beam instrument using an identical solvent-filled cell in the reference beam. The percentage of I and II in each mixture was then calculated from extinction coefficients previously determined at each wave length. These data are summarized in Table I.

Isomerization Study.—The isomerization of I to II was carried out at 61.2, 80.1 and 100.0° by thermostating solutions of known concentration of I in *n*-decane. Samples were removed for analysis (done as described previously) at times which gave a good conversion–time curve at each temperature. A plot of $\ln X_e/(X_e\text{-}X)$ *vs.* time for each temperature is shown in Fig. 1. Thermodynamic values and rate data are summarized in Tables II and III, respectively.

Lithium Aluminum Hydride Reduction.—Bromine was added to butadiene in chloroform at −15° in the manner previously described. After addition of the bromine was complete the chloroform was flashed off under reduced pressure at the reaction temperature and tetrahydrofuran was added to replace the chloroform. Lithium aluminum hydride in tetrahydrofuran was added at −18 to −15° and a temperature of −15° was maintained for two hours. The reaction mixture was then heated to reflux temperature (67°) and held at that temperature for three hours. The reaction products were distilled into a cold trap (Dry Ice–acetone), weighed and analyzed by gas chromatography (Fig. 2). Only one product was formed, *trans*-2-butene, and the material balance on the butadiene was 99%.

Figure 2 also contains data obtained from the lithium aluminum hydride reduction of a mixture of 3,4-dibromo-1-butene and 1,4-dibromo-2-butene. Similar treatment of 92.5% 3,4-dibromo-1-butene and pure 1,4-dibromo-2-butene gave *trans*-2-butene as the only product with a yield of 95% or higher. Analysis of a mixture of the three olefins possible (1-butene, *cis*- and *trans*-2-butene) and of a 97% *trans*- 3% *cis*-2-butene mixture are given in Fig. 3.

The gas chromatographic equipment used for analysis consisted of a 10 ft. × 1/4 in. copper column with dinonyl phthalate on fire brick as the packing. The detector unit was a Gow-Mac thermal conductivity cell and helium was the carrier gas.

Acknowledgment.—The authors are indebted to The Robert A. Welch Foundation for the financial support of this research and to W. H. R. Shaw for valuable discussions concerning the kinetic studies.

AUSTIN 12, TEX.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

The Formation of Linear Polymers from Diene Monomers by a Cyclic Polymerization Mechanism. III. A Study of the Structure of Cyclic Polymers of Certain Unsymmetrical 1,6- and 1,7-Dienes[1,2]

BY MARTIN D. BARNETT,[3a] ALLAN CRAWSHAW[3b] AND GEORGE B. BUTLER

RECEIVED APRIL 25, 1959

The methyl allyl, methyl 2-butenyl and methyl 3-butenyl mixed esters of maleic and fumaric acid have been synthesized and polymerized in bulk using benzoyl peroxide to afford a series of low molecular weight linear polymers containing 37–77% residual unsaturation. The properties of the polymers indicated that polymerization had occurred by an intramolecular–intermolecular mechanism leading, in part, to a poly-[3(5)-methylene-4-carbomethoxy-δ-valerolactone] or (in the case of the 3-butenyl esters) to a poly-[3(5)-methylene-4-carbomethoxy-ε-caprolactone] structure. In addition, poly-(methyl allyl maleate) and poly-(methyl 2-butenyl maleate) showed absorption at 1780 cm.$^{-1}$ characteristic of a γ-butyrolactone ring system. This band was lacking in the corresponding fumarates. Possible explanations of the various modes and relative degrees of cyclization in the polymers are presented.

Recent work[4–10] has verified the original proposal[11] that certain monomers containing a 1,6-diene system can, on polymerization, undergo an alternating intramolecular–intermolecular chain propagation or cyclization, leading to the formation of saturated linear chains containing alternating six-membered rings and methylene groups. In addition, extensions of this new chain propagation mechanism to diene systems capable of forming rings containing more than six carbon atoms[12] as well as into the copolymer field[13] have now been reported.

Work in this area thus far has been largely limited to the study of symmetrical 1,6-dienes. Unsymmetrical 1,6-dienes, however, also should be capable of homopolymerization *via* cyclization, especially those monomers containing double bonds of comparable reactivity toward copolymerization. Although the homopolymerizations of such unsymmetrical 1,6-dienes as allyl acrylate,[14] allyl methacrylate[15,16] and substituted allyl methacrylates[17] have been reported, there appears to have been no previous study directed specifically toward verification of the presence of cyclic units in the polymer derived from such dienes. Unsaturated esters of maleic and fumaric acid seemed particularly suited for such a study because systems of this type should permit a qualitative comparison of the relative reactivities of various unsaturated alcohols as well as a comparison of the degree of cyclization in the *cis–trans* isomers.

---

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract Number AF18(603)-116. Reproduction in whole or in part is permitted for any purpose of the United States government.

(2) This paper was presented before the Division of Polymer Chemistry, American Chemical Society, Boston, Mass., April, 1959.

(3) (a) Post-doctoral fellow, 1958–1959; (b) Post-doctoral fellow, 1956–1958.

(4) G. B. Butler, A. Crawshaw and W. L. Miller, THIS JOURNAL, **80**, 3615 (1958).

(5) A. Crawshaw and G. B. Butler, *ibid.*, **80**, 5464 (1958).

(6) C. S. Marvel and R. D. Vest, *ibid.*, **79**, 5771 (1957).

(7) C. S. Marvel and R. D. Vest, *ibid.*, **81**, 984 (1959).

(8) C. S. Marvel and J. K. Stille, *ibid.*, **80**, 1740 (1958).

(9) J. F. Jones, *J. Polymer Sci.*, **33**, 7 (1958).

(10) J. F. Jones, *ibid.*, **33**, 15 (1958).

(11) G. B. Butler and R. J. Angelo, THIS JOURNAL, **79**, 3128 (1957).

(12) (a) C. S. Marvel and W. E. Garrison, Jr., *ibid.*, **81**, 4737 (1959); (b) T. Holt and W. Simpson, *Proc. Roy. Soc.* (*London*), **A238**, 154 (1956); (c) M. Oiwa and Y. Ogata, *J. Chem. Soc. Japan*, **79**, 1506 (1958).

(13) W. H. Schuller, J. A. Price, S. T. Moore and W. M. Thomas, *J. Chem. Eng. Data*, **1**, in press (1959).

(14) L. Gindin, S. Medvedev and E. Flesher, *J. Gen. Chem.* (*U.S.S.R.*), **19**, a127 (1949).

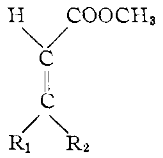
(15) E. R. Blount and B. E. Ostberg, *J. Polymer Sci.*, **1**, 230 (1946).

(16) S. G. Cohen, B. E. Ostberg, D. B. Sparrow and E. R. Blount, *ibid.*, **3**, 264 (1948).

(17) G. M. Bristow, *Trans. Faraday Soc.*, **54**, 1064 (1958).

Table I

Physical Properties of Monomers,



Compd.	R₁	R₂	Yield, %	Boiling point °C.	Boiling point Mm.	n^{22}_D	d^{22}	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Ia	H	$—COOCH_2CH{=}CH_2$	39	80–81	1.0	1.4580	1.1031	56.46	56.35	5.94	5.90
Ib	H	$—COOCH_2CH{=}CHCH_3$	21	73.5–75	0.6	1.4580	1.0762	58.68	58.60	6.57	6.68
Ic	H	$—COOCH_2CH_2CH{=}CH_2$	48	71.5–72	0.6	1.4561	1.0730	58.68	58.79	6.57	6.59
IIa	$—COOCH_2CH{=}CH_2$	H	62	69.5–70.5	1.1	1.4590	1.0990	56.46	56.48	5.94	6.15
IIb	$—COOCH_2CH{=}CHCH_3$	H	61	71–71.5	0.7	1.4622	1.0683	58.68	58.86	6.57	6.72
IIc	$—COOCH_2CH_2CH{=}CH_2$	H	72	63.5–64.5	0.6	1.4580	1.0651	58.68	58.57	6.57	6.73

Table II

Physical Properties of Polymers

Polymer	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Approximate softening point, °C.	Inherent viscosity, concn., g./100 ml.
Poly-Ia	56.46	56.51	5.94	5.84	95	0.061 (0.306)
Poly-Ib	58.68	58.34	6.57	6.58	110	.036 (.297)
Poly-Ic	58.68	58.56	6.57	6.58	105	Not detd.
Poly-IIa	56.46	56.59	5.94	5.91	100	Not detd.
Poly-IIb	58.68	58.70	6.57	6.60	75	.044 (.243)
Poly-IIc	58.68	58.44	6.57	6.39	100	.072 (.262)

Experimental[18]

Fumaryl Chloride Monomethyl Ester (III).—A procedure which obviates the necessity of isolating methyl hydrogen fumarate[19] or separating III from fumaryl chloride by fractional distillation[20] is: A mixture of 392.0 g. (4.0 moles) of maleic anhydride and 800 ml. of dry methanol was allowed to stand at room temperature overnight and the excess methanol removed under reduced pressure. To the residue was added cautiously with swirling a mixture of 375 ml. of thionyl chloride and 400 ml. of dry benzene and the slurry heated to reflux. The mixture became homogeneous within 1.0 hr. and refluxing was continued for an additional 18.0 hr. After removal of solvent and excess thionyl chloride under reduced pressure there was obtained 394.3 g. of faintly yellow liquid, b.p. 93–95° (29–30 mm.). Redistillation yielded 332.0 g. (56%) of colorless acid chloride (III), b.p. 83–84° (24 mm.), reported[20] b.p. 70–71° (14 mm.).

Preparation of Monomers. (a) **Methyl Alkyl Maleates (Ia, b, c).**—The synthesis of methyl 3-butenyl maleate illustrates the procedure followed. A mixture of 29.4 g. (0.30 mole) of maleic anhydride and 200 ml. of dry methanol was allowed to stand at room temperature overnight and the excess methanol removed under reduced pressure. To the residual methyl hydrogen maleate was added 21.6 g. (0.30 mole) of 3-buten-1-ol,[21] 150 ml. of dry benzene, 1.0 g. of *p*-toluenesulfonic acid and 0.5 g. of shiny copper wire and the mixture refluxed under a Dean–Stark trap until the theoretical amount of water had been collected (*ca.* 24 hr.). After extracting the mixture with three 50-ml. portions of 10% sodium bicarbonate solution, water, and drying over anhydrous sodium sulfate there was obtained upon distillation 38.0 g. of colorless liquid, b.p. 80–85° (1.0 mm.). Redistillation afforded 26.6 g. (48%) of methyl 3-butenyl maleate (Ia), b.p. 71.5–72° (0.6 mm.). The physical properties of the methyl alkyl maleates (Ia,b,c) are recorded in Table I.

(b) **Methyl Alkyl Fumarates (IIa,b,c).**—The preparation of methyl 3-butenyl fumarate illustrates the general method. To a stirred solution of 22.0 g. (0.30 mole) of 3-buten-1-ol,[21] 23.7 g. (0.30 mole) of dry pyridine and 200 ml. of dry ether contained in a 1-l., three-necked flask fitted with a dropping funnel, stirrer and condenser (calcium chloride tube) was added dropwise 44.5 g. (0.30 mole) of redistilled acid chloride III over a 1.5-hr. period. The reaction mixture rapidly darkened and deposited pyridine hydrochloride. When addition was complete the mixture was refluxed for 1.0 hr., 100 ml. of water added, and the ether layer washed with water, 10% sodium bicarbonate solution, water, and dried over anhydrous sodium sulfate. Distillation afforded 42.5 g. of colorless product, b.p. 65–67° (0.6 mm.), which was redistilled to give 39.8 g. (72%) of methyl 3-butenyl fumarate (IIc), b.p. 63–64° (0.6 mm.). The physical properties of the methyl alkyl fumarates (IIa,b,c) are recorded in Table I.

A strong absorption band at 965–970 cm.$^{-1}$ characteristic of a *trans* structure was found in the infrared spectra of the fumarates (*trans*-acid bond) and methyl 2-butenyl maleate (*trans*-alcohol bond). This band was absent in the other maleates.

Mass Polymerizations.—The general method was to heat approximately 10.0 g. of monomer containing the appropriate amount of benzoyl peroxide (Table III) in a screw-capped bottle under dry nitrogen at 62–63° for a period just short of the gel time (Table III). The soluble polymers were obtained by pouring the polymerized mixture into pentane, decanting the clear supernatant liquid, dissolving the semisolid residue in acetone and reprecipitating the polymer from pentane. This was repeated twice and the residual solid dried at room temperature for 12–24 hr. at 0.5 mm. After being finely ground, the polymer was dried at 0.5 mm. for an additional 12–24 hr.

The polymers were soluble in chloroform, carbon tetrachloride, acetone, acetic acid and acetonitrile and insoluble in ether, methanol, ethanol, cyclohexane, benzene and pentane. The analyses and approximate softening points of the polymers are presented in Table II. The infrared data are presented in the Discussion.

Determination of Residual Unsaturation.—The method of Siggia[22] was modified as follows. An iodine flask was charged with 50 ml. of glacial acetic acid, a 20–25% excess of 0.1 *N* potassium bromate–potassium bromide solution (as determined by previous titration for residual alcohol unsaturation), 5 ml. of 6 *N* sulfuric acid and the solution stirred magnetically for 2–3 min. A 10-ml. aliquot of polymer solution (prepared by dissolving *ca.* 1 g. of polymer in glacial acetic acid and diluting to 100 ml.) was added rapidly and the mixture stirred in the dark for 10 min. Fifteen milliliters of 20% potassium iodide solution was added, stirring continued for another minute, and the solution rapidly titrated with 0.05 *N* sodium thiosulfate (starch end-point) to give residual alcohol unsaturation.

To determine residual acid unsaturation an iodine flask was charged with 50 ml. of glacial acetic acid, an amount of

---

[18] All melting and boiling points are uncorrected. Infrared spectra were recorded using a Perkin-Elmer model 21 double beam spectrophotometer. Analyses were carried out by Galbraith Laboratories, Knoxville, Tenn., or by Weiler and Strauss, Oxford, England.

[19] H. Erlenmeyer and W. Schoenauer, *Helv. Chim. Acta*, **20**, 1008 (1937).

[20] R. E. Lutz, This Journal, **52**, 3423 (1930).

[21] Prepared by the lithium aluminum hydride reduction of vinylacetic acid according to the method of R. T. Arnold, R. W. Amidon and R. M. Dodson, This Journal, **72**, 2871 (1950).

[22] S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 69.

0.1 *N* bromate-bromide solution exactly equivalent to the residual alcohol unsaturation, 5 ml. of 6 *N* sulfuric acid and the solution stirred magnetically for 2–3 min. A 10-ml. aliquot of polymer solution was introduced and stirring continued in the dark for 10 min. Then, while keeping the flask as shielded from light as possible, an excess of 0.1 *N* bromate-bromide solution was added, followed by a mixture of 25 ml. of glacial acetic acid and 25 ml. of 0.2 *N* mercuric sulfate solution. The mixture was stirred in the dark for 1.0 hr., after which 15 ml. of 2 *N* sodium chloride solution and 15 ml. of 20% potassium iodide solution were added, stirring continued for 2–3 min., and the solution titrated with 0.05 *N* sodium thiosulfate to give residual acid unsaturation.

A blank was run using 50 ml. of glacial acetic acid and about one-half the volume of bromate-bromide solution necessary for the titration of the total residual unsaturation.

The above procedure was checked on each of the six monomers.

Gel Times and Percentage Conversion at Gelation.—The gel time of each monomer was determined by heating a 1-g. sample containing the requisite amount of initiator under dry nitrogen at 62°. The percentage conversion was determined under the same conditions using 4–5 one-gram samples of monomer in small screw-capped vials. Samples were removed periodically, carefully poured into pentane, and the precipitated polymer filtered onto previously weighed sintered glass funnels. The polymer was washed thoroughly with pentane and dried at room temperature and 0.5 mm. overnight. A plot of time *vs.* weight of polymer gave an essentially straight line which, upon extrapolation to the gel time, afforded percentage conversion. The results are recorded in Table III.

TABLE III

GEL TIMES, PERCENTAGE CONVERSION AT GELATION AND CATALYST-TO-MONOMER RATIO

Polymer	Gel time, hr.	Conversion at gelation, %	Benzoyl peroxide as % of monomer
Poly-Ia	9	18	2
Poly-Ib	[a]	>28[a]	2
Poly-Ic	8.25	12	2
Poly-IIa	11.5 (1)[b]	9	0.1
Poly-IIb	56	17	2
Poly-IIc	12 (1)[b]	14	0.1

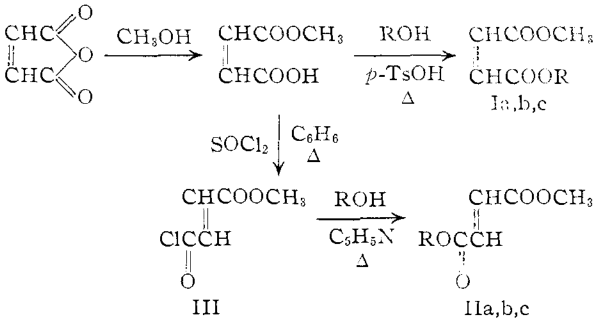
[a] No gelation after 243 hr. The "% conversion at gelation" represents the yield of soluble polymer after this period of heating at 62°. [b] Using 2% benzoyl peroxide.

Viscosity Measurements.—The inherent viscosities of the polymers were determined in glacial acetic acid at 30.0° using an Ubbelohde viscometer. The values are recorded in Table II.

Results and Discussion

The syntheses of the mixed maleate and fumarate esters are summarized in Fig. 1. Fumaryl chloride monomethyl ester (III) could not be obtained in good yield by published procedures.[19,20] However, refluxing a benzene solution of methyl hydrogen maleate and thionyl chloride readily afforded III.[23]

The polymerizations were initiated by benzoyl peroxide at 62° and carried out in bulk to yield relatively low melting, non-hygroscopic white powders readily soluble in acetone, chloroform and a number of other polar solvents. Inherent viscosity measurements (Table II), together with the known tendency for allyl groups to terminate chains through degradative chain transfer,[24] indicated that the polymers were of low molecular weight.



a, R = $-CH_2CH{=}CH_2$
b, R = $-CH_2CH{=}CHCH_3$
c, R = $-CH_2CH_2CH{=}CH_2$

Fig. 1.—Synthesis of monomers.

Residual alcohol and acid unsaturation was determined by bromine titration essentially according to Siggia.[22] The slightly modified procedure (see Experimental) was first checked by titration of the monomers. The analytical data obtained by titration of the polymers are summarized in Table IV. The approximate percentage cyclization was assumed to be the difference between *total* residual unsaturation and 100%, for, if linear polymerization but no cyclization had occurred, the total residual unsaturation would be 100%. Any further loss of unsaturation may be accounted for by three processes: (1) cross-linking, (2) branching and (3) cyclization. Since, from the physical properties of the polymers, cross-linking has not taken place and branching has occurred to, at most, a few per cent., it follows that cyclization must account for essentially all of the "lost" unsaturation.

TABLE IV

ANALYTICAL DATA DERIVED FROM BROMINE TITRATIONS

Polymer	Residual alcohol bond, %	Residual acid bond, %	Approximate % cyclization
Poly-Ia	35.8 ± 0.9	15.3 ± 2.7	49
Poly-Ib	21.1 ± .6	18.6 ± 2.1	60
Poly-Ic	32.8 ± .1	29.2 ± 0.2	38
Poly-IIa	29.3 ± .4	7.76 ± .22	63
Poly-IIb	69.7 ± .6	6.52 ± .20	23
Poly-IIc	43.4 ± .2	14.4 ± .3	43

The infrared spectra of the six soluble polymers (potassium bromide pellet) showed considerable absorption in the C=C stretching region (1625–1655 cm.$^{-1}$) as well as a strong absorption band at 1720–1755 cm.$^{-1}$. Saturated esters (1735–1750 cm.$^{-1}$),[25] α,β-unsaturated esters (1717–1730 cm.$^{-1}$),[25] δ-valerolactone (1740 cm.$^{-1}$)[26] and ϵ-caprolactone (1727 cm.$^{-1}$)[26] all absorb in this latter region. In addition, poly-(methyl allyl maleate) (poly-Ia) and poly-(methyl 2-butenyl maleate) (poly-Ib) exhibited a band at 1780 cm.$^{-1}$ indicating the presence of a γ-butyrolactone ring system.[27] Molecular models indicate somewhat less steric hindrance to attack of the allyl radical at C_2 of the maleate ester (A) than at C_1.

---

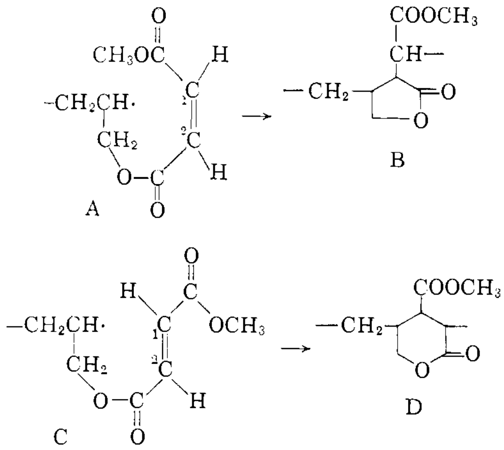
(23) During the course of this work Spatz and Stone [*J. Org. Chem.*, **23**, 1559 (1958)] described the thiourea-catalyzed isomerization of methyl hydrogen maleate to the fumarate. Treatment of the fumarate with thionyl chloride yields III.[19]

(24) R. L. Laible, *Chem. Revs.*, **58**, 807 (1958).

(25) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 153.

(26) H. K. Hall and R. Zbinden, THIS JOURNAL, **80**, 6428 (1958).

(27) Reference 26 gives 1775 cm.$^{-1}$ for γ-butyrolactone.



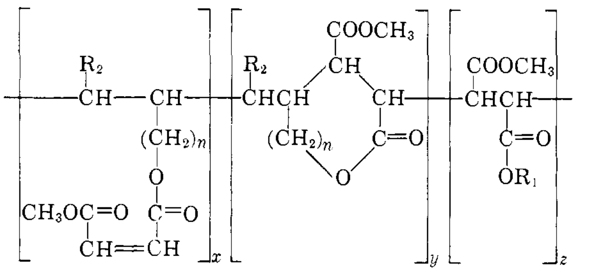
Hence, formation of both the γ-butyrolactone (B) and the δ-valerolactone (D) seems likely. On the other hand, steric factors greatly favor attack at C_1 in the fumarate ester C to form D with the virtual exclusion of B.

The data in Table IV have been transposed to Tables V and VI where tentative average structures for the linear poly-(methyl alkyl maleates) and poly-(methyl alkyl fumarates), respectively, have been proposed on the basis of 20 monomer units per chain. It is most likely that both acid and alcohol bonds are attacked by the initiator. We have arbitrarily assumed, however, that in all cases initial attack occurs at an alcohol carbon (the terminal methylene carbon in the allyl and 3-butenyl esters, the γ-carbon in the 2-butenyl esters) with subsequent attack of the free radical on the acid double bond to form, in the case of the allyl and 2-butenyl polymers, a 6-membered lactone ring and, in the 3-butenyl compounds, a 7-membered lactone ring. Tables III and IV indicate that the fumarate esters polymerize more readily than do the maleates and, in addition, have a greater tendency to polymerize through the acid bond than do the corresponding *cis* isomers. This has been observed previously by Lewis and Mayo[28] who attributed the diminished reactivity of the maleates toward homo- and copolymerization to their decreased ability to assume a planar configuration and, thus, to stabilize the activated complex by resonance with the carbonyl groups. The greater percentage cyclization in poly-(methyl allyl fumarate) (poly-IIa) and poly-(methyl 3-butenyl fumarate) (poly-IIc) as compared to the corresponding *cis* isomers (poly-Ia and poly-Ic, respectively) reflects the increased reactivity of the fumarate *vs.* maleate double bond toward a double bond of more comparable reactivity. That the allyl polymers (poly-Ia and poly-IIa) show a greater percentage cyclization than do the corresponding 3-butenyl compounds (poly-Ic and poly-IIc, respectively) would appear to be a direct consequence of the relative ease of formation of 6- *vs.* 7-membered rings.

The case of the 2-butenyl monomers (Ib and IIb) presents an interesting example of extremes in bond reactivities. In Ib the double bonds are extremely unreactive toward homopolymerization (acid–acid or alcohol–alcohol bonding) and, thus, copolymerization becomes favored. On the other hand, IIb possesses two double bonds situated at the opposite ends of the reactivity spectrum with which we are concerned. Accordingly, while the 2-butenyl bond has little tendency to either homo- or copolymerize the fumarate bond now has enhanced reactivity (relative to the maleate bond) and the predominant mode of polymerization is homopolymerization through the acid bond with a concomitant decrease in cyclization. It will be noted that those polymers containing the greatest degree of cyclization are derived from monomers which possess double bonds of comparable reactivity (allyl and fumarate bonds in IIa, 2-butenyl and maleate bonds in Ib) and that the diminution of cyclization in poly-Ic and poly-IIc is very likely due to the formation of a 7-membered ring rather than to any great difference in reactivity between the allyl and 3-butenyl groups.[29]

TABLE V

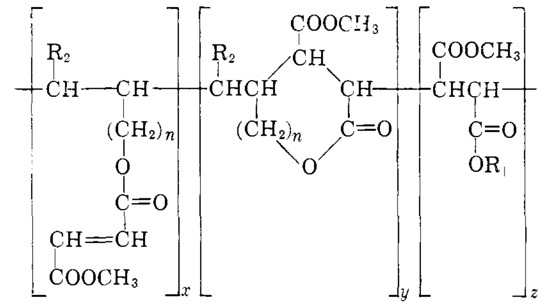
PROPOSED AVERAGE STRUCTURES FOR POLY-(METHYL ALKYL MALEATES)



Polymer	R_1	R_2	*n*	*x*	*y*	*z*
Poly-Ia	$—CH_2CH{=}CH_2$	—H	1	3	10	7
Poly-Ib	$—CH_2CH{=}CHCH_3$	—H	1	4	12	4
Poly-Ic	$—CH_2CH_2CH{=}CH_2$	$—CH_3$	2	6	7.5	6.5

TABLE VI

PROPOSED AVERAGE STRUCTURES FOR POLY-(METHYL ALKYL FUMARATES)



Polymer	R_1	R_2	*n*	*x*	*y*	*z*
Poly-IIa	$—CH_2CH{=}CH_2$	—H	1	1	13	6
Poly-IIb	$—CH_2CH{=}CHCH_3$	—H	1	1	5	14
Poly-IIc	$—CH_2CH_2CH{=}CH_2$	$—CH_3$	2	3	8.5	8.5

GAINESVILLE, FLA.

---

[28] F. M. Lewis and F. R. Mayo, THIS JOURNAL, **70**, 1533 (1948).

[29] Indirect evidence for similar reactivities of the allyl and 3-butenyl groups may be found in the recent work of Bristow[17] who studied the homopolymerization of some substantial allyl methacrylates. For mean molecular weights of 7000 the values of *K* (rate constant for radical addition to the allylic group/rate constant for radical addition to the methacrylate group) for the allyl, 3-butenyl and 2-butenyl groups, respectively, were: 2.60×10^{-2}, 3.14×10^{-2}, 5.50×10^{-3}.