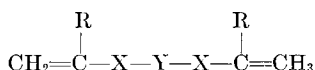


## Copolymerization of Methacrylic Anhydride with Vinyl Monomers

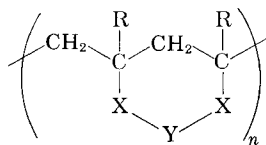
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### INTRODUCTION

It is well known that unconjugated divinyl monomers are crosslinking agents in vinyl polymerizations.<sup>1a</sup> Certain compounds, such as diallyl phthalate<sup>2</sup> and ethylene diacrylate,<sup>3</sup> undergo substantial cyclization during polymerization, with the result that 40-75% of the divinyl compound used is incapable of crosslinking. Recently, several papers<sup>4</sup> have shown that certain 1,6-diolefins of the general type

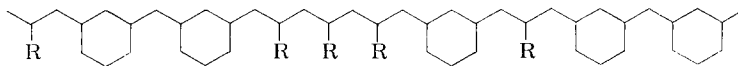


(where R, X, and Y are substituents) can be homopolymerized by either free-radical or ionic mechanisms to form *soluble* cyclopolymers with little or no residual unsaturation. The repeating units have been shown by chemical methods to be:



Methacrylic anhydride is a typical polymerizable 1,6-diolefin and is known to form a soluble cyclopolymer by free-radical initiation.<sup>5</sup>

The purpose of this work was to study how methacrylic anhydride would act as a crosslinker when copolymerized with other common comonomers by a free-radical mechanism. Would the copolymer be an insoluble gel or a soluble random "cyclopolymers," perhaps of the following schematic structure?



How would the experimental conditions or the nature of the comonomer affect the formation of sol or gel? In seeking answers to these questions it was hoped also that the nature of cyclopolymerization could be better understood.

Generally, the formation of a soluble or insoluble copolymer from a vinyl-divinyl pair by a free-radical mechanism depends on the following five major factors: (a) chemical reactivities of the two monomers in copolymerization, (b) ratio of the two monomers in charge, (c) degree of dilution, or the concentration of the monomer mix in a solvent, (d) conversion, and (e) backbone chain length. In the present study the first three factors were experimented with, while the remaining two were held more or less constant. The work consisted of copolymerization of methacrylic anhydride with a variety of commontypes of vinyl monomers under a variety of experimental conditions. The copolymers obtained were characterized by their identities, solubilities, and conversions. The results will be discussed in terms of the reactivity ratios of the vinyl-. .divinyl system studied, and of the effects of monomer ratio, dilution, and conversion on soluble copolymer formation.

### THEORY

In examining the kinetics of copolymerization of a divinyl monomer and a vinyl monomer one may treat it as a general case involving a three-component system.<sup>6</sup> In the propagation step, nine addition steps involving the following six species are possible:

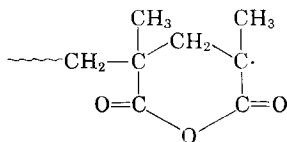
$M_1$  = methacrylic group belonging to methacrylic anhydride

$M_2$  = methacrylic group of the structure:  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}-\text{O}-\text{CO}-\dot{\text{C}}(\text{CH}_3)\text{CH}_2\sim$

$M_3$  = comonomer

$m_1\cdot$  = chain radical of the structure:  $\sim\text{CH}-\text{C}(\text{CH}_3)\text{CO}-\text{O}-\text{CO}-\text{C}(\text{CH}_3)=\text{CH}_2$

$m_2\cdot$  = chain radical of the structure:



$m_3\cdot$  = chain radical ending in comonomer.

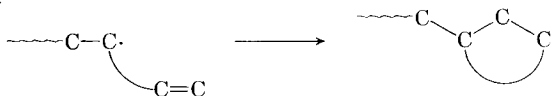
A general treatment would give a complex composition equation for a ternary system.

For the special case in which the divinyl compound undergoes extensive cyclization, a simpler solution for the composition equation may be obtained by considering the kinetic requirements for producing a soluble copolymer. A detailed kinetic treatment for the homopolymerization of ethylene dimethacrylate was recently reported by Aso.<sup>7</sup>

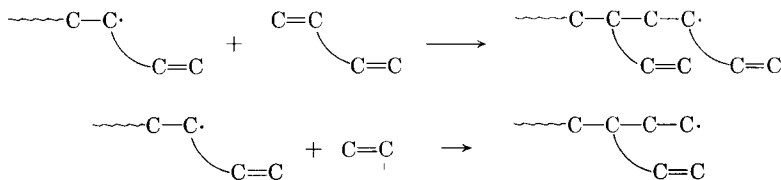
In order to form a soluble copolymer, whether linear or branched, of moderate molecular weight, the reaction rate between  $m_1\cdot$  and  $M_2$  must

be very much greater than that between  $m_1\cdot$  and  $M_1$  or  $M_3$ . The fate of  $m_1\cdot$  may be represented schematically as follows:

Fast reaction



Slow reaction



The first reaction leads to the cyclization of the divinyl monomer, forming a six-membered ring. It is believed to be a unimolecular reaction.

The second and third reactions may be called "interruption" reactions because, when they occur, the cyclization of the divinyl monomer is interrupted and the pendent vinyl group belonging to the penultimate unit would then be unlikely to cyclize easily because of the necessity of forming a ring having more than six members. A fraction of these pendent vinyl groups is expected to participate later in copolymerization with another growing chain, leading eventually to gelation. Gelation is known to occur readily, requiring at gel point one crosslink unit per weight-average chain.<sup>8a</sup> The maximally tolerable degree of the interruption reaction is about 0.1–0.2% for an average backbone chain length of 1000 units.

Thus, to form a soluble copolymer the cyclization reaction involving  $m_1\cdot$  and  $M_2$  must be considerably faster than the interruption reactions between  $m_1\cdot$  and  $M_1$  and between  $m_1\cdot$  and  $M_3$ . One therefore allows that the reaction rates  $k_{11}[m_1\cdot][M_1]$  and  $k_{13}[m_1\cdot][M_3]$  be zero. As  $M_2$  is busily engaged in cyclization with  $m_1\cdot$  and is unable to participate in reactions with  $m_2\cdot$  and  $m_3\cdot$ , the reaction rates  $k_{22}[m_2\cdot][M_2]$  and  $k_{32}[m_3\cdot][M_2]$  are also assumed to be zero.

In standard treatment of a ternary system, the rates of disappearance of  $M_1$  and  $M_2$  are respectively:

$$-dM_1/dt = k_{11}[m_1\cdot][M_1] + k_{21}[m_2\cdot][M_1] + k_{31}[m_3\cdot][M_1]$$

$$-dM_3/dt = k_{13}[m_1\cdot][M_3] + k_{23}[m_2\cdot][M_3] + k_{33}[m_3\cdot][M_3]$$

Since  $k_{11}[m_1\cdot][M_1]$  and  $k_{13}[m_1\cdot][M_3]$  are now assumed to be zero, it follows that

$$dM_1/dM_3 = (k_{21}[m_2\cdot][M_1] + k_{31}[m_3\cdot][M_1]) / (k_{23}[m_2\cdot][M_3] + k_{33}[m_3\cdot][M_3]) \quad (1)$$

Likewise, the steady-state condition

$$k_{21}[m_2\cdot][M_1] + k_{32}[m_3\cdot][M_2] = k_{13}[m_1\cdot][M_3] + k_{23}[m_2\cdot][M_3]$$

may be reduced to the following (since  $k_{34}[m_3\cdot][M_2] = 0$ ):

$$k_{21}[m_2\cdot][M_1] = k_{23}[m_2\cdot][M_3] \quad (2)$$

Substitution of eq. (2) into eq. (1) gives:

$$dM_1/dM_3 = (M_1/M_3)(r_2M_1 + M_3)/(r_3M_3 + M_1) \quad (3)$$

where  $r_2 = k_{21}/k_{23}$  and  $r_3 = k_{33}/k_{31}$  (4)

At low conversions, the copolymer composition equation for the present special vinyl-divinyl system becomes:

$$m_1/m_3 = (M_1/M_3)[(r_2M_1 + M_3)/(r_3M_3 + M_1)] \quad (5)$$

where  $m_1$  and  $m_3$  are, respectively, the molar concentrations of the methacrylic group and the comonomer in the copolymer formed.

Equation (5) is similar in form to the common copolymer composition equation for a binary system, except that it is expressed in terms of molar concentrations of the comonomer,  $M_3$ , and the methacrylic group,  $M_1$  (twice the concentration of the divinyl compound), and of the reactivity ratios  $r_2$  (a measure of the competition between the methacrylic group,  $M_1$ , and the comonomer,  $M_3$ , for the ring radical,  $m_2\cdot$ ) and  $r_3$  (a measure of the competition between  $M_3$  and  $M_1$  for the chain radical ending in the comonomer,  $m_3\cdot$ ). Since the present three-component system is considered under the assumption of extensive cyclization, the end result, reminiscent of that for a binary system, is not surprising.

## EXPERIMENTAL

### Materials

Unless otherwise specified, commercially available monomers were used without further purification. Other monomers were purified by fractional distillation and stored at 5°; the physical constants, given here, checked well with reported values.

*Methacrylic anhydride* (MAN) was prepared by a known procedure;<sup>9</sup> b.p. 82° (8 mm.), 59° (1 mm.);  $n_D^{20}$  1.4538.

ANAL. Calc. for  $C_8H_{10}O_3$ : C, 62.3; H, 6.49. Found: C, 62.8; H, 6.53.

*Methyl methacrylate* (MMA), *n-hexyl methacrylate* (HMA), *ethyl acrylate*, Rohm & Haas Co., uninhibited.

*Lauryl methacrylate*, Rohm & Haas Co., inhibited with 0.01% hydroquinone.

*Styrene*, Dow Chemical Co., technical grade.

*Acrylonitrile*, American Cyanamid Co., uninhibited.

*2-Chloroethyl vinyl ether*, Union Carbide Corporation, reagent grade.

*Benzyl vinyl sulfide*, prepared by the research laboratories of Rohm & Haas Co., b.p. 125° (25 mm.),  $n_D^{20}$  1.5809.

*n-Butyl vinyl sulfone*, prepared by the research laboratories of Rohm & Haas Co., b.p. 102–103° (1.5 mm.),  $n_D^{20}$  1.4619.

*Vinyl acetate*, Celanese Corporation, b.p. 72–73°,  $n_D^{20}$  1.3947.

*Allyl chloroacetate*, prepared according to the procedure of Robertson et al.,<sup>10</sup> b.p. 164–165°,  $n_D^{20}$  1.4453.

*Diisobutylene*, Atlantic Refining Co.

*Allyl benzyl ether*, prepared by the research laboratories of Rohm & Haas Co.,  $n_D^{20}$  1.5096.

*Dimethyl sulfoxide* (DMS), Stepan Chemical Company, reagent grade. Two lots were used: one lot was fractionated, b.p. 189°,  $n_D^{20}$  1.4774; the other lot was used as received,  $n_D^{20}$  1.4780.

*Benzene*, Brothers Chemical Co., reagent grade.

### General Procedure

**Solution Polymerization.** The copolymerizations were conducted in a 500-ml. three-necked flask equipped with a reflux condenser, stirrer, and glass stopper. In general, the reaction mixture consisted of 10–20 g. of the monomer mixture containing 1.0% benzoyl peroxide (based on monomer) in benzene solution. The polymerizations were allowed to run at 80° for 18–64 hrs., and were followed by an isolation procedure (occasionally, additional 1.0% quantities of benzoyl peroxide were added to the reaction mixture when the polymerization rate was slow). If the polymer precipitated from the reaction medium because of insolubility in benzene, the powdery precipitate was isolated by filtration, washed with three 300-ml. portions of either hexane or benzene (“A1” or “A2” respectively, in the tables), and finally dried in vacuum at 55° for 16 hr. If the polymer remained soluble in the solvent or was in the form of a loose gel, it was isolated by precipitation in a nonsolvent. Hexane (“B1” in the tables; at 10:1 nonsolvent/solution ratio) and methanol (“B2” in the tables; at 5:1 nonsolvent/solution ratio) were used. After being stirred for 2–3 hrs., the polymer was isolated by filtration and washed with the nonsolvent twice more. The polymers were dried in vacuum at 55° for 16 hr. Polymer-solvent mixtures that were difficult to filter were dried by evaporation under diminished pressure.

**Bulk Polymerization.** Monomer mixture in 5–10-g. lots, containing 1.0% benzoyl peroxide (based on total monomer weight), were polymerized in polyethylene-lined screw-cap vials in air at 65–70° for 18–64 hr. The solid polymer was pulverized and tested for solubility in dimethyl sulfoxide. If the polymer was soluble, it was precipitated from a dimethyl sulfoxide solution by either hexane or methanol, and was washed and dried as described above.

**Reactivity Ratios.** The reactivity ratio experiments were conducted according to a standard procedure<sup>1b</sup> at 60° in about 50% benzene solutions.

### Characterization of Copolymers

**Solubility.** All the samples used in solubility tests were in the form of powder or small granules. A 0.2–0.3-g. portion of the polymer was heated with 10 ml. of dimethyl sulfoxide in a test tube. In most cases the polymer dissolved within 1 min. at 130–150°. Occasionally, in the case of bigger granules, higher temperatures (up to boiling) and longer times of heating (up to 5 min.) were required for complete solution. These polymers were regarded as “soluble.” Polymers remaining as swollen gels even after prolonged periods of boiling (>15 min.) were considered “insoluble.”

**Elementary Analysis.** Elementary analyses were done on all compounds. Carbon–hydrogen analyses for several polymers unfortunately gave erratic results and were not used in this work.

**Infrared Spectroscopy.** Chloroform-soluble polymers were examined either in chloroform solution or as film; chloroform-insoluble, but dimethyl sulfoxide-soluble, polymers were examined as mull in Nujol.

## RESULTS AND DISCUSSION

### Effects of Monomer Ratio and Dilution on Solubility of Copolymer

Copolymerizations of methacrylic anhydride with methyl methacrylate, *n*-hexyl methacrylate, and other monomers were made with wide variations in charge ratio and concentration. The results are shown in Tables IA–C, respectively. For reasons that will be given, the solubilities of the copolymers obtained may be attributed largely to the effects of dilution and monomer ratio alone for each specific pair of monomers studied.

It is well known that shortening of the backbone chain length of a vinyl-divinyl copolymer will delay gelation,<sup>8a</sup> that polymerization in solution will result, in general, in lowered molecular weight,<sup>8b</sup> and that certain monomers and solvents will cause extensive chain transfer.<sup>8b</sup> The systems used in our work involved monomers and a solvent that are generally considered not chain-transferring. The change in backbone chain length due to dilution effect, when compared with the effects of monomer ratio and dilution on gelation, is believed to be of a minor order.

For a given vinyl-divinyl reaction, conversion means the build-up of crosslinks. Therefore, under otherwise identical conditions, a given copolymer may remain soluble at low conversions but become insoluble at high conversions. This was seen in our study (two runs in Table IB). However, with a few exceptions, the conversions listed in Tables IA and B are of 60% or higher. By considering the results obtained at high conversions, one is now able to determine principally the effects of monomer ratio and dilution alone.

The results in Tables IA and B show that, depending on the experimental conditions chosen, both soluble and insoluble copolymers were obtained at high conversions. The solubilities of the copolymers obtained for the methacrylic anhydride–methyl methacrylate and methacrylic anhydride–

TABLE IA  
Copolymerization of Methacrylic Anhydride and Methyl Methacrylate<sup>a</sup>

Experimental conditions				Results		
MAN/MMA <sup>b</sup>		MMA <sup>b</sup> concn.		Isolation method	Wt.-% conv.	Soly. in DMS <sup>b</sup>
By wt.	By moles	% <sup>c</sup>	moles/l. <sup>d</sup>			
3.0/97	2/98	10	1.0	B1	95	S
3.0/97	2/98	18	1.8	A1	65	I
5.0/95	3/97	10	1.0	B1	61	S <sup>e</sup>
5.0/95	3/97	30	2.9	—	—	I
10/90	6/94	10	0.97	A1	67	I
10/90	6/94	30	2.8	A1	17	I
20/80	14/86	5.0	0.46	A1	70	I
30/70	22/78	25	2.10	A2	80	I
30/70	22/78	10	0.89	A1	49	I
70/30	60/40	10	0.75	A1	91	I
80/20	72/28	5.0	0.36	A1	69	S
90/10	85/15	40	2.7	A2	99	S
95/5.0	93/7	10	0.66	A2	90	S <sup>e</sup>
95/5.0	93/7	20	1.2	A1	88	S

<sup>a</sup> Polymerizations conducted at 65–80° with benzoyl peroxide catalyst.

<sup>b</sup> Abbreviations: see "Experimental" section.

<sup>c</sup> Expressed as milliliters of combined monomers per 100 ml. of solution at 25°, assuming a density of monomers of 1; benzene solvent.

<sup>d</sup> Expressed as moles of combined monomers per liter of solution.

<sup>e</sup> Infrared absorptions at 1815 and 1745 cm.<sup>-1</sup>, characteristic of the anhydride ring, and at 1735 cm.<sup>-1</sup> corresponding to C=O of the acrylic ester unit; the relative intensities were in approximate agreement with that based on charge.

*n*-hexyl methacrylate pairs, as influenced by dilution and monomer ratio, are shown graphically in Figure 1 (from data in Tables IA and B).

The ordinate is expressed, with a few minor approximations, in moles of combined monomers per liter; it represents extreme dilution near the origin and pure monomer (bulk) at the other end. In Figure 1, a dashed curve (*ABC*), defined by the preparative conditions, is drawn to suggest areas of gel formation and of soluble copolymer formation at substantial conversions. In other words, the curve means that, for a given monomer ratio, dilution favors the formation of soluble copolymers and that at a given dilution level soluble copolymers are more apt to be formed if either component in the initial charge is in large excess. The curve, however, is not symmetrical and is concave. Apparently, methyl methacrylate and *n*-hexyl methacrylate are similar in copolymerization tendencies to methacrylic anhydride.

The nature of the curve observed may be interpreted in the light of the analysis of the interruption reactions discussed in the theoretical section. The fact that dilution aids the formation of soluble copolymers can be readily explained by noting that dilution does not change the cyclization rate which, being unimolecular, does not depend on the concentration of

TABLE IB  
Copolymerization of Methacrylic Anhydride and *n*-Hexyl Methacrylate<sup>a</sup>

Experimental conditions				Results		
MAN/HMA <sup>b</sup>		HMA conc.		Isolation method	Wt.-% conv.	Soly. in DMS
By wt.	By moles	% <sup>c</sup>	moles/l. <sup>d</sup>			
5/95	6/94	10	0.59	B2	23	S <sup>e</sup>
20/80	22/78	20	1.2	A2	71	I
20/80	22/78	10	0.60	B2	47	S
20/80	22/78	10 <sup>f</sup>	0.60	B2	44	S
30/70 <sup>j</sup>	32/68	10	0.65	B2	24	S <sup>g</sup>
30/70 <sup>j</sup>	32/68	10	0.65	B2 <sup>h</sup>	84	I
30/70	32/68	16 <sup>f</sup>	0.96	B2 <sup>h</sup>	50	I, S <sup>i</sup>
30/70	—	100	—	—	>90	I
50/50	53/47	5	0.30	A2	66	S
50/50	53/47	10	0.61	A2	78	I
70/30	72/28	10	0.63	A2	80	S <sup>g</sup>
70/30	—	100	—	—	>90	I
90/10	91/9	10	0.64	A2	83	S
95/5	96/4	30	1.9	A2	84	S

<sup>a</sup> Polymerizations conducted at 65–80° with benzoyl peroxide as catalyst.

<sup>b</sup> Abbreviations: see "Experimental" section.

<sup>c</sup> Expressed as milliliters of combined monomers per 100 ml. of solution at 25°, assuming a density of monomers of 1. Benzene used as solvent.

<sup>d</sup> Expressed as moles of combined monomers per liter of solution.

<sup>e</sup> Soluble in benzene, chloroform.

<sup>f</sup> Toluene as solvent.

<sup>g</sup> Infrared absorptions at 1815 and 1745 cm.<sup>-1</sup> characteristic of the anhydride ring, and at 1735 cm.<sup>-1</sup> corresponding to C=O of the acrylic ester unit. The relative intensities were in approximate agreement with that based on charge.

<sup>h</sup> Solution in form of loose gel.

<sup>i</sup> Borderline case.

<sup>j</sup> Soluble at low conversions, insoluble at high conversions.

M<sub>2</sub>. On the other hand, the interruption rates  $k_{13}[m_1 \cdot][M_3]$  and  $k_{11}[m_1 \cdot][M_1]$  are dependent on  $[M_1]$  and  $[M_3]$ . Dilution means decrease of  $[M_1]$  and  $[M_3]$  and would therefore retard the interruption reactions. The relative retardation of the interruption reactions without impairment of the cyclization reaction results in a net gain in the ease of forming soluble copolymers.

The formation of soluble copolymers at either of the extreme monomer ratios and at any degree of dilution can likewise be rationalized. The left-half portion (*AB*) of the curve, perhaps typical of any conventional vinyl-divinyl pair, denotes the greater tendency to form soluble copolymers as the mole fraction of the divinyl component is decreased. The curve is very steep near the ordinate, because it must approach point *A* where the copolymer practically becomes a homopolymer and is, accordingly, soluble at all levels of dilution. The right-hand portion of the curve can be explained by considering the two interruption reaction rates  $k_{13}[m_1 \cdot][M_3]$



TABLE IC  
Copolymerization of Methacrylic Anhydride and Other Monomers<sup>a</sup>

Experimental conditions <sup>c</sup>			Results		
Comonomer (M <sub>3</sub> )	MAN/M <sub>3</sub> by wt.	Vol.-% in benz. <sup>b</sup>	Isola- tion method	Wt.-% conv.	Soly. in. DMS <sup>c</sup>
Styrene	5/95	10	B1	40	S <sup>d</sup>
Styrene	10/90	10	B1	25	S <sup>d</sup>
Styrene	30/70	10	A1	70	I
Styrene	50/50	10	A1	90	I
Styrene	70/30	10	A1	95	I
Styrene	90/10	10	A1	97	S
Lauryl methacrylate	20/80	16 <sup>e</sup>	B2	78	S <sup>f</sup>
Lauryl methacrylate	30/70	10 <sup>e</sup>	B2	52	S <sup>f</sup>
Ethyl acrylate	5/95	10	B1	27	S <sup>d</sup>
Ethyl acrylate	5/95	40	A2	35	I
Ethyl acrylate	70/30	25	A2	71	I
Vinyl acetate	50/50	100	—	—	S
Vinyl acetate	64/36	10	A2	68	S
Diisobutylene	10/90	10	A2	10	S
Diisobutylene	30/70	10	A2	29	S
Diisobutylene	70/30	10	A2	65	S

<sup>a</sup> Polymerizations were conducted at 65–85° with benzoyl peroxide catalyst.

<sup>b</sup> Expressed as milliliters of combined monomers per 100 ml. of solution at 25°, assuming a density of monomers of 1; benzene solvent.

<sup>c</sup> Abbreviations: see "Experimental" section.

<sup>d</sup> Soluble in benzene, chloroform.

<sup>e</sup> Toluene as solvent.

<sup>f</sup> Soluble in toluene.

and  $k_{11}[m_1][M_1]$ . As  $[M_3]$  is decreased by increasing the mole fraction of methacrylic anhydride in the initial charge, the rate  $k_{13}[m_1][M_3]$  is decreased accordingly. At the same time, though the monomer charge is rich in methacrylic anhydride, the other interruption rate,  $k_{11}[m_1][M_1]$ , for some unknown reason remains negligible or zero. The basis of this view is that pure methacrylic anhydride itself, in the absence of any comonomer, can be cyclopolymerized without gelation; if the interruption rate were appreciable, the homopolymer would be crosslinked. Hence, as the monomer charge in a copolymerization reaction approaches pure methacrylic anhydride at a given dilution level and high conversion, the copolymer formed is more likely to be soluble.

Tables IA–C show the effects of dilution and monomer ratio on the solubilities of copolymers prepared from several other vinyl–divinyl pairs. The results, though scanty and scattered, show the general trend illustrated in Figure 1.

### Reactivity Ratios of Methacrylic Anhydride with Vinyl Monomers

Benzyl vinyl sulfide, 2-chloroethyl vinyl ether, allyl urea, and allyl chloroacetate have been selected for reactivity ratio determinations.

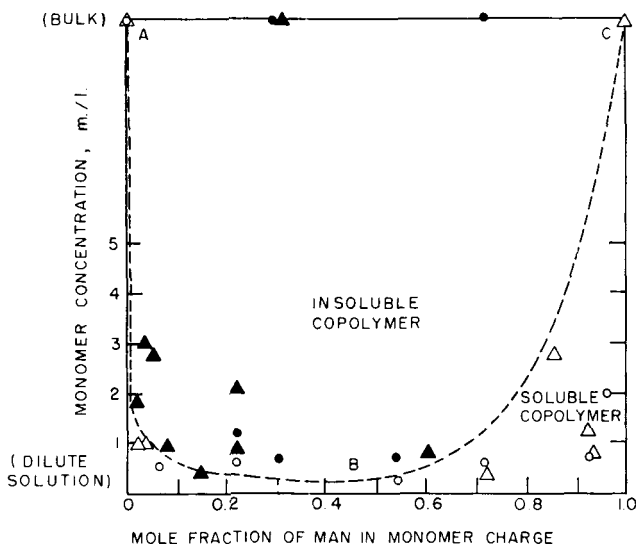


Fig. 1. Effect of dilution and charge ratio on solubility of copolymers MAN-MMA (triangles) and MAN-HMA (circles). Open symbols, soluble; solid symbols, insoluble. Polymerizations conducted at 65–80°, at high conversions, and in benzene solutions.

By standard practice,<sup>1b</sup> the compositions of low conversion polymers, obtained at various charge ratios, were calculated from appropriate elementary analyses. The copolymerizations were conducted in benzene solutions at 60°, and all the copolymers isolated were found soluble in dimethylsulfoxide. By using eq. (5) and an intersection method<sup>1c</sup>,  $r_2$  and  $r_3$  were evaluated. The analytical results are shown in Tables IIA–D; the  $r_2$ ,  $r_3$  values, in Table III. For purposes of comparison, published reactivity ratios of corresponding methyl methacrylate–comonomer pairs, also determined at 60°, are listed in Table III. Where identical pairs cannot be cited, values for the most closely related comonomers are given.

It should be noted that the terpolymer, eq. (5), was based on the assumption that all the rate constants for the various gelation reactions were zero.

TABLE IIA  
Analytical Results for Methacrylic Anhydride and Benzyl Vinyl Sulfide ( $M_3$ )

Mole ratio <sup>a</sup> in charge, $M_1/M_3$	% conv.	% S		Mole ratio in polymer, $m_1/m_3$
0.200/0.900 <sup>b</sup>	13.3	12.36	12.43	0.830/0.585
0.400/0.800	8.65	11.17	11.32	0.926/0.537
0.600/0.700 <sup>b</sup>	11.9	10.50	10.48	1.01 /0.500
0.800/0.600	7.95	9.91	10.09	1.15 /0.475
1.00 /0.500 <sup>b</sup>	9.23	9.13	8.83	1.14 /0.425
1.20 /0.400	7.90	8.38	8.46	1.19 /0.403
1.40 /0.300 <sup>b</sup>	7.20	7.03	7.08	1.32 /0.337

<sup>a</sup>  $M_1 = 2[\text{MAN}]$ .

<sup>b</sup> Polymerization *in vacuo*.

Data in Tables IA–C had just shown that gelation did occur, depending on the conditions of polymerizations; hence the  $r_2$  and  $r_3$  values obtained from eq. (5) were only approximate. They would serve, however, as a useful qualitative basis for subsequent discussion.

TABLE IIB  
Analytical Results for Methacrylic Anhydride and Allyl Chloroacetate ( $M_3$ )

Mole ratio in charge, $M_1/M_3$	% conv.	% Cl		Mole ratio in polymer, $m_1/m_3$
0.200/0.900	2.94	4.79	4.69	1.60/0.200
0.400/0.800	4.28	1.93	1.80	1.83/0.082
0.600/0.700	6.41	1.25	1.33	1.88/0.058
1.20 /0.400	6.94	0.50	0.56	1.95/0.023

TABLE IIC  
Analytical Results for Methacrylic Anhydride and Chloroethyl Vinyl Ether ( $M_3$ )

Mole ratio in charge, $M_1/M_3$	% conv.	% Cl		Mole ratio in polymer, $m_1/m_3$
0.200/0.900 <sup>a</sup>	12.6	10.27	10.29	1.22/0.389
0.600/0.700 <sup>a</sup>	10.0	5.22	5.13	1.60/0.200
0.800/0.600	11.2	3.87	3.87	1.70/0.15
1.00 /0.500 <sup>a</sup>	11.5	3.71	3.62	1.71/0.143
1.20 /0.400	11.2	2.26	2.08	1.83/0.084
1.40 /0.300 <sup>a</sup>	10.7	1.84	1.91	1.85/0.072
1.60 /0.200	9.73	1.05	1.04	1.92/0.038

<sup>a</sup> Polymerization *in vacuo*.

TABLE IID  
Analytical Results for Methacrylic Anhydride and Allyl Urea ( $M_3$ )

Mole ratio in charge, $M_1/M_3$	% conv. <sup>a</sup>	% N		Mole ratio in polymer, $m_1/m_3$
0.200/0.900	7.62	3.54	3.64	1.62/0.189
0.400/0.800	10.9	2.07	1.81	1.79/0.105
1.00/0.500	8.65	0.48	0.42	1.93/0.034

<sup>a</sup> Dioxane, instead of benzene, as the diluent.

Table III shows that in the cases of the vinyl sulfide and allyl acetate as comonomers, the reactivity ratios  $r_2$ ,  $r_3$  for the methacrylic anhydride–comonomer pairs resemble  $\langle r_1 \rangle$ ,  $\langle r_2 \rangle$  for the corresponding methyl methacrylate–comonomer pairs. (The notation  $\langle \rangle$  refers to a conventional binary systems.) Some minor difference between  $r_2$  and  $\langle r_1 \rangle$ , however, exists when a vinyl ether is the comonomer. One may recall that

$$r_2 = k_{21}/k_{23}; \quad \langle r_1 \rangle = k_{[MMA\cdot][MMA]}/k_{[MMA\cdot][M_3]}$$

Since  $r_2$  and  $\langle r_1 \rangle$  are of a similar order of magnitude for several comonomers ( $M_3$ ), then  $k_{23} \propto k_{[MMA\cdot][M_3]}$ .

TABLE III  
Comparison of Reactivity Ratios of Methacrylic Anhydride and Methyl Methacrylate  
with Related Vinyl Monomers (60°)

Monomer, (M <sub>3</sub> )	Methacrylic anhydride		Methyl methacrylate, $\langle M_1 \rangle^a$		Monomer, $\langle M_2 \rangle$
	$r_2^b$	$r_3^b$	$\langle r_1 \rangle$	$\langle r_2 \rangle$	
Benzyl vinyl sulfide	0.8 ± 0.1	∞0	1.0	0.03	Methyl vinyl sulfide <sup>c</sup>
2-Chloroethyl vinyl ether	6.1 ± 0.3	∞0	37	0.01	Ethyl vinyl ether <sup>d</sup>
Allyl urea	28 ± 2	∞0	—	—	—
Allyl chloroacetate	42 ± 2	∞0	50	0	Allyl chloroacetate <sup>e</sup>

<sup>a</sup> The marks  $\langle \rangle$  denote a binary, copolymer system.

<sup>b</sup> Calculated from eq. (5) with the data of Table II.

<sup>c</sup> Calculated from the respective  $Q, e$  values<sup>1d</sup>. MMA: see ref. 13a. Methyl vinyl sulfide: see ref. 14.

<sup>d</sup> Calculated from the respective  $Q, e$  values<sup>1d</sup>. Ethyl vinyl ether: see ref. 15.

<sup>e</sup> See ref. 16;  $\langle r_2 \rangle$  value assumed.

It is interesting to note that maleic anhydride, which resembles the cyclized anhydride structurally, is known to form 1:1 alternate copolymers with allyl acetate<sup>11</sup> and evidently with ethyl vinyl ether;<sup>12</sup> this requires  $\langle r_1 \rangle$  to be 0 in both cases.<sup>13b</sup> The difference in  $r_2$  (42) and  $\langle r_1 \rangle$  (0) between the two respective methacrylic anhydride-comonomer and maleic anhydride-comonomer pairs probably is due to the fact that maleic radical does not add to its own monomer.

### Effect of the Reactivity of the Comonomer on the Solubility of the Copolymer

The previous sections have described the effects of monomer ratio and dilution on the solubility of the copolymer of methacrylic anhydride and a given comonomer, as well as the results of a few reactivity ratio determinations. It is now appropriate to examine the effects of different comonomers alone on the soluble-polymer formation.

A series of copolymerizations involving methacrylic anhydride and several comonomers was carried out under identical conditions. The mole ratio of methacrylic anhydride to the comonomer in all cases was arbitrarily fixed at 32/68 and the polymerizations were made both in bulk and 65–70° and in 10% benzene solutions at 80°. The results, expressed in terms of solubility, conversion, and identification, are shown in Table IV.

With the exception of diisobutylene, the comonomers shown in column 1 may be roughly grouped together to form two classes, styrene to ethyl acrylate and vinyl *n*-butyl sulfone to allyl benzyl ether. The first group of comonomers is characterized by the fact that all the copolymers made from this group were insoluble when the polymerization was conducted in bulk (column 3). When the copolymerizations were made in 10% benzene solutions and at substantial conversions, the copolymers obtained

from lauryl methacrylate, acrylonitrile, and ethyl acrylate now became soluble (column 6). The transition of insoluble to soluble products is due to the dilution effect which was described earlier. The second group of comonomers is characterized by these observations: (a) the copolymerizations of these comonomers with methacrylic anhydride in either bulk or solution, with one exception, yielded soluble products; (b) the conversions in most cases were moderate to poor; and (c) by comparing the conversions with the weight fraction of methacrylic anhydride present in charge (columns 2 and 7), the copolymers obtained appeared to consist chiefly of the anhydride. (All the polymers in this group except, perhaps, that from diisobutylene were genuine copolymers, because both elementary analysis and infrared spectroscopy showed the definite presence, though in small quantities, of the comonomer in the purified products.) Gel formation from allyl chloroacetate and methacrylic anhydride in bulk suggests that monomer pairs in this group may or may not give soluble copolymers in bulk, depending on the conversion.

As discussed earlier, gelation would result if the cyclization of methacrylic anhydride were interrupted by the reaction between  $m_1\cdot$  and either  $M_1$  or  $M_3$ . Reaction between  $m_1\cdot$  and  $M_1$  is not expected to occur because no gelation results when methacrylic anhydride is allowed to homopolymerize. Therefore gelation in a copolymerization between methacrylic anhydride and a comonomer is principally caused by the interruption reaction between  $m_1\cdot$  and  $M_3$ . It appears instructive to correlate the solubility data with  $k_{13}$ , the rate constant of the reaction between  $m_1\cdot$  and  $M_3$ , or by any means that might suggest the relative values of  $k_{13}$ .

In considering the resonance and polar nature of  $m_1\cdot$  and  $m_2\cdot$ , one finds that these two radicals are rather similar. There appears to be no a priori reason to expect that the rate constants  $k_{13}$  and  $k_{23}$ , involving the same comonomer  $M_3$ , would be appreciably different. It may be assumed that  $k_{13} \sim k_{23}$ . The previous section has shown that  $k_{23}$  is proportional to  $k_{[MMA\cdot][M_3]}$  for several comonomers. Thus the relative ease of the interruption reaction may be indirectly reflected by  $k_{[MMA\cdot][M_3]}$ . The latter can be obtained and sometimes approximated from the literature as the reciprocal of the reactivity ratio of methyl methacrylate in binary MMA- $M_3$  systems, allowing  $k_{[MMA\cdot][MMA]}$  to be unity (Table IV, column 9).

An attempt will now be made to correlate the solubility data with  $k_{[MMA\cdot][M_3]}$ . Since only a qualitative comparison is intended, such distracting factors as minor temperature difference, uncertainty in some reactivity ratios, and heterogeneous copolymerization from benzene solutions are assumed to be impertinent.

As seen by the arrangement of the comonomers in column 1 and the  $k_{[MMA\cdot][M_3]}$  values in column 9, Table IV, a qualitative parallel relation may be made between an increasing tendency to form soluble, cyclized copolymers (see also columns 3 and 6) and a decreasing order of  $k_{[MMA\cdot][M_3]}$ . This relationship supports the assumption that the more reactive the

TABLE IV. Copolymerizations of Methacrylic Anhydride with Vinyl Monomers under the Same Experimental Conditions

Comonomer, M <sub>3</sub>	MAN/M <sub>3</sub> , <sup>a</sup> by wt.	In bulk <sup>b</sup>		In 10% benzene solution <sup>e</sup>		k <sub>[MMA-1][M<sub>3</sub>]<sup>f</sup></sub>	Ref.
		Soly. in DMS <sup>c</sup>	% conv. <sup>d</sup>	Ident. of product	Soly. in DMS	% conv. <sup>d</sup>	Ident. of product
Styrene	41/59	I	80 <sup>g</sup>	—	I	87	—
Methyl methacrylate	42/58	I	80 <sup>g</sup>	—	I	95	—
n-Hexyl methacrylate	30/70	I	80 <sup>g</sup>	—	I	84	—
Lauryl methacrylate	23/77	I	80 <sup>g</sup>	—	S	73	—
Acrylonitrile	63/37	I	80 <sup>g</sup>	—	S	68	5.7% N
Ethyl acrylate	42/58	I	80 <sup>g</sup>	—	S	89	—
Vinyl n-butyl sulfone	33/67	S	21	5.0% S	S	51	6.6% S
Vinyl acetate	46/54	S	47	( <sup>h</sup> )	S	54	( <sup>h</sup> )
2-Chloroethyl vinyl ether	41/59	S	31	7.7% Cl	S	58	9.0% Cl
Allyl chloroacetate	35/65	I	37	3.3% Cl	S	28	3.0% Cl
Allyl benzyl ether	33/67	S	35	( <sup>i</sup> )	S	32	( <sup>i</sup> )
Diisobutylene	40/60	S	40	( <sup>i</sup> )	S	42	—

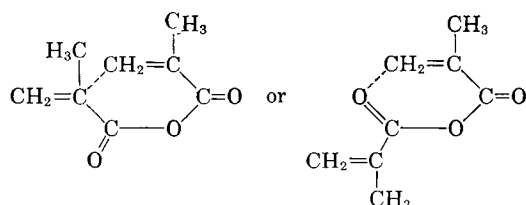
<sup>a</sup> All ratios are 32/68 by moles. <sup>b</sup> 65–70°. <sup>c</sup> DMS: dimethyl sulfoxide. <sup>d</sup> Based on total weight of charge. <sup>e</sup> Per cent based on monomer mixture by volume; 80°. <sup>f</sup> Calcd. from the reactivity ratio of MMA for M<sub>3</sub> at 60° allowing  $k_{[MMA-1][MMA]} = 1$ . See text. <sup>g</sup> Estimated. <sup>h</sup> Strong IR absorption at 1240 cm.<sup>-1</sup> corresponding to C—O stretching vibrations of the vinyl acetate unit. See ref. 17. <sup>i</sup> Weak to medium absorptions at 1125, 1070, 735, and 700 cm.<sup>-1</sup> corresponding to the benzyl unit. Absorptions more intense for the sample prepared in bulk than for that in solution. <sup>j</sup> Presence of diisobutylene unit not certain. <sup>k</sup> Assumed. <sup>l</sup> See ref. 18. <sup>m</sup> Calc. for methyl vinyl sulfone, see footnote (<sup>c</sup>), Table III. <sup>n</sup> Calc. for vinyl ethyl ether, see footnote (<sup>d</sup>), Table III. <sup>o</sup> Footnote (<sup>c</sup>), Table III.

interruption reaction between  $M_3$  and  $m_1\cdot$  (as reflected from  $k_{[MMA]\cdot[M_3]}$ ), the greater the tendency to gel.

Thus, in order to produce soluble copolymers from methacrylic anhydride and a comonomer, the comonomer should be a rather unreactive compound which reacts with methacrylic anhydride radical only slowly. By the same token the conversion of the copolymerization will generally be low. Hence it appears very difficult to obtain a soluble copolymer of methacrylic anhydride and any conventional vinyl monomer under these combined conditions: (a) polymerization in bulk or in moderately concentrated solutions, (b) high conversion, and (c) approximately equimolar ratios.

The mystery of cyclopolymerization itself, however, still remains unsolved. When methacrylic anhydride is homopolymerized, the product is soluble, indicating that the interruption reaction between  $m_1\cdot$  and  $M_1$  does not occur. On the other hand, if a vinyl monomer such as methyl methacrylate is copolymerized with methacrylic anhydride, the copolymer is insoluble provided that, as shown in this work, the ratio of the two monomers and the dilution level are not too extreme. An interpretation advanced herewith is that methyl methacrylate intercepts  $m_1\cdot$ , resulting eventually in crosslinking. The inference is that methyl methacrylate is considerably more reactive than methacrylic anhydride toward  $m_1\cdot$ . Why should there be such a difference in reactivity between a methacrylic group belonging to methyl methacrylate and another methacrylic group belonging to methacrylic anhydride? Structure similarity between the two methacrylic groups does not make the difference in their reactivities obvious.

One could conjecture that perhaps the methacrylic anhydride molecule exists in a loosely coordinated manner where the normal reactivity of the methacrylic groups is thereby modified by the ring conformation:



We have no data to test this hypothesis.

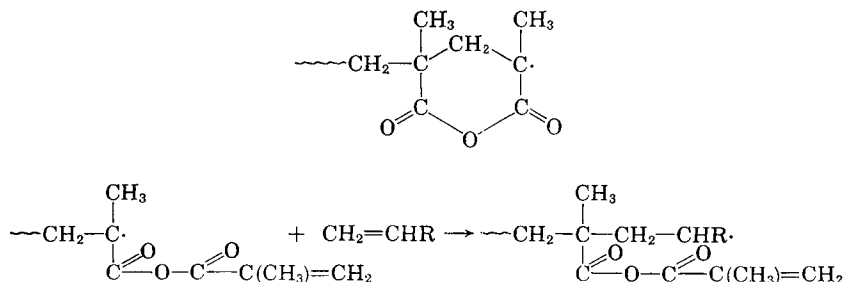
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### Synopsis

Copolymerizations of methacrylic anhydride and a variety of common types of vinyl monomers were conducted in bulk and in solution at 60–80° with benzoyl peroxide catalyst. The copolymers were characterized by conversion, solubility in hot dimethyl sulfoxide, elementary analysis, and infrared spectroscopy. A copolymer composition equation was derived for a special divinyl–vinyl system in which the divinyl monomer would cyclize extensively during polymerization and give rise to soluble, although perhaps branched, copolymers. The results showed that both soluble and insoluble copolymers were obtained, depending on the comonomer used and experimental conditions under which the copolymerization was carried out. In general, soluble copolymers were formed under the following conditions: (a) the less reactive the comonomer in free radical copolymerizations; (b) the greater the dilution; (c) the greater the difference in the moles of the two components in charge; and (d) the lower the conversion. According to reactivity ratio determinations and a comparison with published data, the anhydride ring radical behaved like a methyl methacrylate radical. The key step which led to gelation was believed to be “ring interruption” by the comonomer ( $\text{CH}_2 = \text{CHR}$ ):



The question why methacrylic anhydride does not gel in homopolymerization, however, still remains unresolved.



### Résumé

On a effectué la copolymérisation d'anhydride méthacrylique et de divers monomères vinyliques en masse et en solution à 60–80°C en présence de peroxyde de benzoyle comme catalyseur. Les copolymères étaient caractérisés par leur degré de conversion et leur solubilité dans le sulfoxyde de diméthyle bouillant et cela au moyen d'analyses élémentaires et par spectroscopie infrarouge. Une équation de composition du copolymère a été dérivée pour un système spécial divinyl-vinylique dans lequel le monomère divinylque était fortement cyclisé pendant la polymérisation donnant formation à des copolymères solubles bien que parfois ramifiés. Les résultats ont démontré qu'on obtient des copolymères solubles et insolubles suivant le comonomère employé et les conditions expérimentales dans lesquelles la copolymérisation a été effectuée. En général les copolymères solubles ont été obtenue d'autant mieux que (a) la réactivité du comonomère est faible en copolymérisation radicalaire, (b) la dilution est plus grande, (c) la différence molaire des deux composants au départ est plus élevée, (d) le degré de conversion est faible. Par la détermination des rapports de réactivité et la comparaison avec des données connues, il résulte que le radical anhydride cyclique se comporte comme un radical de méthacrylate de méthyle. L'étape-clef qui provoque la gélification est l'empêchement à la cyclisation provoqué par le comonomère ( $\text{CH}_2=\text{CHR}$ ). Le problème reste toutefois entier en ce qui concerne l'absence de gélification de l'anhydride méthacrylique en cours de son homopolymérisation.

### Zusammenfassung

Es wurden Copolymerisationen von Methacrylsäureanhydrid mit mehreren üblichen Vinylmonomeren in Substanz und in Lösung bei 60–80° mit Benzoylperoxyd als Katalysator durchgeführt. Die Copolymeren wurden durch Umsatzbestimmung, Löslichkeit in heissem Dimethylsulfoxyd, Elementaranalyse und Infrarotspektroskopie charakterisiert. Es wurde eine Gleichung für die Copolymerzusammensetzung für ein spezielles Divinyl-Vinyl System abgeleitet, in dem das Divinylmonomere während der Polymerisation unter Bildung von löslichen, aber vielleicht verzweigten Copolymeren in starkem Ausmass cyclisiert. Die Ergebnisse zeigten, dass sowohl lösliche als auch unlösliche Copolymere erhalten werden, je nach dem verwendeten Comonomeren und den experimentellen Bedingungen, unter denen die Copolymerisation durchgeführt wurde. Im allgemeinen werden um so mehr lösliche Copolymere gebildet, (a) je reaktionsträger das Comonomere bei Radikalcopolymerisation, (b) je grösser die Verdünnung, (c) je grösser der molare Unterschied der beiden verwendeten Komponenten und (d) je geringer der Umsatz ist. Aus Bestimmungen des Reaktivitätsverhältnisses und durch Vergleich mit Literaturdaten ergab sich, dass sich das Anhydridringradikal wie ein Methilmethacrylatradikal verhält. Als Schlüsselreaktion, die zur Gelbildung führt, wird die "Ringunterbrechung" durch das Comonomere ( $\text{CH}_2=\text{CHR}$ ) betrachtet. Die Frage, warum Methacrylsäureanhydrid bei der Homopolymersation kein Gel bildet, bleibt jedoch ungelöst.

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