

## Experimental Study of Copolymerization. IV\*

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We have investigated the copolymerization behavior of fourteen monomer pairs. The systems investigated and the reactivity ratios ( $r_1$  and  $r_2$ ) obtained are given in Table I.

TABLE I

System	$M_1$	$M_2$	$r_1$	$r_2$
I	Vinylidene chloride	Indene	0.40	0.33
II	<i>o</i> -Chlorostyrene	Indene	3.50	0.0
III	Vinylidene chloride	Coumarin	<sup>a</sup>	0.0
IV	Vinylidene chloride	Methacrylic acid	0.15	3.0
V	<i>o</i> -Chlorostyrene	Methacrylic acid	0.12	0.70
VI	Methyl methacrylate	2-Vinylpyridine	0.33	0.70
VII	Vinyl acetate	2-Vinylpyridine	0.0	30
VIII	Methyl methacrylate	Methyl $\alpha$ -chloroacrylate	0.30	1.2
IX	Acrylonitrile	Methyl $\alpha$ -chloroacrylate	0.15	2.0
X	Vinyl chloride	<i>tert</i> -Butylethylene	5.	0.0
XI	Vinyl acetate	1,1-Dichloro-2,2-difluoro-ethylene	0.6	0.0
XII	Vinyl acetate	Acrylonitrile	0.07	6.0
XIII	Vinyl chloride	Diethyl maleate	0.9	0.0
XIV	Styrene	Hexachlorobutadiene	•	0.0

\* Very large.

Note: Estimated errors in above values are  $\pm 15\%$  of reported values.

## EXPERIMENTAL

The preparation of most of the monomers used has already been described.<sup>1</sup> The others are described below.

*Coumarin* (m.p. 71°C.) was purchased from Eimer & Amend, and used as received.

*Indene* (m.p.  $-2.0^\circ\text{C}.$ ) was obtained from Barrett Division, Allied Chemical & Dye Corp. The sample had been purified by recrystallization and was used as received.

*1,1-Dichloro-2,2-Difluoroethylene* was obtained from E. I. du Pont de Nemours & Co., Inc. The brass cylinder in which it was shipped was con-

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nected to a Dry Ice trap, and the contents allowed to distil over at room temperature. Subsequent handling was similar to that used for vinyl chloride.<sup>1</sup>

*Methyl  $\alpha$ -chloroacrylate* was prepared from methyl  $\alpha,\beta$ -dichloropropionate, which was purchased from Eastman Kodak Co. The method described in *Experimental Plastics and Synthetic Resins* was used.<sup>2</sup>

A sample of 40% *methacrylic acid* in aqueous solution containing 0.1% hydroquinone was supplied by Rohm & Haas Co. 100 ml. of this material was shaken with 25 g. of sodium chloride in a 500 ml. separatory funnel. Two layers formed. The lower layer, consisting essentially of sodium chloride and water, was discarded. 5 g. of sodium chloride were added to the material in the funnel and shaken. A sludge of sodium chloride and water formed and was discarded. The crude methacrylic acid thus obtained was dried over calcium chloride for 15 hours and distilled at 4 mm. Practically all of the material came over in the range 44–46°C. The purity of the product was determined by titration. Found: 52.7% COOH; theoretical 52.3%.

*Diethyl maleate* (Eastman Kodak) was purified by vacuum distillation (b.p. 104–6°C. at 14 mm.).

*o*-Chlorostyrene (Dow) was purified by vacuum distillation.

*tert*-Butylethylene was obtained from Professor Newell C. Cook of Pennsylvania State College. It was distilled over sodium immediately before use.

2-Vinylpyridine (Reilly Coal Tar Products) was purified by vacuum distillation.

Hexachlorobutadiene (Eastman Kodak) was purified by vacuum distillation.

All copolymerizations were carried out in sealed Pyrex test tubes at 70°C.

## SYSTEM I

### ( $M_1$ ) VINYLIDENE CHLORIDE-( $M_2$ ) INDENE

Tube	$M_1$	% Cl	$m_1$	% conversion	Time, days
1	0.096	60.31	0.151	16.5	82
2	0.213	47.21	0.314	10.4	82
3	0.341	Sample lost			
4	0.458	38.92	0.423	5.41	82
5	0.623	30.27	0.542	1.56	82
6	0.798	21.60	0.666	0.587	82
7	0.843	14.77	0.767	0.350	22

The  $M_2$  values for samples 1, 2, and 4 have been corrected for high conversion according to the approximate formula:

$$M_2 (\text{av.}) = M_2 + \frac{1}{2} (M_2 - m_2) (\text{conversion})$$

Samples 1 through 6 contained 0.1% benzoyl peroxide. Sample 7 contained no catalyst. Polymers 1–6 were precipitated three times with

methanol using methyl ethyl ketone as solvent. Sample 7 was precipitated twice.

All  $M_2$  values have been corrected for high conversion. The copolymers were purified by precipitating three times with methanol, using benzene as solvent.

### SYSTEM II

#### $(M_1)$ *o*-CHLOROSTYRENE- $(M_2)$ INDENE

Tube	$M_2$	% Cl	$m_2$	% conversion	Time, hrs.
1	0.160	24.20	0.064	21.20	27
2	0.315	22.48	0.141	12.68	27
3	0.452	22.42	0.144	10.08	27
4	0.598	20.25	0.239	6.67	27
5	0.730	19.42	0.275	3.79	27
6	0.854	16.87	0.381	1.66	33

### SYSTEM III

#### $(M_1)$ VINYLIDENE CHLORIDE- $(M_2)$ COUMARIN

Tube	$M_2$	% Cl	% conversion <sup>a</sup>	Time
2	0.101	70.6	2.40	0 hrs. 50 min.
4	0.305	67.9	4.47	2 15
3	0.332	70.8	3.37	1 50
5	0.391	71.0	4.94	2 15
1	0.611	70.0	11.20	7 0

<sup>a</sup> Based on vinylidene chloride monomer.

All tubes contained 0.1% benzoyl peroxide by weight. The polymers precipitated from the monomer mixtures in the form of fine white powders. No solvent could be found, and all were purified by prolonged extraction with boiling acetone. A mixture was also prepared containing 90.0 mole per cent coumarin. After 50 hours in the thermostat, the material had turned red. No residue remained upon extraction with hot water.

### SYSTEM IV

#### $(M_1)$ VINYLIDENE CHLORIDE- $(M_2)$ METHACRYLIC ACID

Tube	$M_2$	% Cl	$m_2$	% conversion	Time
1	0.130	43.94	0.428	1.24	5 hrs. 10 min.
2	0.269	30.66	0.609	0.56	7 25
3	0.412	21.12	0.735	1.06	8 25
4	0.546	15.24	0.811	5.85	8 10
5	0.690	9.76	0.880	5.39	7 10
6	0.845	4.01	0.951	3.48	4 45

0.1% benzoyl peroxide was used in each case. The copolymers precipitated from the monomer mixtures in the form of fine white powders. No suitable solvent could be found, and all were purified by prolonged extraction with hexane.

SYSTEM V. ( $M_1$ ) *o*-CHLOROSTYRENE-( $M_2$ ) METHACRYLIC ACID

Tube	$M_2$	% Cl	$m_2$	% conversion	Time
1	0.147	17.98	0.405	5.13	3 hrs. 10 min.
2	0.274	15.95	0.493	4.11	3 10
3	0.380	14.85	0.538	8.43	2 30
4	0.551	13.09	0.606	4.74	2 30
5	0.688	10.30	0.705	4.04	3 10
6	0.890	3.74	0.904	4.99	4 35

0.2% benzoyl peroxide was used in each case. The copolymers were purified by precipitating three times with hexane, using methyl ethyl ketone as solvent.

SYSTEM VI. ( $M_1$ ) METHYL METHACRYLATE-( $M_2$ ) 2-VINYLPYRIDINE

Tube	$M_2$	% N	$m_2$	% conversion	Time, min.
1	0.909	11.76	0.877	4.7	5
2	0.722	10.10	0.748	3.7	5
3	0.556	8.69	0.640	6.5	10
4	0.348	6.00	0.438	5.9	15
5	0.249	4.94	0.360	6.3	20
6	0.132	3.28	0.237	7.8	25

0.2% benzoyl peroxide was used in each case. The copolymers were purified by precipitating three times with hexane, using methyl ethyl ketone as solvent.

SYSTEM VII. ( $M_1$ ) VINYL ACETATE-( $M_2$ ) 2-VINYLPYRIDINE

Tube	$M_2$	% N	$m_2$	% conversion	Time
1	0.90	12.84	0.97	12	1 hr.
2	0.69	12.85	0.97	11	2 hrs.
3	0.49	12.48	0.93	6	2 hrs.
4	0.30	12.34	0.92	2	6 days
5	0.15	11.81	0.87	2	6 days

The copolymers were purified by precipitating three times with petroleum ether, using methyl ethyl ketone as solvent.

SYSTEM VIII. ( $M_1$ ) METHYL METHACRYLATE-( $M_2$ ) METHYL  $\alpha$ -CHLOROACRYLATE

Tube	$M_2$	% Cl	$m_2$	% conversion	Time
1	0.142	9.51	0.284	4.39	25 hrs. 25 min.
2	0.282	12.84	0.392	7.85	23 20
3	0.418	18.03	0.568	6.06	23 20
4	0.555	21.64	0.698	5.43	10 10
5	0.717	24.26	0.796	3.40	3 25
6	0.859	26.00	0.863	3.58	3 25

No catalyst was used in preparing these polymers. They were purified by precipitating three times with heptane, using dioxane as solvent.

## SYSTEM IX

( $M_1$ ) ACRYLONITRILE-( $M_2$ ) METHYL  $\alpha$ -CHLOROACRYLATE

Tube	$M_2$	% Cl	$m_2$	% conversion	Time	
1	0.098	15.16	0.319	2.00	22 hrs.	30 min.
2	0.195	19.93	0.480	2.50	3	20
3	0.311	22.72	0.599	4.57	2	10
4	0.458	24.99	0.713	2.36		45
5	0.615	26.13	0.778	2.18		45
6	0.783	27.53	0.865	1.49	3	35

0.1% benzoyl peroxide was used in tubes 1-5. No catalyst was used in 6. The copolymers were purified by precipitating twice with hexane, using acetone as the solvent.

## SYSTEM X

( $M_1$ ) VINYL CHLORIDE-( $M_2$ ) *tert*-BUTYLETHYLENE

Tube	$M_1$	% Cl	$m_2$	% conversion	Time, hrs.
1	0.560	44.5	0.17	7.1	158
2	0.300	53.2	0.05	5.1	11
3	0.733	No polymerization after one month			
4	0.155	54.5	0.03	4.0	3

0.2% benzoyl peroxide was used in each tube. The copolymers were purified by precipitating three times with methanol, using acetone as solvent.

## SYSTEM XI

( $M_1$ ) VINYL ACETATE-( $M_2$ ) 1,1-DICHLORO-2,2-DIFLUOROETHYLENE

Tube	$M_2$	% Cl	$m_2$	% conversion	Time	
1	0.835	30.00	0.454	1.11	6 hrs.	5 min.
2	0.646	28.11	0.419	9.52	1 hr.	35
3	0.387	21.21	0.299	12.9	1	35
4	0.055	10.39	0.135	18.6	1	35

0.1% benzoyl peroxide was used in tubes 2, 3, and 4. No catalyst was added to 1. The copolymers were purified by precipitating three times with hexane, using benzene as solvent. All  $M_2$  values have been corrected for high conversion.

## SYSTEM XII

 $(M_1)$  VINYL ACETATE- $(M_2)$  ACRYLONITRILE

Tube	$M_1$	% N	$m_2$	% conversion	Time, min.
1	0.104	10.37	0.512	2.8	105
2	0.213	15.45	0.696	1.8	50
3	0.406	18.12	0.782	2.7	50
4	0.491	20.62	0.855	4.6	50
5	0.676	22.20	0.896	6.0	50
6	0.881	26.30	0.981	2.3	70

0.3% benzoyl peroxide was used in each case. The copolymers were purified by precipitating three times with methanol, using dimethylformamide as solvent.

## SYSTEM XIII

 $(M_1)$  VINYL CHLORIDE- $(M_2)$  DIETHYL MALEATE

Tube	$M_1$	% Cl	$m_2$	% conversion	Time
1	0.088	44.8	0.088	8.8	3 hrs. 30 min.
2	0.182	35.7	0.176	11.3	3 30
3	0.315	29.9	0.247	5.7	4 30
4	0.548	21.5	0.372	4.5	7 15
5	0.732	15.9	0.481	2.2	14 15

0.25% benzoyl peroxide was used in each tube. Samples 1 through 3 were purified by precipitation with methanol, using methyl ethyl ketone as solvent. Samples 4 and 5 were purified by precipitation with 80% methanol, 20% water, using methyl ethyl ketone as solvent.

## SYSTEM XIV

 $(M_1)$  STYRENE- $(M_2)$  HEXACHLOROBUTADIENE

Tube	$M_1$	% Cl	$m_2$	% conversion	Time
1	0.10	2.4	0.08	2.1	1 hr.
2	0.31	Trace	0.00	2.4	1 30 min.
3	0.52	Trace	0.00	1.9	1 30
4	0.70	Trace	0.00	2.7	5 hrs.
5	0.89	Trace	0.00	3.5	26

0.2% benzoyl peroxide was used in each case. The copolymers were purified by precipitating three times with methanol, using methyl ethyl ketone as solvent.

## DISCUSSION

The copolymerization of indene with vinylidene chloride indicates that indene can add to its own free radical at an appreciable rate. This was not altogether unexpected, as the thermal polymerization of indene has

been reported at 120, 170, and 188°C.<sup>3</sup> We have verified the polymerization of indene at 70°C. A small amount of polymer formed after 18 days in the 70° thermostat. It precipitated as a fine powder upon pouring into methanol.

Coumarin, on the other hand, behaves as an inert diluent with vinylidene chloride. The chlorine analyses indicate that if coumarin enters the polymer at all, it does so to an exceedingly small extent.

Methacrylic acid was copolymerized with vinylidene chloride and with *o*-chlorostyrene with the aim of comparing it with methyl methacrylate. The relative reactivities of these two monomers with the vinylidene chloride and *o*-chlorostyrene free radicals are indicated in Table II. It is

TABLE II

Radical	Monomer	
	Methyl methacrylate	Methacrylic acid
Vinylidene chloride.....	4.1	6.7
<i>o</i> -Chlorostyrene.....	2	8.3

seen that methacrylic acid is about 50% more reactive than methyl methacrylate toward the vinylidene chloride radical, and is over 4 times as reactive toward the *o*-chlorostyrene radical. This would indicate that the carboxyl group leads to a somewhat greater reactivity, and a somewhat more positive polarity of the double bond than the carbomethoxyl group.

The data on the copolymerization of 2-vinylpyridine with methyl methacrylate and with vinyl acetate indicate that it is quite similar to styrene in reactivity.

Methyl  $\alpha$ -chloroacrylate was copolymerized with methyl methacrylate and with acrylonitrile in order to compare its behavior with that of methyl methacrylate. The relative reactivities are in Table III. We see that methyl  $\alpha$ -chloroacrylate is more reactive than methacrylate toward the

TABLE III

Radical	Monomer	
	Methyl methacrylate	Methyl $\alpha$ -chloroacrylate
Acrylonitrile.....	7	7
Methyl methacrylate.....	1	3
Methyl $\alpha$ -chloroacrylate.....	0.8	1

methyl methacrylate free radical, and that they are about equally reactive toward the acrylonitrile and methyl  $\alpha$ -chloroacrylate free radicals. This would imply that the double bond of methyl  $\alpha$ -chloroacrylate is somewhat more reactive and more positive than that of methyl methacrylate.

The system vinyl chloride/*tert*-butylethylene was investigated because of the possibility that *tert*-butylethylene would show a behavior significantly different from that of other olefins because of the absence of  $\alpha$ -methylenic

hydrogen atoms. However, it was observed that this monomer copolymerized with vinyl chloride in a fashion very similar to that previously reported for 1-pentene.<sup>1</sup> Thus it did not polymerize by itself at 70°C. in the presence of benzoyl peroxide, and inhibited the polymerization of vinyl chloride.

The behavior of 1,1-dichloro-2,2-difluoroethylene indicates that it does not add to itself at a significant rate in the vinyl acetate copolymer. This nonreactivity may be attributed to steric hindrance of the halogen atoms. Similar results are reported in a recent paper.<sup>4</sup> However, these authors were able to polymerize this compound by using acetyl peroxide as catalyst at a temperature of 135°C.

As would be expected, acrylonitrile is much more reactive than vinyl acetate in copolymerization. Diethyl maleate is about as reactive as vinyl chloride toward the vinyl chloride free radical, but does not add to itself, probably because of steric hindrance. Hexachlorobutadiene is extremely unreactive. Again, we attribute this behavior to steric effects.

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### Résumé

Les résultats expérimentaux obtenus pour quatorze copolymérisations sont indiquées. L'addition de l'indène à un radical indénique est confirmée. Ce monomère inhibe intensément la polymérisation du chlorure de vinylidène. La coumarine se comporte comme un diluant inerte à l'égard de la polymérisation du chlorure de vinylidène. L'effet des groupes suivants sur la réactivité de la double soudure est examinée: carboxyle, 2-pyridyle, tertiaire-butyle.

### Zusammenfassung

Es werden experimentelle Resultat für 14 copolymere Systeme angegeben. Die Selbstaddition von Indol wurde untersucht. Dieses Monomere inhibiert Vinyliden stark. Cumarin benimmt sich bei der Polymerisation von Vinylidenchlorid als inertes Verdünnungsmittel. Der Effekt der folgenden Gruppen: Carboxyl, 2-Pyridyl, tert-Butyl wird auf die Reaktionsfähigkeit der Doppelbindung geprüft.

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