tion, and to Amelia Saldaña and Delia Ortegon for their technical assistance.

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Fatty Acid Esters of 3-Butene-1,2-diol. III. The Polymerization of Erythryl Divalerate[1]

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Since the diacetate of 3-butene-1,2-diol (erythryl diacetate) was shown previously[2] to yield a homopolymer similar in degree of polymerization to polyallyl acetate,[3] it was of interest to check the allylic behavior of the erythryl esters by a more detailed study of another monomer. Erythryl divalerate therefore was heated with benzoyl peroxide for a study of (a) the rate of disappearance of monomer and of peroxide and (b) the nature and molecular weight of the product. Brief studies also were made of the copolymerization of erythryl divalerate with styrene.

TABLE I

POLYMERIZATION OF ERYTHRYL DIVALERATE AT 80° WITH BENZOYL PEROXIDE AS INITIATOR

Bz_2O_2 concn., %	k,[a] hr.$^{-1}$	dM/dP
2.31	0.197	19.0
4.47	.217	13.2
7.45	.228	8.8

[a] First-order velocity constants for the decomposition of benzoyl peroxide, obtained by the method of least squares from the data of Fig. 1.

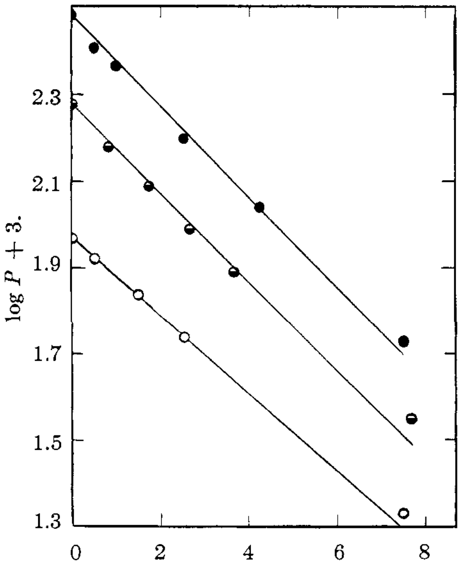


Fig. 1.—Pate of decomposition of benzoyl peroxide in polymerizing erythryl divalerate at 80°. Initial concn. of Bz_2O_2: ○, 2.31%; ◒, 4.47%; ●, 7.45%.

For the kinetic studies, solutions of benzoyl peroxide in erythryl divalerate, at three different concentrations, were heated at 80° and analyses were made for monomer and peroxide after varying intervals of time. The results are shown in Table I and in Fig. 1.

Figure 1 shows that the decomposition of benzoyl peroxide in erythryl divalerate is an unimolecular reaction up to at least 77% completion. The values of the first order rate constants are close to those reported[3,4] for allyl acetate under similar conditions.

A graph of the monomer concentration against peroxide concentration (Fig. 2) shows that in any given polymerization the ratio of dM/dP is constant for benzoyl peroxide and erythryl divalerate, as was observed[3,4] for other allyl esters.

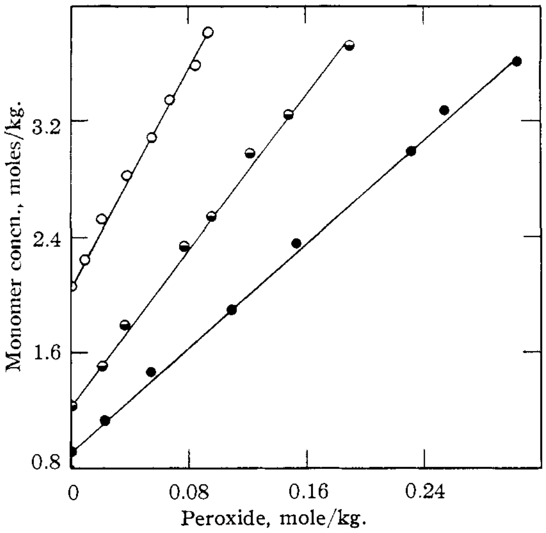
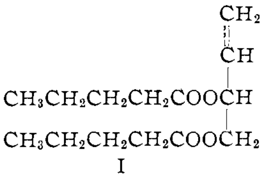
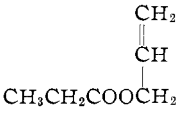


Fig. 2.—Monomer concn. plotted against polymer concn. in the polymerization of erythryl divalerate: initial concn. of Bz_2O_2, ○ = 2.31%; ◒, 4.47%; ●, 7.45%.

The values of dM/dP observed for erythryl divalerate are lower than those reported[3,4] for most other allyl esters at comparable concentrations of benzoyl peroxide. For example, the dM/dP values for erythryl divalerate are 25–35% lower than those for allyl acetate, and about 15% lower than those for allyl propionate This lowering of the dM/dP value may be due to an increased ease of degradative chain transfer at the α-position of the erythryl divalerate (I), where there is a tertiary hydrogen atom, while the allyl ester II has only secondary hydrogen at this position.


$$\begin{array}{r} CH_2 \\ \| \\ CH \\ | \\ CH_3CH_2CH_2CH_2COOCH \\ | \\ CH_3CH_2CH_2CH_2COOCH_2 \end{array}$$

I


$$\begin{array}{r} CH_2 \\ \| \\ CH \\ | \\ CH_3CH_2COOCH_2 \end{array}$$

II

Moreover, there is increased opportunity for radical attack on the erythryl ester, since there are two carbonyl groups in the erythryl ester next to which attack can occur with the formation of a new reso-

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[1] From the Master's Thesis of Stewart C. Brown, University of Delaware, 1954.

[2] E. Dyer, T. G. Custer, W. C. Meisenhelder, THIS JOURNAL, **71**, 2728 (1949).

[3] P. D. Bartlett and R. Altschul, *ibid.*, **67**, 812, 816 (1945).

[4] N. C. Gaylord and F. R. Eirich, *ibid.*, **74**, 334, 337 (1952).

nance stabilized radical, whereas there is only one such position in the allyl ester.

The homopolymer formed by heating erythryl divalerate at 80° in the presence of 5% of benzoyl peroxide was a viscous liquid with a degree of polymerization of about 5. Since the homopolymer of erythryl diacetate[2] had a D.P. of 17.7, it appears that increasing the size of the acid residues decreases the molecular weight of erythryl ester polymers. The same trend was noted[4] in comparing the homopolymers of allyl acetate and allyl propionate (of D.P. 12 and 10, respectively). The very low molecular weight of the polyerythryl divalerate is in accord with the kinetic evidence for the occurrence of extensive degradative attack in the case of the erythryl ester.

A brief study of the copolymerization of erythryl divalerate with styrene gave results (shown in Table II) which are similar to those obtained with other saturated erythryl esters.[2] For example, copolymers of erythryl diacetate and styrene prepared from 1:1 and 1:1.7 monomer mixtures (molar ratios of ester to styrene) had ester to styrene ratios of 1:22 and 1:17, respectively.

TABLE II

COPOLYMERIZATION OF ERYTHYL DIVALERATE WITH STYRENE AT 80° FOR 48 HOURS USING 5% INITIATOR

Run	A	B	C
Ester:styrene in charge,[a] moles	1:2	1:1	1:2
Yield of polymer,[b] %	47	25	46
Melting range[c] of polymer, °C.	100–126	94–118	100–126
Chlorine in polymer, %	. .	5.0	1.8
Sapn. no. of polymer	48.6	63.3	46.0
Ester:styrene in polymers,[d] moles	1:23	1:20	1:25

[a] Total weight of monomers, about 14 g. per run. Initiator, benzoyl peroxide in A, *p*-chlorobenzoyl peroxide in B and C. [b] Based on total monomers. [c] From first sintering point to free flow in a 1-mm. capillary melting point tube. [d] Values corrected for presence of *p*-chlorobenzoyl groups in polymer.

Experimental

Erythryl Divalerate.—This ester was prepared according to the method of Whitmore and Krems,[5] using erythrol and *n*-valeryl chloride (Eastman Kodak Co.). The erythrol was made from butadiene monoxide[6] obtained by a modification of the method of Kadesch.[7] The average yield of erythryl divalerate from four preparatory runs was 39.4% of product, b.p. 127° at 2 mm., $n^{20}D$ 1.4378; acid no., 0; peroxide no., 0; iodine no., 99.8 (calcd. 99.1); sapn. no., 428 (calcd. 438).

Kinetic Studies.—Tubes containing 2 to 3 g. of a solution of recrystallized benzoyl peroxide (99.5% pure by iodimetric analysis) and erythryl divalerate were sealed under nitrogen and heated at 80 ± 0.7°. After varying periods of time (shown in Fig. 1) the tubes were removed from the bath, chilled, and duplicate samples removed for determination of residual monomer by the catalytic Wijs method[8] and for peroxide by the iodimetric method of Nozaki.[9] Control experiments showed both methods to be accurate to within 1% for solutions containing up to 10% of benzoyl peroxide in the ester.

Homopolymerization.—Two samples of erythryl divalerate (of total weight 19 g.) containing 5% by weight of benzoyl peroxide were heated at 80° for 48 hr. in sealed tubes containing high purity nitrogen. The combined contents were then dissolved in benzene, and freed from peroxides by three washings with 9% sodium carbonate followed by salt solution and water. After removal of the solvent, the unchanged monomer was distilled off at 3 mm. pressure. The residue was a viscous liquid, obtained in 65% yield, which could not be solidified nor further purified. The recovery of monomer was 21%.

Anal. Calcd. for $C_6H_5COO(C_{14}H_{24}O_4)_5$: mol. wt.. 1403; iodine no., 0; sapn. no., 439.1. Found: mol. wt. (CCl_4, b.p.), 1452; iodine no., 5.6; sapn. no., 491.5.

Copolymerization.—Copolymers of erythryl divalerate and styrene,[10] prepared as indicated in Table II, were freed from initiator as above and the solid polymers precipitated from benzene with methanol. The composition of the copolymers was determined from saponification analyses, with correction for the probable content of saponifiable initiator groups. The assumption was made that 60% of the chloride-containing groups in copolymers prepared with *p*-chlorobenzoyl peroxide consisted of *p*-chlorobenzoate groups. This is based on the findings of Bartlett and Altschul.[3] When benzoyl peroxide was the initiator, it was assumed that the same proportionate amount of saponifiable initiator residues could be present.

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[5] W. F. Whitmore and I. J. Krems, THIS JOURNAL, **71**, 2427 (1949).

[6] Pariselle, *Ann. chim. phys.*, **8**, 24, 389 (1911).

[7] R. G. Kadesch, THIS JOURNAL, **68**, 41 (1946).

[8] H. D. Hoffman and C. E. Green, *Oil and Soap*, **16**, 239 (1939).

[9] K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **18**, 583 (1946).

[10] Supplied through the courtesy of the Dow Chemical Co.

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The Thermal Decomposition of the Bis-pyridinium Salts of Tetramethylene and Pentamethylene Dibromides

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The reaction of tetramethylene dibromide or pentamethylene dibromide with pyridine has been reported by Hartwell and Pogorelskin[1] to yield hygroscopic solids. The bromides could not be characterized as the anhydrous salts except by conversion to tetramethylene-α,δ-bis-pyridinium perchlorate and pentamethylene-α,ϵ-bis-pyridinium perchlorate. Gautier and Renault[2] obtained from the reaction of tetramethylene dibromide with pyridine a crystalline salt of well-defined melting point, but these authors failed to report any analyses for the compound.

In the repetition of this work, treatment of the dihalides with pyridine either with or without methanol as solvent yielded crystalline salts which were stable to the atmosphere for several weeks. The compound I formed from tetramethylene dibromide was identical with that reported by Gautier and Renault,[2] and analysis of the products from both reactions indicated that only the bis-pyridinium bromides had been formed. Limiting the quantity of pyridine to a 1:1 molar ratio also produced only the bisquaternary salts and no monoaddition salt could be isolated.

The thermal decomposition of alkyl pyridinium salts leads normally to the removal of pyridine hydrobromide producing the corresponding alkene. On heating these salts at 230–270°, two moles of pyridine hydrobromide were lost and compound I yielded butadiene while pentamethylene-α,ϵ-bis-

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[1] J. L. Hartwell and M. A. Pogorelskin, THIS JOURNAL, **72**, 2040 (1950).

[2] J. A. Gautier and J. Renault, *Compt. rend.*, **225**, 682 (1947).