

ing with benzene in a liquid-liquid extractor for six hours. After having been dried 24 hours over solid potassium hydroxide, the benzene was removed by fractional distillation through a column 30 cm. long packed with glass helices. The *d*-2-aminomethyltetrahydropyran was then distilled through a short unpacked column, redried and redistilled to give 0.8 g. (50%), b.p. 167-169°, $[\alpha]_D^{25} + 8.3^\circ$ (homogeneous, $l = 1$ dm.).

The resolved *d*-amine was also characterized by converting 0.10 g. to 0.06 g. (45%) of *N*-benzoyl-*d*-2-aminomethyltetrahydropyran, m.p. 112-113°, $[\alpha]_D^{25} + 28.3^\circ$ (chloroform, $c 2.9$).

Resolution of *dl*-2-Tetrahydropyranylacetic Acid.—To 52.6 g. of quinine in 450 cc. of hot benzene there was added 23.3 g. of II in 15 cc. of the same solvent. The hot solution was filtered, allowed to crystallize at 20°, and cooled to 5° for two days. The crystals were washed with three 10-cc. portions of cold benzene to yield 59.0 g. (79%) of mixed quinine 2-tetrahydropyranylacetates, m.p. 140-150°, $[\alpha]_D^{25} - 133.2^\circ$ (ethanol, $c 0.4$). A second crop of 9.9 g., m.p. 130-135°, $[\alpha]_D^{25} - 123.7^\circ$ (ethanol, $c 0.4$) was not further purified. After eight recrystallizations from benzene, the physical properties were essentially constant, m.p. 162-163°, $[\alpha]_D^{25} - 136.3^\circ$ (ethanol, $c 0.7$). The yield of quinine *l*-2-tetrahydropyranylacetate was 10.1 g. (28%).

Anal. Calcd. for $C_{27}H_{35}O_5N_2$: C, 69.23; H, 7.69; N, 5.90. Found: C, 69.00; H, 7.72; N, 6.10.

The salt was hydrolyzed by dissolving 10.0 g. in 50 cc. of chloroform and shaking with 60 cc. of 2 *N* aqueous sodium hydroxide. The chloroform layer was washed with two 20-cc. portions of water. The combined aqueous phase was then extracted with chloroform in a liquid-liquid extractor

for four hours. The basic solution was finally neutralized to methyl orange indicator with 1.5 *N* hydrochloric acid and extracted with fresh chloroform for six hours. Distillation of the chloroform solution gave 3.4 g. (74%) of *l*-2-tetrahydropyranylacetic acid (IIa), b.p. 120-125° (4 mm.). One recrystallization from petroleum ether, b.p. 60-90°, gave a product melting at 37-38°, $[\alpha]_D^{25} - 5.67^\circ$ (ethanol, $c 15$).

D-Desoxyephedrine was somewhat less satisfactory as a resolving agent. After preparation in, and five recrystallizations from butanone, the physical properties of the salt were essentially constant. At the end of seven, the yield of *D*-desoxyephedrine *l*-2-tetrahydropyranylacetate was 30%, m.p. 103-104°, $[\alpha]_D^{25} + 2.00^\circ$ (ethanol, $c 6.5$).

Anal. Calcd. for $C_{17}H_{27}O_3N$: C, 69.62; H, 9.21; N, 4.78. Found: C, 69.63; H, 9.28; N, 4.68.

Hydrolysis of 4.5 g. of salt gave 0.13 g. (3%) of impure IIa, m.p. 36-37°, $[\alpha]_D^{25} - 4.54^\circ$ (ethanol, $c 6$).

***d*-2-Aminomethyltetrahydropyran (VIa) by the Hofmann Reaction.**—By means of the procedure outlined for the conversions of the racemic mixtures, 3.0 g. of IIa was converted to 2.0 g. (74%) of *d*-2-tetrahydropyranylacetamide (Va), m.p. 84-85°, $[\alpha]_D^{25} + 12.5^\circ$ (ethanol, $c 1.6$).

Anal. Calcd. for $C_7H_{13}O_2N$: C, 58.74; H, 9.09; N, 9.79. Found: C, 58.90; H, 9.30; N, 9.30.

Application of the Hofmann reaction to 2.0 g. of Va gave 1.0 g. of VIa, b.p. 167-169°, $\alpha_D^{25} + 6.40^\circ$ (homogeneous, $l = 1$ dm.).

The *N*-benzoyl derivative was also formed, m.p. 111-113°, $[\alpha]_D^{25} + 25.4^\circ$ (chloroform, $c 1.75$).

CHICAGO 14, ILLINOIS

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

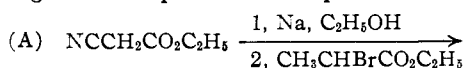
The Synthesis and Polymerization of Some 2-Methyl-3-alkyl-1,3-butadienes¹

BY C. S. MARVEL AND J. A. FULLER

Three new 2-methyl-3-alkyl-1,3-butadienes have been prepared and polymerized in an emulsion system. Polymerization rates of the new dienes are lower than that of dimethylbutadiene. Determination of 1,4-addition in the polymers by the perbenzoic acid method indicates a value of 95% for poly-2-methyl-3-*n*-butyl-1,3-butadiene.

Two factors which may account for the superiority of natural rubber in several of its properties are the regularity of the 1,4-structure of the chain and the slight dissymmetry of the individual isoprene units. Emulsion polybutadiene is composed of approximately 80% 1,4-units² while emulsion poly-2-alkylbutadienes contain 85% 1,4-units.³ Emulsion polydimethylbutadiene also has 85% of its units linked in the 1,4-manner but the greater symmetry of the units apparently results in a rise in the brittle point⁴ of the material. This study was undertaken to see whether the amount of 1,4-addition could be increased by the presence of larger alkyl substituents on the monomer. The two substituents on each monomer prepared were unlike in order to avoid properties associated with symmetry.

The preparation of the monomers by the following reactions presented no special difficulties.

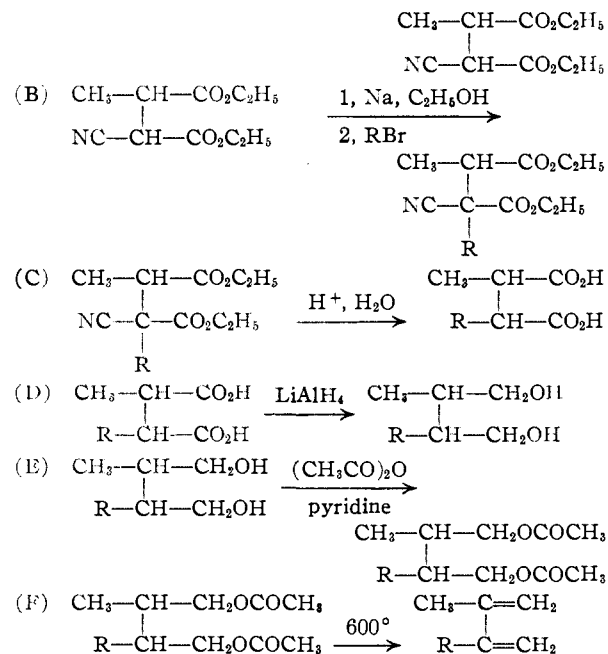


(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the U. S. Government Synthetic Rubber Program.

(2) I. M. Kolthoff, T. S. Lee and M. A. Mairs, *J. Polymer Sci.*, **2**, 220 (1947).

(3) C. S. Marvel, J. L. R. Williams and H. E. Baumgarten, *ibid.*, **4**, 583 (1949).

(4) G. Salomon and C. Koningsberger, *ibid.*, **2**, 522 (1947).



Each monomer contained a methyl substituent to make possible a closer comparison with known polymers. The R groups selected for the alkylating agents were ethyl, isopropyl and *n*-butyl.

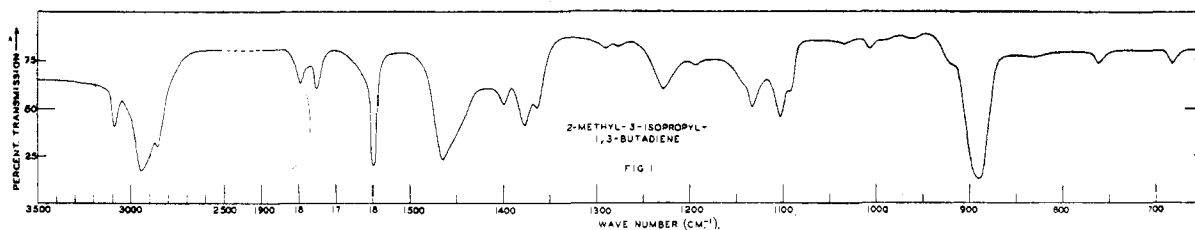


Fig. 1.

The observation was made by Berner and Leonardsen⁵ that the use of diethyl malonate in Reaction A results in extensive dehydrohalogenation of the α -bromo ester and that the main product in this case is a glutaric acid derivative. Hence, we used the cyanoester.

Preliminary experiments with lithium aluminum hydride indicated that good yields of the diols could be obtained from the succinic acids. In larger scale reductions, however, appreciable amounts of the acids containing the isopropyl or the *n*-butyl substituent were converted to γ -lactones. These two products had almost identical infrared absorption spectra.⁶ Both absorbed strongly at 1774 cm^{-1} , characteristic of lactones, and had no other functional groups. These products and the conditions favoring their formation were not investigated further.

The conditions for pyrolysis described in the preparation of 2-alkylbutadienes⁸ were modified slightly for this investigation. The heated column was packed with glass helices instead of glass beads, and the column temperature was maintained at 600° instead of 575°. It was found that a feed rate of one drop per second allowed less carbonization to take place than the rate of one drop every six seconds as previously described. The over-all yields of the dienes were: 2-methyl-3-ethyl-1,3-butadiene, 18%; 2-methyl-3-*n*-butyl-1,3-butadiene, 11.5%; 2-methyl-3-isopropyl-1,3-butadiene, 8.6%.

These materials all form adducts with maleic anhydride. The diene structures were confirmed by their infrared spectra. In each instance there was strong absorption at 1600 and at 890 cm^{-1} . The former frequency is characteristic of a conjugated diene, while the latter is characteristic of an unsymmetrically disubstituted ethylene ($\text{CH}_2=\text{C}<$). Conspicuously absent from all the spectra was absorption at 910 and 990 cm^{-1} . These two frequencies are associated with monosubstituted ethylenes ($\text{CH}_2=\text{CH}-$). This combination of facts excludes those structures which might be obtained if a rearrangement of the double bonds occurred during the pyrolysis.

In addition to the absorption frequencies mentioned above, the isopropyl group of 2-methyl-3-isopropyl-1,3-butadiene was detectable by its absorption at 1399 and 1363 cm^{-1} . The spectrum of this monomer is illustrated in Fig. 1. Table I summarizes the properties of the three dienes prepared.

Since the nature of the polymerization medium and the catalyst may have a profound effect on the

(5) E. Berner and R. Leonardsen, *Ann.*, **538**, 1 (1939).

(6) We are indebted to Miss Elizabeth Petersen for the infrared absorption curves and their interpretation.

TABLE I
2-METHYL-3-ALKYL-1,3-BUTADIENES

Substance	B.p., °C.	n_D^{20}	M. p. of maleic anhydride adduct, °C.
2-Methyl-3-ethyl-1,3-butadiene	93-94.5	1.441	67-68
2-Methyl-3-isopropyl-1,3-butadiene	108-109	1.4415	108-108.5
2-Methyl-3- <i>n</i> -butyl-1,3-butadiene	142-144	1.4472	120-121

character of a polymer, it was considered necessary to use the same type system employed for polydimethylbutadiene and the poly-2-alkylbutadienes which were previously subjected to 1,4-addition determination. The effect of the unlike alkyl groups should thus be more readily detected. The polymerization recipe used is a modification of the Mutual GR-S recipe and is described below.

Table II summarizes the polymers obtained. Since 2-alkylbutadienes are slower in this recipe than is butadiene, the low polymerization rates are not unexpected. The polymers were soluble in benzene.

TABLE II
POLYMERIZATION OF 2-METHYL-3-ALKYL-1,3-BUTADIENES
MEBd = 2-methyl-3-ethyl-1,3-butadiene; MIBd = 2-methyl-3-isopropyl-1,3-butadiene; MBBd = 2-methyl-3-*n*-butyl-1,3-butadiene.

No.	Monomers	Modifier (parts per hundred parts monomer)	Time, hr.	Conversion, %	Inherent viscosity
FL-71	MEBd	0.1	24	47	0.22
73	MEBd	.03	27	46	.51
75-1	MEBd	.01	36	33	.12
75-2	MEBd	.005	36	0	..
90	MEBd	.15	72	67	.22
77	MEBd(75), styrene(25)	.01	24	23	.25
87	MEBd	.1	48	64	.52
88-1	MIBd	.1	48	0	..
88-2	MIBd	.1	96	18	.08
91	MIBd(75), styrene(25)	.1	67	48	.26
89-1	MBBd	.1	48	63	.16
89-2	MBBd	.1	96	73	.23
92	MBBd(75), styrene(25)	.1	67	74	.17

The low inherent viscosities of the polymers indicate that they are "self-modifying." This effect has been noted with the 2-alkylbutadienes.⁹

Samples of poly-2-methyl-3-ethyl-1,3-butadiene (FL-90, Table II) and poly-2-methyl-3-*n*-butyl-1,3-butadiene (FL-89-2, Table II) were examined by

TABLE III
DETERMINATION OF 1,4-ADDITION

Sample	Initial molarity of double bonds	Initial molarity of perbenzoic acid	Ml. $\text{Na}_2\text{S}_2\text{O}_8$ (0.05118 N)				
			0.1 (hr.)	0.25 (hr.)	1.5 (hr.)	3 (hr.)	4.5 (hr.)
FL-89-2	0.02028	0.03008	13.35	10.78	10.60	10.55	10.55
FL-90	.02012	.03008	13.88	11.90	11.75	11.65	11.60
Blank	0	.03008	29.35	29.37	29.35	29.34	29.35

the procedure of Kolthoff and Lee⁷ to determine the amount of 1,2- and 1,4-addition which had occurred. The results of these analyses are given in Table III and Fig. 2.

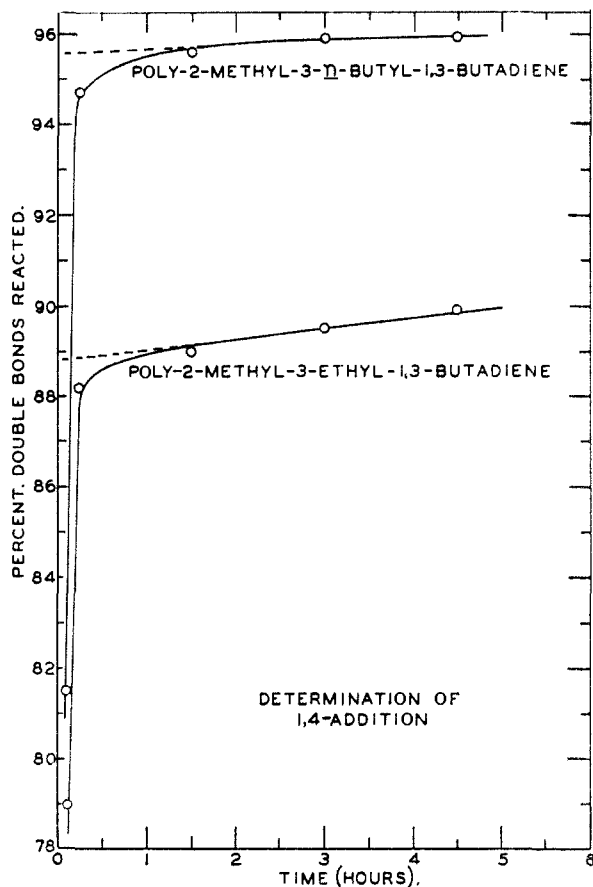


Fig. 2.

The conclusion reached here is that the presence of the two alkyl groups definitely influences the amount of 1,4-addition. Furthermore, the increase in 1,4-addition is mostly due to steric factors. The amount of 1,4-addition was increased by substituting a *n*-butyl group for an ethyl group while the inductive factors remained practically the same.

In calculating the per cent. of double bonds reacted it was assumed that the polymer contained one double bond per monomer unit. This assumption seems justified on the basis of total unsaturation values reported for emulsion polyisoprene and emulsion 2-alkylbutadienes.^{2,3}

Experimental

Diethyl α -Methyl- α' -cyanosuccinate.⁵—To a stirred solution of 30.5 g. (1.33 g. atoms) of sodium in 500 ml. of absolute ethanol was added dropwise 150 g. (1.33 moles) of

freshly distilled ethyl cyanoacetate, followed by 240 g. (1.33 moles) of ethyl α -bromopropionate (Eastman Kodak Co.) as soon as the reaction mixture was neutral to litmus. Most of the ethanol was removed by distillation and the residue was washed with water and dried over anhydrous magnesium sulfate. Distillation gave 194.8 g. (69%) of colorless oil boiling at 108–113° (1 mm.); n_D^{20} 1.4362.

Diethyl α -Methyl- α' -cyano- α' -alkylsuccinates.—These derivatives were prepared by adding diethyl α -methyl- α' -cyanosuccinate to a solution of an equivalent amount of sodium in absolute ethanol and treating the resulting solution with an excess of the appropriate alkyl bromide. Quantities up to 3 moles of ester were employed. The reaction mixtures were worked up in the usual way and the products isolated by distillation.

Diethyl α -Methyl- α' -cyano- α' -ethylsuccinate.⁶—B.p. 118–123° (1.5 mm.); n_D^{20} 1.4362; yield 78%.

Diethyl α -Methyl- α' -cyano- α' -isopropylsuccinate.—B.p. 113–115° (1 mm.); n_D^{20} 1.4462; yield 61%. *Anal.* Calcd. for $\text{C}_{13}\text{H}_{21}\text{O}_4\text{N}$: C, 61.16; H, 8.29. Found: C, 61.08; H, 8.42.

Diethyl α -Methyl- α' -cyano- α' -*n*-butylsuccinate.—B.p. 124–125° (1 mm.); n_D^{20} 1.4462; yield 72%. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{23}\text{O}_4\text{N}$: C, 62.43; H, 8.61. Found: C, 62.10; H, 8.77.

α -Methyl- α' -alkylsuccinic Acids.—The free acids were prepared by refluxing the diethyl α -methyl- α' -cyano- α' -alkylsuccinates with concentrated hydrochloric acid until a homogeneous solution was obtained or until the phases were no longer cloudy. On cooling, the major portions of the products were isolated by filtration. Additional product was obtained by concentration and ether extraction of the filtrates.

α -Methyl- α' -ethylsuccinic Acid.⁵—M.p. range 145–160°; yield 86%.

α -Methyl- α' -isopropylsuccinic Acid.—M.p. range 105–120°; yield 79%. *Anal.* Calcd. for $\text{C}_9\text{H}_{11}\text{O}_4$: C, 55.16; H, 8.10. Found: C, 54.90; H, 8.06.

α -Methyl- α' -*n*-butylsuccinic Acid.—M.p. range 85–105°; yield 97%. *Anal.* Calcd. for $\text{C}_9\text{H}_{11}\text{O}_4$: C, 57.46; H, 8.57. Found: C, 57.46; H, 8.53.

2-Methyl-3-Alkyl-1,4-butanediols.—The disubstituted succinic acids were converted to the corresponding 1,4-butanediols by adding dropwise an ethereal solution of the acid to a stirred solution of a twofold excess of lithium aluminum hydride. The mixture was stirred 30 minutes and then treated with water to destroy excess hydride. The complex was hydrolyzed with dilute hydrochloric acid and the products were isolated by ether extraction and distillation. Quantities up to 1.3 moles of disubstituted succinic acid were employed.

2-Methyl-3-ethyl-1,4-butanediol.—B.p. 98–101° (1 mm.); n_D^{20} 1.4570; yield 93%. *Anal.* Calcd. for $\text{C}_7\text{H}_{13}\text{O}_2$: C, 63.59; H, 12.20. Found: C, 63.87; H, 12.15.

2-Methyl-3-isopropyl-1,4-butanediol.—B.p. 103–105° (1 mm.); n_D^{20} 1.4590; yield 51%. *Anal.* Calcd. for $\text{C}_8\text{H}_{15}\text{O}_2$: C, 65.75; H, 12.42. Found: C, 66.17; H, 12.47.

γ -Butyrolactone by-product.—B.p. 60–62° (1 mm.); n_D^{20} 1.4447.

2-Methyl-3-*n*-butyl-1,4-butanediol.—B.p. 109–111° (0.8 mm.); n_D^{20} 1.4581; yield 56%. *Anal.* Calcd. for $\text{C}_9\text{H}_{17}\text{O}_2$: C, 67.45; H, 12.58. Found: C, 67.36; H, 12.56.

γ -Butyrolactone by-product.—B.p. 69–72° (1 mm.); n_D^{20} 1.4434.

2-Methyl-3-alkyl-1,4-butanediol Diacetates.—These derivatives were prepared by allowing the diols to stand with acetic anhydride in excess at or near the reflux temperature for several hours. A small quantity of pyridine was added as catalyst. The products were isolated by distillation.

2-Methyl-3-ethyl-1,4-butanediol Diacetate.—B.p. 83–85° (1 mm.); n_D^{20} 1.4352; yield 95%. *Anal.* Calcd. for $\text{C}_{11}\text{H}_{20}\text{O}_4$: C, 61.09; H, 9.32. Found: C, 60.87; H, 9.33.

2-Methyl-3-isopropyl-1,4-butanediol Diacetate.—B.p. 83–85° (0.6 mm.); n_D^{20} 1.4382; yield 95%. *Anal.* Calcd. for $\text{C}_{12}\text{H}_{22}\text{O}_4$: C, 62.58; H, 9.63. Found: C, 62.97; H, 9.75.

2-Methyl-3-*n*-butyl-1,4-butanediol Diacetate.—B.p. 90–92° (0.5 mm.); n_D^{20} 1.4375; yield 95%. *Anal.* Calcd. for $\text{C}_{13}\text{H}_{24}\text{O}_4$: C, 63.90; H, 9.90. Found: C, 64.14; H, 9.84.

2-Methyl-3-alkyl-1,3-butadienes.—A 12-in. Fenske column, with one-eighth inch Pyrex helices packing was suspended vertically in a jacket heater. The top of the

(7) I. M. Kolthoff and T. S. Lee, *J. Polymer Sci.*, **2**, 206 (1947).

column was fitted with a dropping funnel. The receiver at the lower end of the column was vented to a trap. Receiver and trap were packed in solid carbon dioxide. The column was maintained at a temperature of 600° as the substituted butanediol diacetates were added slowly through the dropping funnel. The rate of addition was one drop per second.

When all the material had been added the assembly was allowed to cool and was then washed down with ether, the washings being added to the material in the receiver. The ether solution was washed successively with small portions of water, 10% aqueous sodium carbonate and water and then dried over anhydrous magnesium sulfate. The products were isolated by distillation at atmospheric pressure.

2-Methyl-3-ethyl-1,3-butadiene.—B.p. 93–94.5°; n_D^{20} 1.4441; yield (two passes through column), 45%. *Anal.* Calcd. for C_9H_{12} : C, 87.42; H, 12.58. Found: C, 86.84; H, 12.71.

2-Methyl-3-isopropyl-1,3-butadiene.—B.p. 108–109°; n_D^{20} 1.4415; yield (two passes through column), 55%. *Anal.* Calcd. for C_8H_{14} : C, 87.19; H, 12.81. Found: C, 86.93; H, 12.83.

2-Methyl-3-*n*-butyl-1,3-butadiene.—B.p. 142–144°; n_D^{20} 1.4472; yield (two passes through column), 45%. *Anal.* Calcd. for C_9H_{14} : C, 87.01; H, 12.99. Found: C, 87.24; H, 13.19.

3-Methyl-4-alkyl-1,2,5,6-tetrahydrophthalic Anhydrides.—In a 2-oz. screw-capped bottle were placed 1 g. of maleic anhydride, 25 ml. of dry ether, 1 ml. of the disubstituted butadiene and a few crystals of picric acid. The bottle was capped and rotated for 24 hours in a 50° polymerization bath. The products were recrystallized from low-boiling petroleum ether. The adduct having the *n*-butyl substituent was obtained as the free phthalic acid derivative.

3-Methyl-4-ethyl-1,2,5,6-tetrahydrophthalic Anhydride.—M.p. 67–68°. *Anal.* Calcd. for $C_{11}H_{14}O_7$: C, 68.02; H, 7.27. Found: C, 68.10; H, 7.44.

3-Methyl-4-isopropyl-1,2,5,6-tetrahydrophthalic Anhydride.—M.p. 108–108.5°. *Anal.* Calcd. for $C_{12}H_{16}O_7$: C, 69.21; H, 7.93. Found: C, 69.63; H, 8.25.

3-Methyl-4-*n*-butyl-1,2,5,6-tetrahydrophthalic Acid.—M.p. 120–121°. *Anal.* Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.82; H, 8.62.

Polymerization.—All polymerizations were carried out using the following recipe:

Water	180 parts
Soap (Procter and Gamble silica free flakes)	5
Potassium persulfate	0.3
Dodecyl mercaptan	Variable
Monomer(s)	100

The soap was charged to a 2-oz. screw-capped bottle as a 2.8% solution. Potassium persulfate was then added as a 3% solution followed by dodecyl mercaptan. Monomers were weighed into the bottle on a trip balance. The bottle was flushed for one minute by a stream of nitrogen and then capped using a self-sealing rubber gasket. The reaction was carried out by rotating the bottle end-over-end at 16 r.p.m. in a 50° bath for the required time. The resulting latex was blended with 5 ml. of 2% soap solution containing 10% phenyl- β -naphthylamine and then coagulated by adding 12 ml. of a solution composed of 100 g. of alum, 100 ml. of concentrated hydrochloric acid and 1 l. of water. The raw polymer was washed several times with distilled water and dried for 24 hours at 1 mm.

Evaluation.—Conversions, static solubilities and inherent viscosities were determined by methods described by Frank, Adams, Blegen, Deanin and Smith.⁸

Determination of the amount of 1,4-addition in the polymers was carried out by the method of Kolthoff, Lee and Mairs.⁷ The method consists essentially in treating a known quantity of polymer with a measured excess of perbenzoic acid in a chloroform-benzene mixture. Samples are periodically removed and the unused perbenzoic acid determined iodometrically.

(8) R. L. Frank, E. C. Adams, J. R. Blegen, R. Deanin and P. V. Smith, *Ind. Eng. Chem.*, **39**, 887, 893 (1947).

URBANA, ILLINOIS

RECEIVED SEPTEMBER 24, 1951

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Synthesis and Characterization of Ethylene/Carbon Monoxide Copolymers, A New Class of Polyketones¹

BY M. M. BRUBAKER, D. D. COFFMAN AND H. H. HOEHN

The discovery of the free radical-initiated copolymerization of ethylene and carbon monoxide at superatmospheric pressures has led to the synthesis of a family of polyketones ranging from liquids to microcrystalline linear polymers of high molecular weight. The presence of carbonyl groups and hydrocarbon fragments, as shown by infrared spectra, is consistent with a polyketone structure containing $-\text{CH}_2\text{CH}_2-$ and $-\text{CO}-$ units. Further confirmation of the polyketone structure is furnished by the formation of derivatives characteristic of typical ketones. Hydrogenation of the polyketones yields polyalcohols without cleavage of the polymer chain, reaction with hydroxylamine and with hydrogen cyanide gives the corresponding oximes and cyanohydrins, respectively, and nitric acid oxidation gives rise to polymethylene dicarboxylic acids ranging from glutaric acid through sebacic acid.

Introduction

A study of the free radical chemistry of carbon monoxide led to the discovery that carbon monoxide copolymerizes with ethylene yielding a family of polyketones. The present paper concerns the synthesis and properties of these polyketones which contain $-\text{CO}-$ and $-\text{CH}_2\text{CH}_2-$ units, display the chemical reactivity characteristic of carbonyl compounds, and range from liquids to solid polymers of high molecular weight.

Polyketone Synthesis

The polyketones are conveniently prepared batch-wise by the polymerization of a mixture of

ethylene and carbon monoxide at superatmospheric pressures, employing di-(*t*-butyl) peroxide initiator at 135°. Variables such as pressure, the ratio in which the ethylene and carbon monoxide are employed, the temperature, and the solvent medium profoundly affect the composition, molecular weight and other properties of the polyketones formed.

Pressure.—Progressively higher pressures increase the proportion of carbon monoxide that copolymerizes, lead to higher molecular weight polymers, and result in higher conversions as indicated in Table I.

Monomer Composition.—The proportion in which the carbon monoxide combines with ethylene at 135° may be varied over a wide range by adjusting the ratio of carbon monoxide to ethy-

(1) Presented at the XII International Congress of Pure and Applied Chemistry, New York City, New York, September, 1951.