinylidenchlorid, Vinylacetat – Tetrachloräthylen, Allylchlorid – Vinylidenchlorid, Vinylacetat – Vinylidenchlorid, Methylmethacrylsäure – Vinylchlorid, Penten-1 – vinylchlorid, Allylchlorid – Vinylacetat, Methylmethacrylsäure – 2,5-Dichlorstyrol, Vinylchlorid – Vinylidenchlorid und Vinylchlorid – Dioctylmaleat.