

## Copolymerization of 4-Cyclopentene-1,3-dione with Acrylonitrile and Methyl Methacrylate\*

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### Synopsis

The copolymerization of acrylonitrile and methyl methacrylate with 4-cyclopentene-1,3-dione ( $M_2$ ) is reported. The copolymers were prepared by heating the monomer feeds in sealed tubes with  $\alpha, \alpha'$ -azobisisobutyronitrile. Infrared bands for both the  $\beta$ -diketone and the nitrile, in the case of acrylonitrile, or ester, in the case of methyl methacrylate, indicated that copolymerization had occurred. The acrylonitrile copolymers were insoluble in the common solvents and swelled on treatment with dimethylformamide and dimethylsulfoxide. The methyl methacrylate copolymers were partially soluble in the usual solvents with the solubility and gel content varying with the composition of the copolymers. Solution viscosities indicated high molecular weights. The reduced specific viscosity of the sodium salt of the 0.05 methyl methacrylate copolymer increased with decreasing concentration, a characteristic typical of polyelectrolytes. The compositions of the copolymers were determined from the nitrogen analyses for acrylonitrile copolymers, and the ultraviolet absorption of the  $\beta$ -diketone for the methyl methacrylate copolymers. The molar extinction coefficient of the  $\beta$ -diketone structural unit was estimated from a study of model compounds. The reactivity ratios were evaluated by the usual methods. For the acrylonitrile ( $M_1$ )-4-cyclopentene-1,3-dione ( $M_2$ ) system,  $r_1 = 3.67$ ,  $r_2 = 0.21$ . For the methyl methacrylate ( $M_1$ )-4-cyclopentene-1,3-dione ( $M_2$ ) system  $r_1 = 7.4$ ,  $r_2 = 0.083$ . For each system  $Q$  and  $e$  values for 4-cyclopentene-1,3-dione were evaluated. The average values are  $Q = 0.20$ ,  $e = 1.42$ . The behavior of 4-cyclopentene-1,3-dione is compared with maleic anhydride and *N*-butylmaleimide with respect to the reactivity of the monomer, the reactivity of the radical, and the effective polarity of the double bond.

### INTRODUCTION

It has long been recognized that radicals derived from 1,2-disubstituted ethylenes have a low order of reactivity toward their parent monomers, as illustrated by their extremely low copolymerization reactivity ratios.<sup>1</sup> Many of these monomers, although reactive in copolymerization, do not homopolymerize satisfactorily to give high polymers.<sup>2a</sup> Cyclic five-membered monomers are irregular in their reactivities. Although vinylene carbonate polymerizes readily under mild conditions,<sup>2a</sup> maleic anhydride is quite resistant, and the polymerization has only recently been satisfactorily

\* Taken in part from the Ph.D. dissertation of F. Lynn Hamb (1963), West Virginia University.

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effected under rather severe conditions.<sup>3</sup> In contrast to the low reactivity of maleic anhydride in vinyl homopolymerization, maleimide, a closely related monomer, homopolymerizes rapidly under mild conditions.<sup>4</sup> Apparently the substitution of a  $\text{—NH—}$  group for the  $\text{—O—}$  group in the ring enhances the reactivity of the radical with its own monomer. Since maleic anhydride and maleimide are sterically and electronically similar, it becomes difficult to assign a specific cause to this difference in reactivity in free radical polymerization.

The recent availability<sup>5,6</sup> of 4-cyclopentene-1,3-dione, a monomer similar in structure to maleic anhydride and maleimide, but containing a  $\text{—CH}_2\text{—}$  group in place of the  $\text{—O—}$  or  $\text{—NH—}$ , makes possible through homopolymerization and copolymerization studies further comparisons of the effects of various substituents in the ring on the reactivities of double bonds in cyclic structures. The dione is a very reactive dieneophile in the Diels-Alder reaction and, through its methylene group, readily undergoes acid-catalyzed condensation with aldehydes.<sup>7</sup> In base, polymerization occurs by a proposed anionic mechanism.<sup>7</sup>

The purpose of this paper is to report the free-radical copolymerization of 4-cyclopentene-1,3-dione with acrylonitrile and methyl methacrylate and to compare the reactivity of this monomer with other cyclic monomers, particularly maleic anhydride and maleimide, through reactivity ratios and the Alfrey-Price<sup>8</sup>  $Q$  and  $e$  values.

## EXPERIMENTAL

### Materials

A mixture of 3-cyclopentene-1,2-diol and 4-cyclopentene-1,3-diol was prepared by the peracetic acid oxidation of cyclopentadiene.<sup>9</sup> Oxidation with chromic acid afforded 4-cyclopentene-1,3-dione.<sup>7</sup> The compound was recrystallized three times from ethyl ether and dried before use.

Acrylonitrile (Eastman Organic Chemicals) was passed through a silica gel column just prior to use to remove the hydroquinone inhibitor.<sup>2b</sup>

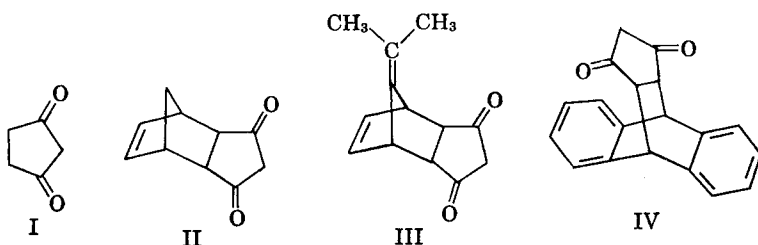
Methyl methacrylate (Matheson, Coleman and Bell) was washed with 5% sodium hydroxide, then with water, and was dried over anhydrous magnesium sulfate. The monomer was distilled at  $50^\circ\text{C./125 mm.}$  just prior to use.

$\alpha,\alpha'$ -Azobisisobutyronitrile (The Borden Chemical Company) was recrystallized from ethyl ether to give white needles, m.p.  $94^\circ\text{C. (dec.)}$ .

Benzene was washed with sulfuric acid, then with water and was dried over calcium chloride. It was distilled through a 30-in. packed column, and the middle fraction was collected and stored over sodium.

### Model Compounds

Compounds I–IV were prepared for use in estimating the molar extinction coefficient of the  $\beta$ -diketone unit in methyl methacrylate copolymers.



Cyclopentane-1,3-dione (I) was prepared by reduction of 4-cyclopentene-1,3-dione with zinc dust in acetic acid.<sup>5</sup>

The Diels-Alder adducts II and IV were prepared by the condensation of 4-cyclopentene-1,3-dione with cyclopentadiene<sup>5</sup> and anthracene,<sup>5,10</sup> respectively.

Compound III was prepared by a Diels-Alder reaction between 2.0 g. (0.019 mole) of dimethylfulvene and 1.5 g. (0.015 mole) of 4-cyclopentene-1,3-dione in 4 ml. of benzene. After three days at room temperature the reaction mixture consisted of a mass of tacky solid. The solid (0.6 g.) was collected and recrystallized from chloroform to yield white crystals of the adduct, m.p. 200–201°C.

ANAL. Calcd.  $C_{13}H_{14}O_2$ : C, 77.20%; H, 6.98%. Found: C, 77.31%; H, 6.85%.\*

### Copolymerization with Acrylonitrile

#### *Polymerization Procedure*

A homogeneous solution of the desired molar ratio of acrylonitrile and 4-cyclopentene-1,3-dione in benzene was charged into a thick-walled tube. The initiator,  $\alpha, \alpha'$ -azobisisobutyronitrile, was added in the amount of 0.015 mole-% of the total charge. The sample was degassed a minimum of three times by alternate cooling in liquid air and warming under low pressure. The tube was sealed under 0.1–0.2 mm. pressure of nitrogen and placed in a constant temperature bath at  $60 \pm 0.1^\circ\text{C}$ . The mixture was heated and stirred until reaction was estimated to have proceeded to 2 or 3% conversion, as evidenced by the precipitation of the polymer. Stirring was accomplished by the agitation of a small bar magnet in the tube by a magnetic stirrer placed outside the bath adjacent to the tube. The tube was opened, and the contents were poured into ethyl ether. After settling, the copolymers were filtered, washed with ether, dried in air, and weighed to determine the per cent conversion.

#### *Characterization and Analysis*

In the infrared spectra of the copolymers a sharp band at  $2240\text{ cm}^{-1}$  (nitrile) and a broad band with its maximum at  $1590\text{ cm}^{-1}$  ( $\beta$ -diketone) are evidence that both monomers participate in the polymerization reaction.

\* Elemental analyses by Galbraith Laboratories, Inc., Knoxville, Tennessee.

The copolymers from all feed compositions have very similar solubility properties. The copolymers are swollen by dimethylformamide and dimethyl sulfoxide. They are insoluble in diethyl carbonate, methanol, benzene, acetone, chloroform, tetrahydrofuran, petroleum ether (30–60°C.), and ethyl ether. The general insolubility and the swelling of the copolymers in dimethylformamide and dimethyl sulfoxide may be indicative of crosslinking between polymer chains.

In the heat of a Bunsen flame the copolymers fuse into brittle pellets. Films of the copolymers, fabricated at 20,000 lb. and 140–150°C., are transparent, amber in color, hard, and very brittle.

TABLE I  
Reactivity Ratio Data for the Copolymerization of  
Acrylonitrile ( $M_1$ ) and 4-Cyclopentene-1,3-dione ( $M_2$ ) in Benzene

$f_1$ Mole fraction $M_1$ in feed	Time, min.	Conversion, %	N, %	$F_1$ mole fraction $M_1$ in polymer
0.90	90	2.79	24.01	0.94
0.80	120	1.62	23.63	0.93
0.60	160	1.85	19.92	0.85
0.40	185	1.63	14.89	0.70
0.25	195	2.06	13.49	0.65
0.15	225	1.64	11.08	0.57
0.05	440	2.30	1.73	0.11

The copolymers were ground to a finely divided state, washed repeatedly with ether, dried in air, and subsequently dried under high vacuum at 80°C. for 4–5 hr. The composition was determined from nitrogen analyses. The polymerization data are presented in Table I.

### Copolymerization with Methyl Methacrylate

#### *Polymerization Procedure*

To the desired ratio of methyl methacrylate and 4-cyclopentene-1,3-dione dissolved in pure dry benzene was added 0.5 mole-% of the total charge  $\alpha, \alpha'$ -azobisisobutyronitrile. The mixture was charged into a thick-walled tube and degassed twice under a low pressure of nitrogen by alternate warming and cooling in a Dry Ice-acetone bath. The tube was sealed and placed in a constant temperature bath at  $65 \pm 1^\circ\text{C}$ . The contents were stirred with a small bar magnet until the polymerization had proceeded to a 2–5% conversion, as evidenced by the increased viscosity. The polymer was precipitated by addition of the mixture to petroleum ether (30–60°C.) for feeds of high methyl methacrylate content or ethyl ether for feeds of low methyl methacrylate content. The precipitated polymers were collected by filtration, dried in air, and weighed. The polymerization data and conversions are reported in Table II.

TABLE II  
Conversion Data for Copolymerization of Methyl Methacrylate ( $M_1$ )  
and 4-Cyclopentene-1,3-dione ( $M_2$ ) in Benzene

$f_1$ Mole fraction $M_1$ in feed	Total feed, moles	Vol. benzene, ml.	Time, min.	Conversion %
1.00	0.040	5	210	30.0
0.95	0.0737	5	30	4.35 <sup>a</sup>
0.90	0.0778	5	30	3.61
0.80	0.100	10	50	6.54 <sup>b</sup>
0.70	0.121	10	35	2.76 <sup>c</sup>
0.60	0.100	5	50	6.61 <sup>d</sup>
0.50	0.0816	10	35	3.25
0.40	0.100	10	65	4.30
0.25	0.100	10	35	3.91
0.15	0.0807	10	35	1.14
0.10	0.0697	12	50	2.08
0.05	0.100	12	55	0.62

<sup>a</sup> Trace of gel.

<sup>b</sup> 12% gel.

<sup>c</sup> 47% gel.

<sup>d</sup> 65% gel.

The copolymers were purified by precipitation into petroleum ether from ethyl acetate solution after separation of any insoluble material. The copolymers from the 0.05, 0.10, 0.15 feeds were not reprecipitated, as these tended to form emulsions. The polymers were dried under reduced pressure over phosphorus pentoxide at 80°C.

#### *Characterization of the Copolymers*

**Spectra.** Infrared absorption bands at 1730  $\text{cm}^{-1}$  (ester) and 1600  $\text{cm}^{-1}$  ( $\beta$ -diketone) indicate the presence of both methyl methacrylate and 4-cyclopentene-1,3-dione structural units in the copolymers. Ultraviolet absorption, characteristic of  $\beta$ -diketones, occurs at 247  $\text{m}\mu$  for ethanol solutions of the copolymers or 255  $\text{m}\mu$  for chloroform solutions.

**Solubility.** In general, the copolymers from feeds above 0.25 mole fraction methyl methacrylate are either partially or completely soluble in ethyl acetate, benzene, chloroform, acetone, tetrahydrofuran, and methyl ethyl ketone, the solubility decreasing progressively with increasing concentration of the dione in the copolymer. On the other hand, the solubility in ethanol and aqueous sodium hydroxide increases with increasing dione content. In dimethylformamide and dimethyl sulfoxide the copolymers are partially soluble over the entire composition range.

In all of the copolymerizations gel was formed, Table II, which showed considerable swelling with various solvents. The occurrence of gel, the amount of which increased with increasing 4-cyclopentene-1,3-dione content, may be a result of crosslinking, possibly through the active hydrogens of the  $\beta$ -diketone unit.

**Softening Behavior.** Clear, flexible films of the copolymers could be cast from ethyl acetate or chloroform solution. The softening point of the films, as determined on a Köffler hot stage, decreased with increasing dione concentration. At higher temperatures the copolymers of low dione content melted to viscous oils (Table III).

TABLE III  
Melting and Softening Behavior of Methyl Methacrylate-  
4-Cyclopentene-1,3-dione Copolymers  
(Films Cast from Chloroform)

Feed composition, mole fraction MMA	Softening point, °C.	High temperature behavior
1.0	145	Viscous, rubbery
0.95	140	Viscous liquid at 290°C.
0.90	135	Viscous liquid at 280°C.
0.80	125	Darkens at 200°C., does not melt
0.70	125	Darkens at 200°C., does not melt

**Solution Viscosity.** The intrinsic viscosities of several of the copolymers and of poly(methyl methacrylate) prepared under similar conditions are compared in Table IV. Although the molecular weights of the copolymers are not known, the high intrinsic viscosities indicate a reasonably high degree of polymerization.

TABLE IV  
Intrinsic Viscosities of Methyl Methacrylate ( $M_1$ )-  
4-Cyclopentene-1,3-dione Copolymers in Chloroform at 30°C.

Feed ratio, mole fraction $M_1$	Intrinsic viscosity of copolymer
1.0	$1.36 \pm 0.05$
0.95	$2.11 \pm 0.05$
0.90	$2.30 \pm 0.05$
0.80	$1.36 \pm 0.07$
0.70	$1.75 \pm 0.05$

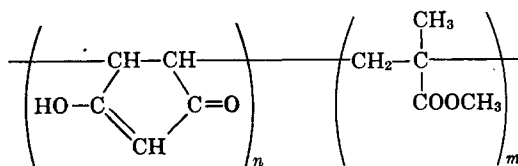
TABLE V  
Viscosity Data for Aqueous Solutions of  
the Sodium Salt of the 0.05  $M_1$  Copolymer

Concentration g./100 ml.	$\eta_{sp}$	$\eta_{sp}/c$
0.1267	0.094	0.742
0.0634	0.059	0.931
0.0422	0.045	1.06
0.0317	0.036	1.13
0.0253	0.031	1.22

The sodium salt of the copolymer from the 0.05 mole fraction feed was prepared by potentiometric titration with sodium hydroxide in 10% aqueous ethanol. The solvent was evaporated, and the copolymer salt was washed quickly with a small amount of water and dried. Viscosity measurements on aqueous solutions of the copolymer salt revealed that the reduced specific viscosity increases with decreasing concentration (Table V), a behavior consistent with the electrolytic nature of the copolymer salt.

### *Analysis of the Copolymers*

**Methods.** Two methods of analysis are indicated by the structure (V) of the copolymer: titration of the  $\beta$ -diketone through its enolic hydrogen or ultraviolet measurements of the conjugated carbonyl.



V

Although potentiometric titration of several of the copolymers in aqueous ethanol provided some analytical data, the low solubility of many of the polymers in solvents suitable for titration prevented this method from being used to cover the entire range of copolymer composition. By using two solvents, ethanol and chloroform, however, it was possible to measure the composition of all but one (0.25 feed) of the copolymers by their ultraviolet absorption.

**Ultraviolet of Model Compounds.** The wavelength and the molar extinction coefficient for the  $\beta$ -diketone structural unit in the copolymer was estimated from the ultraviolet data for model compounds I–IV in two solvents, 95% ethanol and chloroform (Table VI).

From Table VI, the extinction coefficient of the  $\beta$ -diketone structural unit was assigned the values 9290 for ethanol solutions and 3555 for chloroform solutions. These values were taken as the average for compounds

TABLE VI  
Ultraviolet Absorption of Model Compounds

Compound	95% Ethanol			Chloroform		
	Concn., mole/l. $\times 10^5$	$\lambda_{\text{max}}$ , m $\mu$	$\epsilon$	Concn., mole/l. $\times 10^5$	$\lambda_{\text{max}}$ , m $\mu$	$\epsilon$
I	1.98	245	12,000	16.0	246	3,800
II	1.36	263	9,260	16.2	249	6,300
III	1.29	264	9,460	15.8	246	3,510
IV	1.75	265	9,140	16.0	248	3,600

II, III, and IV for ethanol solutions and III and IV for chloroform. Compound I, which lacks substitution at the 4 and 5 positions of the ring and is, therefore, not as closely related to the disubstituted structural unit of the copolymers as were compounds II–IV, was not included in the average. The cause of the high extinction coefficient for compound II in chloroform is not known at this time, but it may be due to a difference in solvent effect on the two possible forms, *exo* and *endo*, both of which might have been present. Minor variations in the wavelength and extinction coefficient with concentration<sup>11</sup> were minimized by maintaining reasonably constant concentrations.

**Copolymer Composition Analysis.** The analytical data for the copolymers are presented in Table VII. The absorbancy,  $A_{(\text{obs})}$ , of the copolymer at  $\lambda_{\text{max}}$  for the  $\beta$ -diketone unit was determined with a Beckman DU quartz spectrophotometer. For the copolymers of low dione content, it was necessary to correct the  $A_{(\text{obs})}$  values for the absorption of the methyl methacrylate units in order to obtain the absorbancy due solely to the dione. This was done in the following way. The extinction coefficient of the methyl methacrylate structural unit for poly(methyl methacrylate) in chloroform was determined at each of the reported wavelengths. These values varied in magnitude between 2 and 6. From the molar extinction coefficient of the dione, an approximate copolymer composition was calculated by assuming  $A_{(\text{obs})} = A_{(\text{M}_2)}$ . The absorbancy arising from the dione units,  $A_{(\text{M}_2)}$ , was then determined from the relationship

$$A_{(\text{M}_2)} = A_{(\text{obs})} - c_{(\text{M}_1)}\epsilon_{(\text{M}_1)}$$

The corrected copolymer composition was then calculated from  $A_{(\text{M}_2)}$ . For the copolymer of high dione content this correction is negligible.

TABLE VII  
Ultraviolet Analytical Data for Copolymers of Methyl Methacrylate ( $\text{M}_1$ ) and 4-Cyclopentene-1,3-dione ( $\text{M}_2$ )

$f_1$ Mole fraction $\text{M}_1$ in feed	Solvent	Concn., g./l.	$\lambda_{\text{max}}$	Absorbance			$F_1$ Mole fraction $\text{M}_1$ in polymer
				Obs.	MMA	$\text{M}_2$	
0.95	$\text{CHCl}_3$	0.8300	259	0.237	0.022	0.215	0.993
0.90	"	0.5600	250	0.250	0.032	0.218	0.990
0.80	"	0.4040	255	0.393	0.016	0.377	0.974
0.70	"	0.2180	252	0.388	0.006	0.382	0.953
0.60	"	0.2900	254	0.873	0.008	0.865	0.920
0.50	"	0.2650	251	1.070	0.009	1.061	0.892
0.40	"	0.0365	252	0.228	0.001	0.227	0.832
0.15	$\text{C}_2\text{H}_5\text{OH}$	0.0160	248	0.585	—	0.585	0.609
0.10	"	0.0200	247	0.905	—	0.905	0.520
0.05	"	0.0150	246	0.822	—	0.822	0.423



## RESULTS

## Copolymerization with Acrylonitrile

In Figure 1 the mole fraction acrylonitrile in the copolymer  $F_1$  is plotted against the mole fraction in the monomer feed  $f_1$ . Treatment of the copolymer equation by the method of Mayo and Lewis<sup>12</sup> provided the series of lines shown in Figure 2. Values of  $r_1$  and  $r_2$  were determined from the

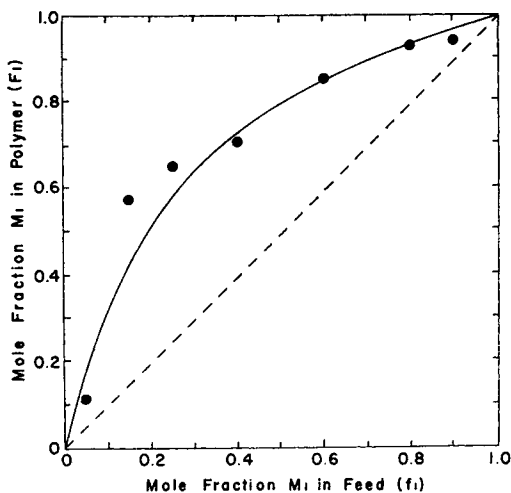


Fig. 1. Copolymerization of acrylonitrile ( $M_1$ ) with 4-cyclopentene-1,3-dione ( $M_2$ ). The solid curve was calculated for  $r_1 = 3.7$ ,  $r_2 = 0.20$ .

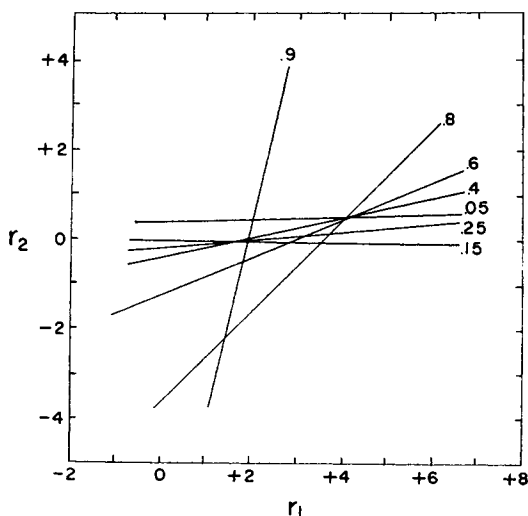


Fig. 2. Mayo-Lewis plot for determining reactivity ratios for the system acrylonitrile ( $M_1$ )-4-cyclopentene-1,3-dione ( $M_2$ ). The numbers at each line are the feed compositions.  $r_1 = 3.5 \pm 0.6$ ,  $r_2 = 0.2 \pm 0.2$ .

TABLE VIII  
Reactivity Ratios for the System  
Acrylonitrile ( $M_1$ ) and 4-Cyclopentene-1,3-dione ( $M_2$ )

No.	Method	$r_1$	$r_2$
1	Mayo and Lewis	$3.0 \pm 1.0$	$0.25 \pm 0.25$
2	Modified Mayo and Lewis, excluding 0.9 data	$3.5 \pm 0.6$	$0.2 \pm 0.2$
3	Fineman-Ross	3.80	0.24
4	Curve-fitting	3.70	0.20
5	Average of 2, 3, and 4	3.67	0.21

region of intersection bounded by the 0.9, 0.8, 0.05, and 0.15 feed lines, an area which includes all of the experimental data. If the somewhat uncertain 0.9 feed line is omitted, the area of intersection becomes bounded by the 0.8, 0.6, 0.15 feed lines, providing modified values of  $r_1$  and  $r_2$ . Although this operation has little effect on  $r_2$ ,  $r_1$  is changed to a significantly higher value (Table VIII).

The solution of the copolymer equation by the method of Fineman and Ross<sup>13</sup> is shown in Figure 3, where the solid line is the least-squares fit to the experimental data. In this case, in order to obtain a real solution it was necessary to exclude the 0.9 feed because its inclusion resulted in a positive intercept on the  $R(\rho - 1)/\rho$  axis giving an impossible negative value for  $r_2$ . The necessity for such an omission provides further justification for similar action in the Mayo-Lewis solution.

With the aid of the IBM 1620 digital computer appropriate values for  $r_1$  and  $r_2$ , taken within the intersection area of the Mayo-Lewis plot, Fig-

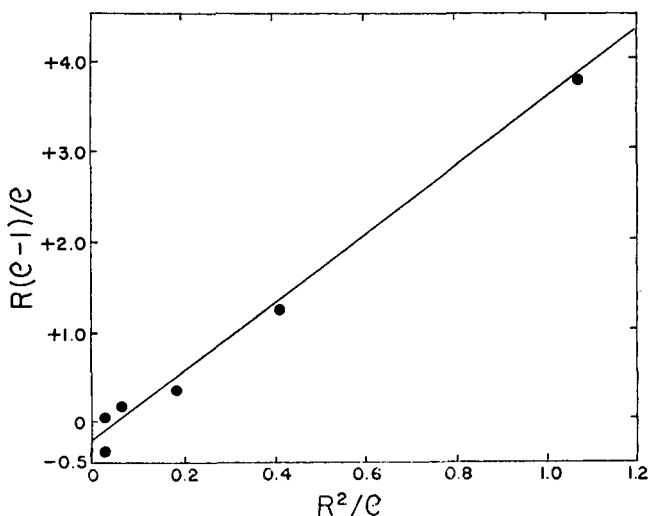


Fig. 3. Fineman-Ross plot for determining reactivity ratios for the system acrylonitrile ( $M_1$ )-4-cyclopentene-1,3-dione ( $M_2$ ).  $r_1 = 3.80$ ,  $r_2 = 0.24$ .

ure 2, were assigned, and  $F_1$  versus  $f_1$  curves were calculated. The solid curve in Figure 1 was judged to represent the best fit to the experimental data. The reactivity ratios as determined by the several methods are compared in Table VIII. The best value of the reactivity ratios is reported as the average of numbers 2, 3, and 4.

### Copolymerization with Methyl Methacrylate

The analytical data of Table VII are presented in Figure 4 as a graph of the mole fraction of methyl methacrylate in the copolymer  $F_1$  versus the

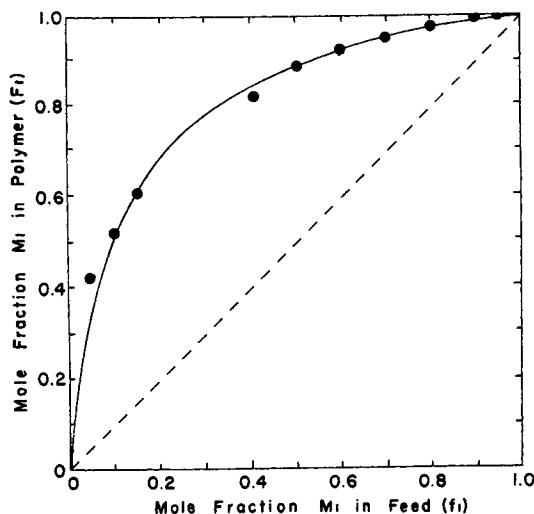


Fig. 4. Copolymerization of methyl methacrylate ( $M_1$ )–4-cyclopentene-1,3-dione ( $M_2$ )  
The solid curve was calculated for  $r_1 = 7.35$ ,  $r_2 = 0.075$ .

mole fraction of methyl methacrylate in the monomer feed  $f_1$ . At all feed compositions the mole fraction of methyl methacrylate is greater in the copolymer than in the feed.

Treatment of the composition data by the method of Mayo and Lewis is shown in Figure 5. The reactivity ratios are taken as the center of the area where the maximum number of intersections occur, an assignment which omits the data for the 0.90, 0.80, and 0.70 feeds. Solution of the

TABLE IX  
Reactivity Ratios for the System Methyl  
Methacrylate ( $M_1$ ) and 4-Cyclopentene-1,3-dione ( $M_2$ )

No.	Method	$r_1$	$r_2$
1	Mayo and Lewis	$7.5 \pm 0.5$	$0.10 \pm 0.05$
2	Fineman-Ross	7.35	0.074
3	Curve-fitting	7.35	0.075
4	Average of 1, 2, and 3	7.4	0.083

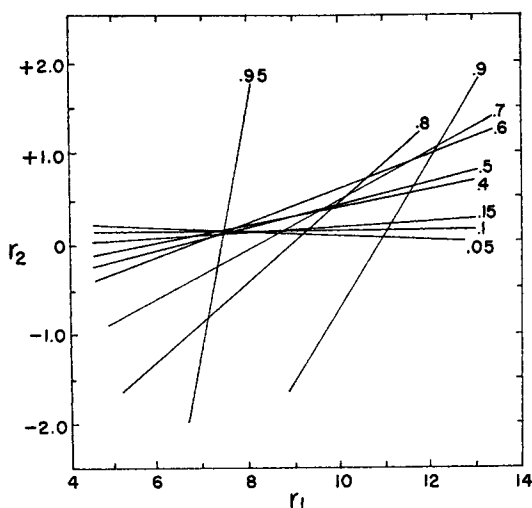


Fig. 5. Mayo-Lewis plot for determining reactivity ratios for the system methyl methacrylate ( $M_1$ )-4-cyclopentene-1,3-dione ( $M_2$ ). The numbers represent feed compositions.  $r_1 = 7.5 \pm 0.5$ ,  $r_2 = 0.10 \pm 0.05$ .

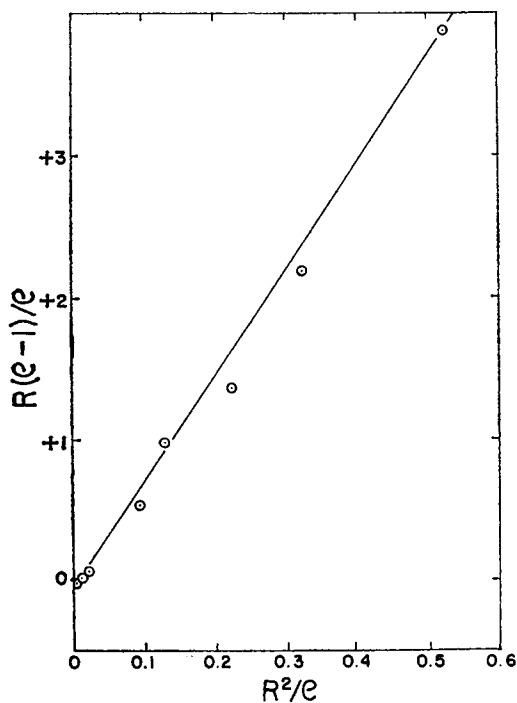


Fig. 6. Fineman-Ross plot for determining reactivity ratios for the system methyl methacrylate ( $M_1$ )-4-cyclopentene-1,3-dione ( $M_2$ ).  $r_1 = 7.35$ ,  $r_2 = 0.074$ .

copolymer equation by the method of Fineman and Ross is shown in Figure 6. Here it was necessary to omit the data for the 0.95 and 0.90 feeds since their inclusion resulted in a positive intercept on the  $R(\rho - 1)/\rho$  axis and a corresponding impossible negative value for  $r_2$ . In the solution by the curve-fitting method, the solid curve in Figure 4 was judged to give the best fit to the experimental data. The reactivity ratios obtained by the three methods are compared and averaged in Table IX.

## DISCUSSION

The  $Q$  and  $e$  parameters for 4-cyclopentene-1,3-dione were calculated by using the values  $Q = 0.50$ ,  $e = 1.23$  for acrylonitrile<sup>14</sup> and  $Q = 0.73$ ,  $e = 0.4$  for methyl methacrylate.<sup>15</sup> These results are compared in Table X and averaged to provide the best  $Q$  and  $e$  values.

TABLE X  
 $Q$  and  $e$  Values for 4-Cyclopentene-1,3-dione

	Copolymerization with		
	Acrylonitrile	Methyl methacrylate	Average
$Q$	0.26	0.13	0.20
$e$	1.74	1.10	1.42

The relative reactivities of acrylonitrile and 4-cyclopentene-1,3-dione with the two polymer radicals are tabulated in Table XI. The corresponding information for maleic anhydride, taken from copolymerization with acrylonitrile ( $M_1$ ) ( $r_1 = 6$ ,  $r_2 = 0$ ),<sup>17</sup> is included for comparison.

TABLE XI  
Relative Reactivities of Monomers with Polymer Radicals

Monomer	Radical	
	Acrylonitrile	4-Cyclopentene-1,3-dione
Acrylonitrile	1	4.8
4-Cyclopentene-1,3-dione	0.27	1
Maleic anhydride <sup>a</sup>	0.16	—

<sup>a</sup> Data of Mayo, Lewis, and Walling.<sup>16</sup>

Both radicals are more reactive toward acrylonitrile monomer than toward the dione. In reaction with the acrylonitrile radical the dione is about 1.7 times more reactive than maleic anhydride. In contrast with maleic anhydride, which resists adding its own kind, the dione radical does have a slight tendency to add dione monomer, as indicated by a reactivity ratio  $r_2$  greater than zero.

The relative reactivities of methyl methacrylate and 4-cyclopentene-1,3-dione with the two polymer radicals are given in Table XII and compared with corresponding information secured from copolymerization studies of methyl methacrylate with maleic anhydride ( $r_1 = 6.7$ ,  $r_2 = 0.02$ );<sup>17</sup> ( $r_1 = 3.5$ ,  $r_2 = 0.03$ );<sup>18</sup> and *N*-butylmaleimide ( $r_1 = 1.33$ ,  $r_2 = 0.12$ ).<sup>19</sup>

TABLE XII  
Relative Reactivities of Monomers with Polymer Radicals

Monomer	Radical			
	Methyl methacrylate	4-Cyclopentene-1,3-dione	Maleic anhydride	<i>N</i> -Butylmaleimide
Methyl methacrylate	1	12	50 <sup>a</sup> , 33 <sup>b</sup>	8.3 <sup>c</sup>
4-Cyclopentene-1,3-dione	0.14	1	—	—
Maleic anhydride	0.15, <sup>a</sup> 0.24 <sup>b</sup>	—	1	—
<i>N</i> -Butylmaleimide	0.75 <sup>c</sup>	—	—	1

<sup>a</sup> Data of de Wilde and Smets.<sup>17</sup>

<sup>b</sup> Data of Blackley and Melville.<sup>18</sup>

<sup>c</sup> Data of Coleman and Conrady.<sup>19</sup>

Comparison of the relative reactivities of methyl methacrylate and 4-cyclopentene-1,3-dione radicals (Table XII) shows that both of these radicals are considerably more reactive with methyl methacrylate monomer than with dione monomer. This behavior is very similar to that observed when acrylonitrile is the comonomer. Comparison of the three cyclic monomers with respect to their reactivity toward the methyl methacrylate radical indicates the following order of reactivity: *N*-butylmaleimide > maleic anhydride ≥ 4-cyclopentene-1,3-dione. The same order of reactivity of the monomers is indicated by their relative *Q* values (Table XIII).

Assuming almost equal reactivities of the dione and maleic anhydride monomers, it then appears that the dione radical is less discriminating than maleic anhydride radical (Table XII), and, hence, would have a greater intrinsic reactivity. The relative *e* values indicate the following order of electron attracting ability of the groups substituted on the double bond of

TABLE XIII  
*Q* and *e* Data for Cyclic Monomers

	4-Cyclopentene-1,3-dione	Maleic anhydride <sup>a</sup>	Maleic anhydride <sup>b</sup>	<i>N</i> -Butylmaleimide <sup>c</sup>
<i>Q</i>	0.20	0.19	0.38	0.94
<i>e</i>	1.42	1.8	1.9	1.75

<sup>a</sup> Data of de Wilde and Smets.<sup>17</sup>

<sup>b</sup> Data of Blackley and Melville.<sup>18</sup>

<sup>c</sup> Data of Coleman and Conrady.<sup>19</sup>

the cyclic monomers: maleic anhydride  $\geq$  *N*-butylmaleimide > 4-cyclopentene-1,3-dione. This is the same order as would be expected from a consideration of the availability of the electrons on the —O—, the —NR—, or the —CH<sub>2</sub>— for participation in a resonance distribution of the charges between the carbonyl groups. The slightly lower  $e$  for the dione indicates less radical stabilization, resulting in lower reactivity of the monomer and a greater reactivity of the product radical.

These studies of the reactions of cyclic five-membered monomers are continuing, and in a future publication will be reported the copolymerization of 4-cyclopentene-1,3-dione with styrene.

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### Résumé

On rend compte de la copolymérisation de l'acrylonitrile et du méthacrylate de méthyle avec la 4-cyclopentène-1,3-dione ( $M_2$ ). Les copolymères ont été préparés en chauffant les réactifs monomériques en tube scellé en présence d' $\alpha,\alpha$ -azo-bis isobutyronitrile. La présence à l'infra rouge de bandes caractéristiques de la  $\beta$  dicétone et du nitrile (dans le cas de l'acrylonitrile) ou de l'ester (dans le cas du méthacrylate de méthyle) indiquent que la copolymérisation a bien eu lieu. Les copolymères d'acrylonitrile sont insolubles dans les solvants habituels et gonflent par traitement au diméthylformamide et au diméthylsulfoxyde. Les copolymères de méthacrylate de méthyle sont partiellement solubles dans les solvants usuels et la solubilité et le contenu en gal varient avec la composition des copolymères. La viscosité des solutions indique des poids moléculaires élevés. La viscosité spécifique réduite du sel sodique du copolymère 0.05 de méthacrylate de méthyle augmente avec la dilution, ce qui est caractéris-

tique des polyelectrolytes. Les compositions des copolymères ont été déterminées par analyse d'azote par les copolymères d'acrylonitrile et par l'absorption ultraviolette de la  $\beta$ -dicétone pour les copolymères de méthacrylate de méthyle. Le coefficient d'extinction molaire de l'unité structurale  $\beta$ -dicétone a été estimé sur la base d'un modèle. Les rapports de réactivité ont été calculés par la méthode ordinaire. Pour le système acrylonitrile ( $M_1$ )-4-cyclopentène-1,3-dione ( $M_2$ )  $r_1 = 3.67$   $r_2 = 0.21$ . Pour le système méthacrylate de méthyle ( $M_1$ )-4-cyclopentène-1,3-dione ( $M_2$ )  $r_1 = 7.4$  et  $r_2 = 0.083$ . Pour chaque système, les valeurs  $Q$  et  $e$  pour la 4-Cyclopentène-1,3-dione ont été calculées. La valeur moyenne de  $Q = 0.20$  et de  $e = 1.42$ . On compare le comportement de la 4-cyclopentène-1,3-dione avec celui de l'anhydride maléique et de la *N*-butylmaleimide en ce qui concerne la réactivité du monomère, celle du radical et le polarité effective de la double liaison.

### Zusammenfassung

Über die Copolymerisation von Acrylnitril und Methylmethacrylat mit 4-Cyclopenten-1,3-dion ( $M_2$ ) wird berichtet. Die Copolymeren wurden durch Erhitzen der Monomermischungen in zugeschmolzenen Röhren mit  $\alpha,\alpha$ -Azo-bisobutyronitril hergestellt, Infrarotbanden für sowohl  $\beta$ -Diketon und Nitril, im Fall von Acrylnitril, als auch Ester, im Fall von Methylmethacrylat, lassen das Eintreten der Copolymerisation erkennen. Die Acrylnitrilcopolymeren waren in üblichen Lösungsmitteln unlöslich und quollen bei Behandlung mit Dimethylformamid und Dimethylsulfoxyd. Die Methylmethacrylatcopolymeren waren teilweise in üblichen Lösungsmitteln löslich, wobei die Löslichkeit und der Gelgehalt von der Copolymerzusammensetzung abhängig waren. Die Lösungsviskosität zeigt ein hohes Molekulargewicht an. Die reduzierte spezifische Viskosität des Natriumsalzes des 0,05 Methylmethacrylatcopolymeren nahm mit abnehmender Konzentration zu, was ein für Polyelektrolyte typisches Merkmal ist. Die Copolymerzusammensetzung wurde für Acrylnitrilcopolymere aus der Stickstoffanalyse und für Methylmethacrylatcopolymere aus der Ultraviolettabsorption des  $\beta$ -Diketons bestimmt. Der molare Extinktionskoeffizient der  $\beta$ -Diketonstruktureinheit wurde durch eine Untersuchung an Modellverbindungen bestimmt. Die Reaktivitätsverhältnisse wurden mit den üblichen Methoden berechnet. Für das Acrylnitril- ( $M_1$ )-4-Cyklopenten-1,3-dion ( $M_2$ )-system ergab sich  $r_1 = 3,67$ ,  $r_2 = 0,21$ . Für das Methylmethacrylat ( $M_1$ )-4-Cyklopenten-1,3-dion ( $M_2$ )-system  $r_1 = 7,4$ ,  $r_2 = 0,083$ . Für jedes System wurden  $Q$ - und  $e$ -Werte von 4-Cyklopenten-1,3-dion berechnet. Der Mittelwert beträgt  $Q = 0,20$ ,  $e = 1,42$ . Das Verhalten von 4-Cyklopenten-1,3-dion wird in bezug auf die Reaktivität des Monomeren, die Reaktivität des Radikals und die Effektivpolarität der Doppelbindung mit Maleinsäureanhydrid und *N*-Butylmaleinimid verglichen.

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