(B) **By Hydrogenation in Alkaline Medium.**—When V was dissolved in aqueous-ethanolic sodium carbonate no absorption of hydrogen was observed. Palladium on Norite was the catalyst.

(C) **By Hydrogenation of V in the Presence of Diethylamine.**—One-half gram of V was treated exactly as in (A) except for the presence of a few drops of diethylamine. The isolation of the products was also carried out in the same manner. The isomer of VI melting at 188–189° was obtained in larger proportion (0.35 g.), while the lower melting isomer, if present at all, was not isolated.

Isomerization of V.—One-half gram of V (m. p. 174–175°) was dissolved in 40 cc. of dry benzene, and a stream of dry hydrogen chloride gas was passed through the solution for one hour. The stoppered flask was then allowed to stand for two days at room temperature before removing the solvent on the steam-bath. The gummy residue solidified after a few minutes (m. p. 115–140°). There seemed to be a negligible difference in the solubility of the sodium salts, hence little purification could be brought about in this way. The regenerated acids were recrystallized from ethanol and ethanol–water combinations. About 350 mg. of the starting acid (V) was recovered in this way. Finally, a small amount of a new acid (tentatively designated as IX) melting at 144–145° was obtained. The amount was too small for satisfactory characterization.

Summary

Two crystalline racemates of 1-ethyl-2-methyl-7-methoxy-1,2,3,4,9,10,11,12-octahydrophenanthrene-2-carboxylic acid (VIa, VIb) have been prepared from ethyl 1-keto-2-methyl-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene-2-carboxylate.[1] These compounds, as well as the intermediate hexahydro acid (V), exhibited strong estrogenic activity in white rats.

KALAMAZOO, MICHIGAN RECEIVED AUGUST 27, 1948

[COMMUNICATION NO. 1180 FROM THE KODAK RESEARCH LABORATORIES]

Heats of Polymerization. IV. Copolymerization[1]

BY L. K. J. TONG AND W. O. KENYON

Introduction

This paper deals with heats of polymerization of a special type of copolymeric system in which the original monomeric units are, for the most part, arranged in the copolymer chain in an alternate sequence. Though this structural limitation definitely simplifies interpretation of the observed heats of polymerization, it is impossible to define and interpret exactly the energy changes, as will be shown. Without such structural limitation, the interpretation would be much more difficult because of the unknown sequence of units along the polymer chain.[1a]

Thus, in general, if a given unsaturate is not capable of homopolymerizing, or does so only very sluggishly under given conditions of temperature and catalyst concentration, but will form copolymers[2] at a fairly rapid rate when a second unsaturate is present, the probability of two units of the first component adding consecutively is very small. If the two monomer units are found to disappear from various monomer compositions at substantially equal molar rates, it is highly probable that the adjacent combined units are different. In terms of copolymerization kinetics as described by Mayo and Lewis[3] this can be interpreted that the reaction of each monomer with radicals that are different is much faster than the reaction of the same monomer with radicals that are similar. The reactions described in this article belong to this category, as subsequent evidence will show. The kinetics of allyl acetate and maleic anhydride copolymerization, also an example of this type of reaction, have been studied and discussed by Bartlett and Nozaki.[4]

Experimental

Vinyl acetate (VA) was purified from a commercial product by fractional distillation through a five-foot column under atmospheric pressure, b. p. 72.2–72.3°.

Maleic anhydride (MA) was Eastman Kodak Co. white label grade product again distilled under reduced pressure and kept in a desiccator over phosphorus pentoxide.

Diethyl maleate (DEM) was Eastman white label grade product again fractionally distilled through a two-foot column under reduced pressure, b. p. 102.5–102.7° (11 mm.) n^{20}D 1.4408. Part of this material was further purified by crystallizing four times in brine and ice mixtures. Each time the unfrozen portion, which amounted to about half the total, was discarded; final product n^{20}D 1.4402, m. p. −8.8°.

Diethyl fumarate (DEF) was Eastman white label grade again distilled through a two-foot column under reduced pressure, b. p. 95.1° (10 mm.), n^{20}D 1.4408. A portion was further purified by crystallizing four times in an ice-bath with about half of the material discarded each time, m. p. 0.6°.

Benzoyl peroxide used as catalyst was Eastman white label grade.

Isopropenyl acetate was purified by washing with saturated sodium chloride solution, with dilute sodium chloride and sodium bisulfate solution, then again with sodium chloride solution. It was dried over magnesium sulfate and fractionated through a ten-inch column, b. p. 97.5°.

The apparatus has been described previously.[5]

The procedures are those described before, with the following modifications: Air was not removed from the reaction system except for one case mentioned later. The earlier practice of flushing the air space with nitrogen will change the composition of the monomer mixtures owing to their differences in vapor pressures. When both compo-

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[1] Presented before the High Polymer Forum at the Chicago, Illinois meeting of the American Chemical Society, 1948.

[1a] Since the original submission of this paper, the kinetics of some of the reactions concerned here have been published by Lewis and Mayo, THIS JOURNAL, **70**, 1533 (1948).

[2] The term "heteropolymers" is sometimes applied when one or more of the monomers will not homopolymerize. This term has unfortunate implications as to the physical homogeneity of the product, so we prefer the term "copolymer."

[3] Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944).

[4] Bartlett and Nozaki, *ibid.*, **68**, 1495 (1946).

[5] Tong and Kenyon, *ibid.*, **67**, 1278 (1945); **68**, 1355 (1946); **69**, 1402 (1947); **69**, 2245 (1947).

TABLE I

2nd component	Vinyl acetate, mole %[a]		No. of runs	P (Millimoles monomeric unit)	Catalyst concentration(s), mole %	k	a	− ΔH kcal./mole
	Monomer	Polymer						
...	100	100	15	4.9 to 33.9	0.018 .035	0.4582	+0.01	21.26 ± 0.22
DEF	79.85	78.70	3	9.6 to 44.4	.21	.4413	− .13	20.48 ± 0.33
DEF	61.52	59.0	13	7.0 to 39.5	.25	.4125	− .13	19.14 ± 0.21
DEF	50.0	53.0	6	13.1 to 35.7	.27 .54	.3917	− .005	18.17 ± 0.32
DEM	74.95	74.0	9	7.4 to 45.1	.11 .22 .45	.4450	− .15	20.65 ± 0.33
DEM	50.0	53.9	14	5.9 to 41.6	.27 .54	.4316	+ .03	20.03 ± 0.29

[a] Weighted average of all runs.

nents were liquid, sufficient quantities were mixed in advance for all the runs having a given composition but the benzoyl peroxide catalyst was added prior to each run. Maleic anhydride, when used, was first added individually to the reaction tubes, then the liquid component containing the catalyst was added. The tube and contents were weighed after each addition.

In all cases the maleic anhydride was completely dissolved before the calorimetric determination by vigorous shaking after a preliminary short warming in the vapor space of the calorimeter. The isopropenyl acetate–maleic anhydride combinations were allowed to react until the heat evolution stopped. Drift corrections were applied as previously described.[5] The other pairs were allowed to react for a predetermined time; the reaction was quenched by cooling in a Dry Ice-methanol-bath, and the extent of reaction was then determined by bromination of unused monomers. The reaction time varied between two to three hours, depending upon the reactants and the catalyst concentration, but in all cases the reactions had become slow at this point. Drifts were determined with blanks every day before the first run was made, and the conditions were adjusted so that drifts were small compared to the average deviations observed.

Analysis of Residual Monomers by Bromination.—In preparation for bromination, the polymers were placed in a flask containing 100 g. of glacial acetic acid after the reaction tubes were broken up while still at low temperature. With gentle shaking, the polymers usually dissolved completely overnight

(a) **Vinyl Acetate.**—Ten cubic centimeters of the dope was added to a flask containing 5 cc. of 6 N H_2SO_4 and 20 cc. of glacial acetic acid. The sample was titrated with a solution of $^1/_{30}$ M $KBrO_3$ and $^1/_5$ M KBr to a yellowish end-point. This method was found accurate to 1% by using a known quantity (about 0.15 g.) of vinyl acetate.

(b) **Diethyl Maleate and Diethyl Fumarate.**—This method, described by Bartlett[4] and Lucas,[6] uses mercuric sulfate as a catalyst. The container is a round-bottomed flask with a ground-glass stopper sealed to a three-way stopcock. One arm is connected by rubber tubing to an aspirator and the other arm is sealed to a short funnel. A measured volume of bromate-bromide solution was pipetted into the flask. The flask was then partially evacuated. Solutions were added to the funnel and drawn into the flask individually in the following order: 10 cc. polymer dope, 5 cc. 6 N H_2SO_4, and 20 cc. 0.2 N $HgSO_4$. The flask was placed in a 60° bath in the dark for twenty minutes, then cooled in a Dry Ice-bath until ice began to form.[7] After the addition of 15 cc. of 2 N NaCl and 15 cc. of 20% potassium iodide solutions, the contents were titrated with 0.1 N thiosulfate with starch indicator. The small amount of iodine or bromine physically absorbed was determined by redissolving the precipitate in a fresh portion of acetic acid and titrating the iodine after addition of potassium iodide solution. The sum of monomeric vinyl acetate and diethyl maleate (or fumarate) was calculated from the total thiosulfate used.

This second analysis was not so accurate as that of vinyl acetate alone, but since the polymerization reactions are about 90% complete, even a sizable percentage error in the analysis of the remaining 10% of monomer would not produce too large an absolute error in the estimation of total polymer. Residual diethyl fumarate or diethyl maleate was determined only in the 50 mole per cent. polymerizations. With excess vinyl acetate, the smaller components were assumed to have reacted completely at the end of the runs, but the residual vinyl acetate monomer was determined. This assumption was justified, since in those instances where the maleate or fumarate was determined, they were found absent within experimental error.

Results and Discussion

Vinyl Acetate and Diethyl Fumarate.—In order to save space, only the results are given for the homopolymerization of VA and the copolymerization of VA with DEF and DEM. The treatment of the data whose results appear in Table I has been previously described.[5]

The linear relationship of W'_{CCl_4} *vs.* P was calculated by the method of least squares. The slopes k of this relationship and the graphical intercepts (5) a are given in Table I. The H values and the standard deviations were obtained from the slope k assuming that all individual deviations are in the W_{CCl_4} values. Tracings from photographic recordings are reproduced in Fig. 1 to illustrate the course of the reactions. Inspection of the curves reveals that each is composed of two similar portions connected in the region which includes a minimum slope corresponding to a minimum reaction velocity.

"Inflection points," when referred to in this article, mean the particular ones occurring in these regions. It is significant that these points occur at W_{CCl_4} values very close to the values indicated by the short horizontal lines which are calculated by the equation $2 \times DEF \times 18.6/46.4$ where 18.6 is the $-\Delta H$ of the equimolar copolymerization of this monomer pair, 46.4 is the heat of vaporization per gram of carbon tetrachloride, and DEF is the number of moles of diethyl fumarate introduced. The agreement indicates that the

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[6] Lucas and Pressman, *Ind. Eng. Chem., Anal. Ed.*, **10**, 140 (1938).

[7] This cooling was found necessary in order to slow down the return of iodine color near the end-point of the final titration.

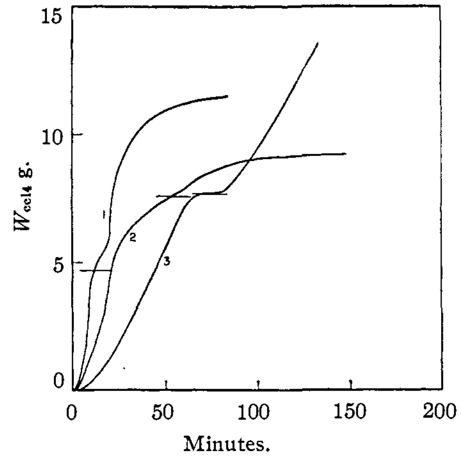

Fig. 1.—Heat evolution *vs.* time; W_{ccl_4} = heat evolved/46.4: (1) 0.21 mole % of catalyst, 5.9 mmoles. of diethyl fumarate, 23.4 mmoles of vinyl acetate; (2) 0.20 mole % of catalyst, 9.51 mmoles of diethyl fumarate, 15.24 mmoles of vinyl acetate; (3) 0.071 mole % of catalyst, 8.74 mmoles of maleic anhydride, 39.0 mmoles of vinyl acetate.

reaction can be interpreted as proceeding in two stages: The first stage is mainly the copolymerization of the two components in a 1:1 ratio, and the second stage is homopolymerization of excess VA. Table II shows the observed and calculated values of W_{CCl_4} at the inflection points. At low percentages of DEF, the observed values are higher than the calculated values, indicating that in a large excess of VA, some homopolymerization of VA occurred simultaneously with the copolymerization in the first stage of the reaction. On the basis of the above reasonings, the $-\Delta H$ observed in systems having excess VA is the sum of the heat of copolymerization resulting in alternating chain units and the heat of homopolymerization of the excess VA.

TABLE II

VINYL ACETATE–DIETHYL FUMARATE INFLECTION POINTS ON POLYMERIZATION CURVES

	Diethyl fumarate monomer in initial mixture		W_{CCl_4} at inflection	
(Cat.)	Mole fraction	Millimoles	Obs.	Calcd.
0.21	0.2015	3.8	3.7	3.2
.21	.2015	5.9[a]	5.5	4.7
.20	.3845	9.5[b]	7.6	7.6
.20	.3845	9.7	7.1	7.8
.20	.3845	10.2	8.1	8.1

[a] Curve 1, Fig. 1. [b] Curve 2, Fig. 1.

It seems strange that the phenomenon of the second induction did not show up in other very similar reactions using VA-DEM, VA-isopropyl fumarate,[8] VA-dimethyl fumarate[8] systems. We suspected that impurities in the material caused this abnormal behavior. DEF was purified by repeated crystallization, and in one run the system was degassed as described by Bartlett and Nozaki but the general characteristics of the curve did not change.

To explain the second induction period, we have considered the possibility that it may be due to the time required to establish a second steady state, but this seems improbable in view of the work of Nozaki and Bartlett[9] who showed that steady states are established in a very short time in the polymerization of vinyl acetate.

The other possibility which suggests itself is the presence of an inhibitor either added initially or generated during the first stage of the reaction. If so, this inhibitor must have the following properties: (1) it does not inhibit the copolymerization; (2) it is not removed during the period of copolymerization; and (3) it inhibits homopolymerization of vinyl acetate. Since additional purification steps failed to remove or change significantly the induction period, it seems likely that the inhibitor is generated during the first stage of the reaction.

Calculations

Let

$-\Delta H$ = observed heat of polymerization per mole of monomeric unit
N_V = moles of vinyl acetate units in polymer
N_F = moles of diethyl fumarate units in polymer

Let

q = heat absorbed by the system
$-\Delta H_V$ = heat of homopolymerization per mole of vinyl acetate
$-\Delta H_{cop.}$ = heat of copolymerization per mole of mixed monomer in 1:1 ratio

$$q = 2N_F \Delta H_{cop.} + (N_V - N_F)\Delta H_V$$

when $N_V > N_F$. Dividing by $N_V + N_F$

$$\frac{q}{N_V + N_F} = \Delta H = \frac{2N_F \Delta H_{cop.}}{N_V + N_F} + \frac{N_V + N_F - 2N_F}{N_V + N_F}\,\Delta H_V$$

Since

$$N_F/(N_V + N_F) = x$$
$$\Delta H = 2x(\Delta H_{cop.} - \Delta H_V) + \Delta H_V$$

which requires ΔH to be linear with respect to x and equal to $\Delta H_{cop.}$ at $x = 0.5$. The value ob-

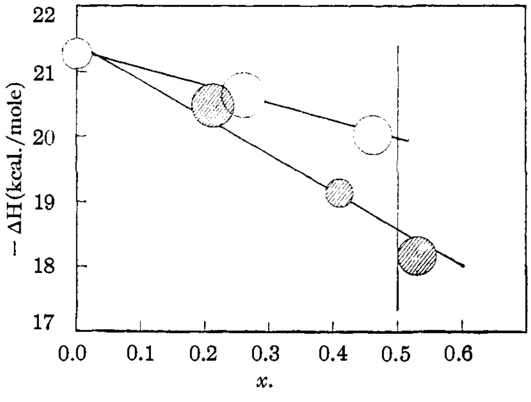

Fig. 2.—Copolymerization of vinyl acetate with diethyl maleate and diethyl fumarate: x = mole fraction of ○, diethyl maleate, ●, diethyl fumarate.

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(8) Tong and Kenyon, unpublished results.

(9) Nozaki and Bartlett, THIS JOURNAL, **68**, 2377 (1946).

tained for this pair is 18.6 kcal./mole, as shown in Fig. 2.

Vinyl Acetate–Diethyl Maleate (DEM).—DEM was not observed to homopolymerize under our conditions of catalysis and temperature. Therefore, in copolymerization, DEM will add only on the radical ending in a VA unit, since it is very unlikely that it will add to a radical ending in a DEM unit. The possibility of adding two or more VA units consecutively cannot be excluded, but if this occurs it will lower the ratio of DEM to VA in the copolymers. Starting with a 50 mole per cent. mixture (Table I), the composition of maleate in the polymer was found to be 46% DEM after the reactions were about 85% complete, showing very little homopolymerization of the VA.

The extrapolated value (using the method of calculation described for VA-DEF) for heat of copolymerization is 20 kcal./mole for this pair of monomers (Fig. 2).

Vinyl Acetate–Maleic Anhydride (MA).—All experiments with this pair of monomers were with excess VA. The copolymer is insoluble in this system. The reaction curves show very flat shoulders (Curve 3, Fig. 1). The amounts of heat evolved up to the inflection point were proportional to the amounts of maleic anhydride initially present. This relationship holds over a wide range of compositions, as shown in Table III. This, again, indicates that the first stage of reaction is copolymerization yielding polymers with alternating units. This reaction proceeded until maleic anhydride was exhausted at the inflection point. With alternating units, the molar amount of VA consumed to the inflection point should equal the amount of maleic anhydride initially present. The very flat shoulder portion of the curve existed long enough to enable a reaction to be stopped in this region. One reaction using 20.9 millimoles of maleic anhydride and 55.8 millimoles of vinyl acetate was quenched at the inflection point by dropping the reaction tube into a Dry Ice–alcohol bath. Analysis for residual VA showed that 20.9 millimoles had reacted. The $-\Delta H_{\text{cop.}}$ of copolymerization was obtained from the equation

$$-\Delta H_{\text{cop.}} = -W_{\text{CCl}_4} \times 46.4/2N_{\text{MA}}$$

where N_{MA} = number of moles of maleic anhydride. Using the data from the last two runs of Table III, $-\Delta H_{\text{cop.}}$ has an average value of 20.2 kcal./mole.

Table III

Vinyl Acetate–Maleic Anhydride

W_{CCl_4} = weight of CCl_4 vaporized at inflection points

(Cat.)	Monomers introduced Vinyl acetate. millimoles	 Maleic anhydride. millimoles	W_{CCl_4}	$\frac{W_{\text{CCl}_4}}{\text{Maleic anhydride reactd.}}$[c]
0.073	38.0	7.27	6.55	0.905
.071	39.0[a]	8.74	7.81	.895
.045	34.7	20.3	17.86	.880
.037	55.8[b]	20.9	17.90	.857

[a] Curve 3, Fig. 2. [b] Reaction quenched at inflection point. [c] Complete reaction assumed.

Isopropenyl Acetate (IPA)–Maleic Anhydride.—The pair reacts differently from the above mixtures involving VA in that IPA did not homopolymerize under our experimental conditions. The situations are very similar to the allyl acetate–maleic anhydride copolymerization described by Bartlett and Nozaki, and many of their conclusions regarding the latter reactions may be applied. The major differences are that the present work was at a higher temperature and a lower catalyst concentration.

The products are insoluble in the monomers or in any solvent tried which is suitable for bromination purposes. Polymerization experiments covering the entire range of composition are shown in Table IV. The reactions were allowed to proceed until heat evolution stopped. If all the reactions were to proceed at a 1:1 ratio until the smaller component is exhausted, then the heat evolved should be proportional to the amount of the smaller component originally present. Under ideal conditions the heat evolved per mole of total starting monomer when plotted against the starting composition should form two straight lines—one through each origin and intersecting at x = 0.5, as shown by the dotted lines on Fig. 3. The experimental points on the IPA-rich side of the diagram do fall on the theoretical line, but those on the MA side fall considerably below the theoretical line. In a large excess of MA, the small amounts of catalyst used probably decompose by chain reactions, as shown by Bartlett and Nozaki,[4] before the IPA can be exhausted. The products formed in IPA-rich systems were colorless, and in the MA-rich systems the products ranged from tan to dark brown. Assuming that the runs on the left-hand branch of the curve represent the idealized condition of 1:1 reaction ratio until the exhaustion of MA, then the extrapolated value of 17.8 at x = 0.5 is the heat of copolymerization for this pair of monomers.

Table IV

Isopropenyl Acetate–Maleic Anhydride

(Cat.)	Initial monomers M, total millimoles	 x, mole fraction maleic anhydride	W_{CCl_4}	$(W_{\text{CCl}_4}/M) \times 46.4$
0.09	52.0	0.110	4.22	3.8
.10	68.0	.110	5.52	3.8
.18	45.7	.264	9.50	9.8
.07	46.3	.313	11.06	11.1
.16	41.7	.315	9.79	10.9
.06	59.2	.397	16.65	13.0
.11	42.6	.495	10.2	11.1
.05	68.0	.506	18.60	12.7
.09	52.5	.614	10.00	8.9
.06	67.9	.740	11.73	8.0
.10	64.1	.742	10.58	7.7
.02	52.4	.788	5.86	5.2

A summary of the heats of copolymerization is given in Table V, in which $-\Delta H_{\text{cop.}}$ represents the heat liberated by the reaction of 0.5 mole of each monomer to form one mole of mixed monomeric units arranged alternately in the copolymer. Since in all cases discussed here every two unsymmetrical units are separated by a symmetrical unit, the effect of head-and-tail type of arrangements on the energy content of the copolymer is believed to be slight.

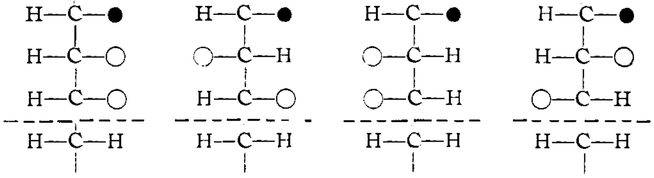
TABLE V

COPOLYMERIZATION WITH ALTERNATING UNITS

	$-\Delta H_{\text{cop.}}$ in kcal.
Vinyl acetate–diethyl fumarate	18.6 ± 0.3
Vinyl acetate–diethyl maleate	20.0 ± .2
Vinyl acetate–maleic anhydride	20.2 ± .4
Isopropenyl acetate–maleic anhydride	17.8 ± .4

If copolymers derived from vinyl acetate–diethyl maleate and vinyl acetate–diethyl fumarate reactions are identical, then the difference in their $-\Delta H_{\text{cop.}}$ values should be equal to one-half the heat of isomerization in changing from diethyl maleate to diethyl fumarate. This was calculated by Williams[10] to be 4.2 kcal./mole (or 2.1 kcal./0.5 mole). The observed difference in $-\Delta H_{\text{cop.}}$ is 1.4 ± 0.5 kcal. The disagreement of 0.7 kcal. between the calculated and observed values is just outside of the standard deviation of our experiments.

If the difference between the observed and calculated value is real, it may indicate that the copolymers VA-DEM and VA-DEF are not structurally identical. Let us consider the arrangements in such polymers of the neighboring groups attached to three adjoining carbon atoms somewhere along the chain which, in turn, are attached to CH_2 groups at each end. It can be seen that there are four possible arrangements (excluding mirror images) where ● = acetyl group and ○ = carbalkoxyl group. This type of isomerism in polymers has been suggested by Staudinger[11] and used by Huggins[12] as a possible explanation of differences in polymer properties resulting from differences in temperature of polymerization. Conceivably fumarates and maleates can lead to products where different arrangements predominate and their interactions may give rise to slight differences in energy content.



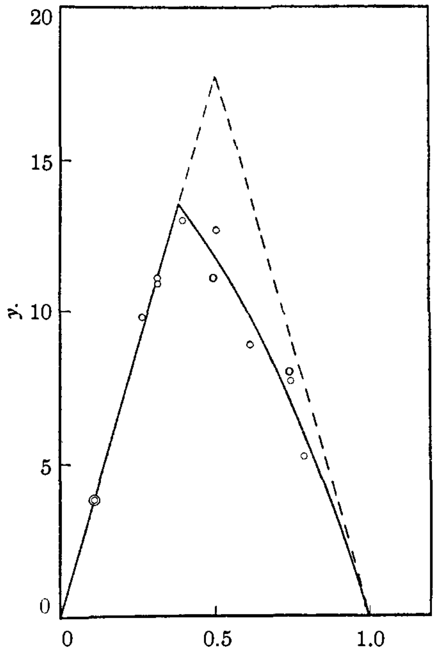


Fig. 3.—Isopropenyl acetate–maleic anhydride copolymerization: y = heat evolved per millimole of initial monomer.

Acknowledgment.—The authors wish to express their appreciation to Dr. M. L. Huggins for helpful discussion and advice in the preparation of certain phases of this article, and to Mr. T. M. Laakso for preparing the isopropenyl acetate used.

Summary

1. The copolymerization of vinyl acetate and isopropenyl acetate with certain difficulty homopolymerizable unsaturates to produce copolymers of substantially alternating monomeric units has been studied.

2. Vinyl acetate appears to copolymerize preferentially in an equimolar ratio with the second monomer until the latter is exhausted, then the residual vinyl ester homopolymerizes.

3. The observed $-\Delta H_{\text{cop.}}$ in kcal./mole for the equimolar systems investigated are: a vinyl acetate–diethyl fumarate 18.6 ± 0.3; vinyl acetate–diethyl maleate 20.0 ± 0.2; vinyl acetate-maleic anhydride 20.2 ± 0.4; and isopropenyl acetate–maleic anhydride 17.8 ± 0.4.

4. After allowance is made for the heat of isomerization of fumaric and maleic esters, a small difference in their heat of copolymerization with vinyl acetate was observed which, if real, may be due to isomeric arrangement of substituent groups along the main skeletal chain.

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[10] Williams, THIS JOURNAL, **64**, 1395 (1942).

[11] Staudinger, "Die Hochmolekularen organischen Verbindungen (Kautschuk und Cellulose)," Julius Springer, Berlin, 1932, p. 114.

[12] Huggins, THIS JOURNAL, **66**, 1991 (1944).

[13] Original manuscript received February 24, 1948.