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°; $n^{20}D$ 1.4441; yield (two passes through column), 45%. *Anal.* Calcd. for C_7H_{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°; $n^{20}D$ 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°; $n^{20}D$ 1.4472; yield (two passes through column), 45%. *Anal.* Calcd. for C_9H_{16}: 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 $C_{11}H_{14}O_3$: 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 $C_{12}H_{16}O_3$: 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.

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(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 Polyketones[1]

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 $-CH_2CH_2-$ and $-CO-$ 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 $-CO-$ and $-CH_2CH_2-$ 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-

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

Table I

Effect of Pressure on the Copolymerization of Carbon Monoxide with Ethylene

Pressure, lb./sq. in.	Carbon monoxide, %	Polyketone[a] Molecular weight	Weight, g.
200	12.6	280	5
1000	28.1	700	18
2660	39.3	2420	80
4500	41.8	3400	170
14,700	44.9	Insoluble	130

[a] Polyketones prepared according to Procedure II.

lene in the mixed monomers. Copolymers obtained at 2000 lb./sq. in. with various proportions of carbon monoxide in the feed are shown in Table II.

Table II

Effect of Monomer Composition on the Copolymerization of Carbon Monoxide with Ethylene

Carbon monoxide, %		Polyketone[a]	
In monomers	In polyketone	Molecular weight	Weight (g.) formed
13	17.8	2250	61
25	28.4	4310	90
33	34.3	1700	104
36	35.7	1420	113
42	36.7	1800	78

[a] Polyketones prepared according to Procedure III.

It will be noted that with a monomer mixture containing 36% carbon monoxide, the monomers combined in the same ratio in which they were present.

Temperature.—The ratio in which carbon monoxide combines with ethylene is also a function of temperature, as shown in Table III.

Table III

Effect of Temperature on the Copolymerization of Carbon Monoxide with Ethylene

	Polyketone[a]	
Temperature, °C.	Carbon monoxide, %	Molecular weight
120	22.8	360
135	18.5	240
150	12.5	280
165	9.1	250

[a] Polyketones prepared according to Procedure IV.

When the temperature at which copolymerization is carried out is increased, the proportion of carbon monoxide combined decreases. The formation of lower molecular weight copolymer with increased temperature is also evident.

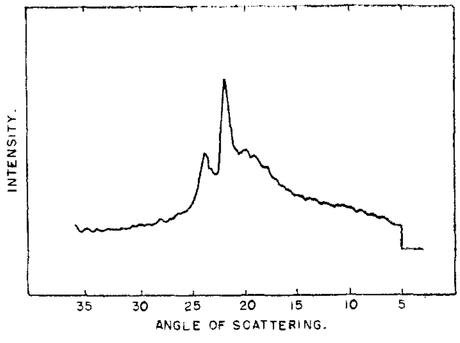

Fig. 1.—X-Ray diffraction of E/CO polyketones–plot of angle of scattering *versus* intensity.

Medium.—The copolymerization of carbon monoxide with ethylene can be carried out in various media. The particular medium employed affects the composition of the copolymer formed and its molecular weight. The results obtained employing benzene or cyclohexane are indicated in Table IV.

Table IV

Effect of Medium on Polyketone[a] Properties

Medium	Carbon monoxide in polyketone, %	Molecular weight
Benzene	13.4	3800
Cyclohexane	9.9	1430

[a] Polyketones prepared according to Procedure V.

Physical Properties of the Polyketones

Crystallinity.—Polyketones obtained by the copolymerization of carbon monoxide and ethylene range from liquids of low molecular weight to crystalline solids displaying the macromolecular properties of toughness and orientability. Polyketones of about 400 molecular weight are mobile liquids. As the molecular weight is increased to 1000–3000, the copolymers range from viscous liquids to crystalline waxes. The crystallinity of a typical wax-like polyketone is shown by the X-ray diffraction data reproduced in Fig. 1. The percentage of crystallinity, estimated from a plot relating intensity to angle of scattering, is about 38%. In crystallinity, these polyketones closely resemble the microcrystalline petroleum waxes. In several instances the crystal size of the polyketones was smaller than that of a typical microcrystalline petroleum wax.

Density.—The density of the polyketones varied with the composition, and increased from 0.934 to 1.105 at 23° as the carbon monoxide content was increased from 12.6 to 36.7%. The densities, melting ranges, and molecular weights of polyketones containing increasing proportions of carbon monoxide are listed in Table V.

Table V

The Density and Melting Range of Polyketones

CO in copolymer, %	Density (23°)	Melting range, °	Molecular weight	Inherent viscosity
12.6	0.934	Liquid at 25°	280	
17.8	.952	70–82	2260	0.15
24.1	.979	70–86	2710	.13
34.3	1.068	70–97	1700	.17
35.7	1.091	76–111	1420	.20
36.7	1.105	70–117	1800	.15

Linearity.—The polyketones show a linear relation between the logarithm of the melt viscosity and the reciprocal of the absolute temperature. A plot illustrating this relationship for a typical polyketone is shown in Fig. 2. This relation is like that displayed by straight-chain condensation polymers.[2] Accordingly, the polyketones are inferred to be essentially linear and free of three-dimensional structures.

Homogeneity.—The copolymers of ethylene and carbon monoxide are mixtures comprising polyketones differing from one another in composition, as judged by the ratios in which the polymer com-

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[2] P. J. Flory, This Journal, **62**, 1067 (1940).

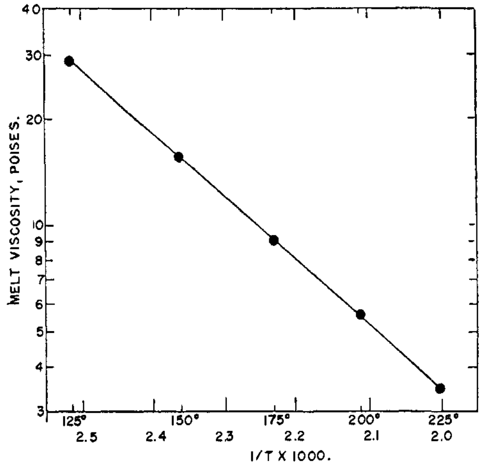

Fig. 2.—Melt viscosity of a polyketone as a function of temperature.

ponents combined, and in chain length. This inhomogeneity, in respect to composition and molecular weight, has been shown by characterization of polymer fractions separated from typical polyketone batches listed in Table VI.

Table VI

Properties of Polyketone Fractions

Polymer	Original polyketone, %	Carbon monoxide in polyketone, %	Molecular weight of polyketone
Original A, hard wax		39.3	2430
Fraction I, soft grease extracted with ether	20	34.2	680
Fraction II, residual hard wax	80	40.1	7760
Original B, oil		28.0	700
Fraction I, mobile liquid extracted with cyclohexane	54	25.2	500
Fraction II, viscous oil extracted with ether	23	31.4	1020
Fraction III, residual soft wax	23	34.1	2050

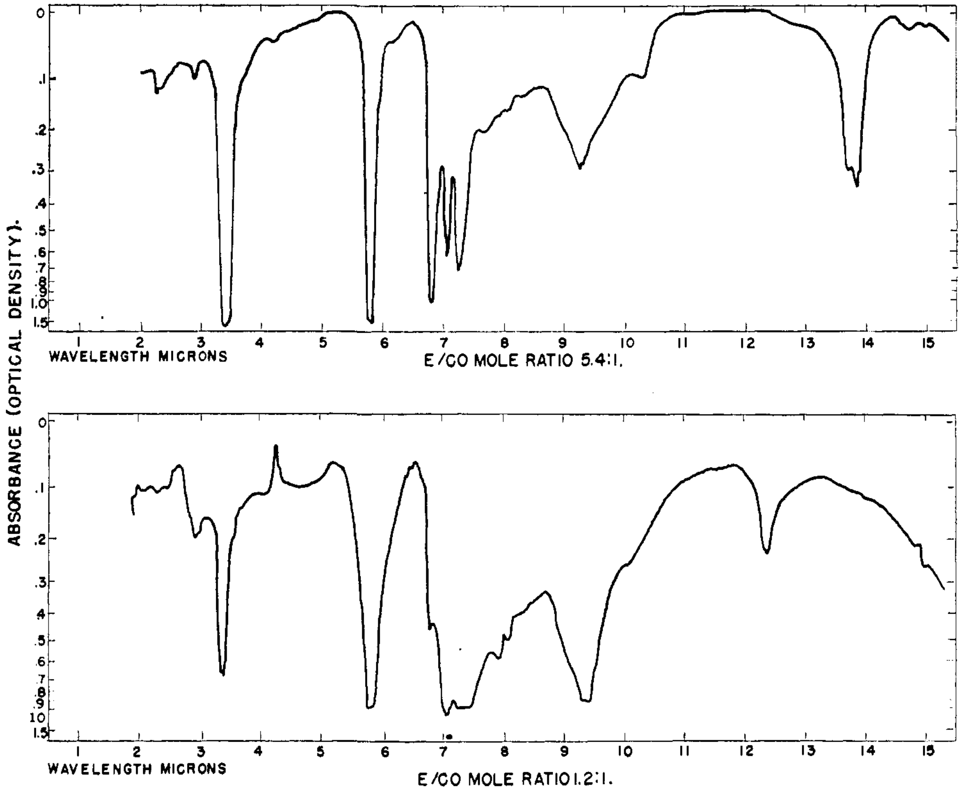

Fig. 3.—Infrared spectra of typical E/CO polyketones.

Structure of the Polyketones

The ketonic character of the ethylene copolymers with carbon monoxide, and also the presence of carbonyl groups alternating with hydrocarbon fragments comprising multiples of ethylene groups, $(-CH_2CH_2-)_n$, have been demonstrated by physical and chemical methods.

Infrared Absorption Spectra.—Typical infrared spectra for representative copolymers are reproduced in Fig. 3. The spectra are consistent with a polyketone structure comprising $-CH_2CH_2-$ and $-CO-$ units. The presence of the ketonic group is inferred from the absorption band at 5.8 μ and its harmonic at 2.9 μ. Other bands due to carbon–hydrogen structures arising from the ethylene component of the copolymer are also present in the spectra. These bands bear a relationship to the infrared absorption bands given by polythene,[3,4] but their location and intensity have been altered by the introduction of carbonyl groups in the chain. The carbon–hydrogen valence vibration absorptions at 3.4 μ were the only bands remaining

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[3] H. W. Thompson and P. Torkington, *Proc. Roy. Soc.* (*London*), **A184**, No. A996, 3 (1945): *Trans. Faraday Soc.*, **XLI**, 246 (1945).

[4] N. Sheppard and G. B. B. M. Sutherland, *Nature*, **159**, 739 (1947).

relatively constant at the low resolution of the spectrophotometer. For example, as the carbonyl concentration was increased, the 6.8 μ band for carbon–hydrogen bending vibration common to most hydrocarbon groups was replaced by two bands at 7.1 and 7.3 μ. These bands have been assigned to methylene structures adjacent to a carbonyl since they are characteristic of α-hydrogen structures. The doublet band at 13.9 μ, shown by higher hydrocarbons and polythene, which indicates four or more carbons in a chain, shifted to shorter wave lengths, became a singlet, decreased in intensity, and disappeared as the mole ratio of ethylene to carbon monoxide was lowered to approach 1:1. A band of higher intensity at 9.3 μ and a new band at 12.4 μ appeared in the spectra of polyketones. These bands do not necessarily require the postulation of new chemical structural units. This assumption is based on the marked non-additive changes in the hydrocarbon bands associated with the change in structure of the vibrating unit of $(-CH_2CH_2-)_n$ as compared with that of $(-CH_2CH_2)_x\underset{|}{C}{=}O$.

Ultraviolet Absorption Spectra.—Typical ultraviolet absorption curves for the copolymers in chloroform solution are shown in Fig. 4. The maximum absorption found at 2700–2800 Å. is like that for the carbonyl in simple ketones. Certain of the copolymers showed absorption also in the region of 2500 Å. The significance of this is not known.

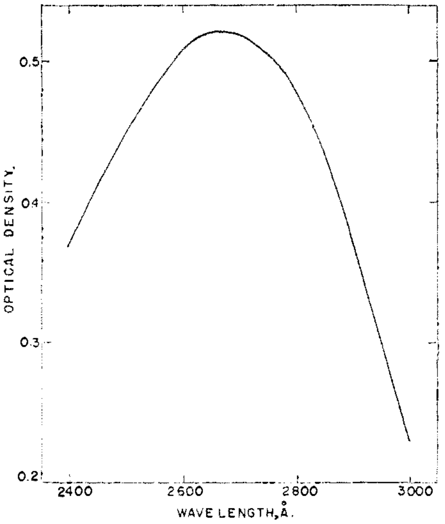


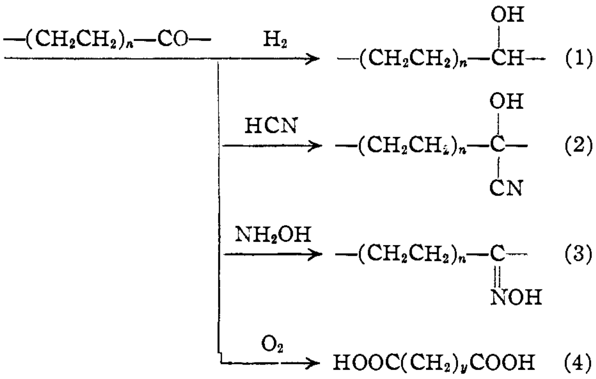
Fig. 4.—Ultraviolet absorption spectrum of a polyketone containing ethylene and carbon monoxide in the mole ratio 1.4:1.

Derivatives of the Polyketones.—The polyketones behave like typical ketones in the reactions they undergo. Representative polyketone derivatives are indicated in Table VII.

Hydrogenation.—Hydrogenation of the polyketones at high pressure using copper chromite catalyst yields hydroxyl-containing polymers having units represented as (1). The composition, molecular weight range and hydroxyl number of the hydrogenation products, and the absence of infrared absorption bands corresponding to the carbonyl group, indicated the essentially complete conversion of the ketone functions to alcohol groups without cleavage of the polyketone chain. The infrared spectrum of a typical polyalcohol derived from a polyketone is shown in Fig. 5.

Table VII

Derivatives of the Polyketones



$$-(CH_2CH_2)_n-CO- \xrightarrow{H_2} -(CH_2CH_2)_n-\overset{OH}{\overset{|}{C}}H- \quad (1)$$

$$\xrightarrow{HCN} -(CH_2CH_2)_n-\underset{CN}{\underset{|}{\overset{OH}{\overset{|}{C}}}}- \quad (2)$$

$$\xrightarrow{NH_2OH} -(CH_2CH_2)_n-\underset{NOH}{\underset{\|}{C}}- \quad (3)$$

$$\xrightarrow{O_2} HOOC(CH_2)_yCOOH \quad (4)$$

Hydrocyanation.—The polycyanohydrin represented as (2) was prepared by treating an ethylene/carbon monoxide copolymer with excess hydrogen cyanide in the presence of potassium cyanide catalyst. The polycyanohydrin was a straw-colored, hard, brittle resin. Analysis indicated that 80% of the carbonyl groups had been converted to cyanohydrin groups.

Oximation.—The polyoxime represented as (3) was prepared by introducing an aqueous solution of hydroxylamine into a solution of the polyketone in an organic solvent. The polyoxime that was separated had a composition corresponding to the conversion of 78% of the carbonyl groups to oxime groups.

Oxidation.—Assignment of a polyketone structure to the copolymers, in which ethylene units separate the carbonyl groups, is supported by the products obtained by oxidation of the polyketones. Nitric acid oxidation of copolymers of ethylene/carbon monoxide mole ratios of 4:1 to 4.6:1 gave polymethylene dicarboxylic acids ranging from glutaric through sebacic acid along with lesser amounts of higher homologs. The acids were characterized by conversion of the mixed crude acids to the dimethyl esters which were separated by fractional distillation. Identification was accomplished by determination of boiling point, refractive index, and saponification number of each ester fraction, and by saponification of selected fractions to obtain the dibasic acids for melting point determination. The melting points observed are listed in Table IX.

Experimental

Synthesis of Polyketones

Procedure 1.[5]—The synthesis of a typical polyketone is illustrated by the following experiment. A 400-ml. silver-lined reactor, capable of withstanding pressures of 1000 atm. was swept free of air by displacement with nitrogen. Into the reactor was introduced 100 ml. of cyclohexane and 3 ml. of di-(*t*-butyl)-peroxide. The reactor was then closed, cooled in a bath of Dry Ice–acetone, evacuated, placed in a mechanical shaker, and connected to a high pressure source of mixed gas consisting of 58% ethylene and 42% carbon

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[5] M. M. Brubaker, U. S. Patent 2,495,286, January 24, 1950.

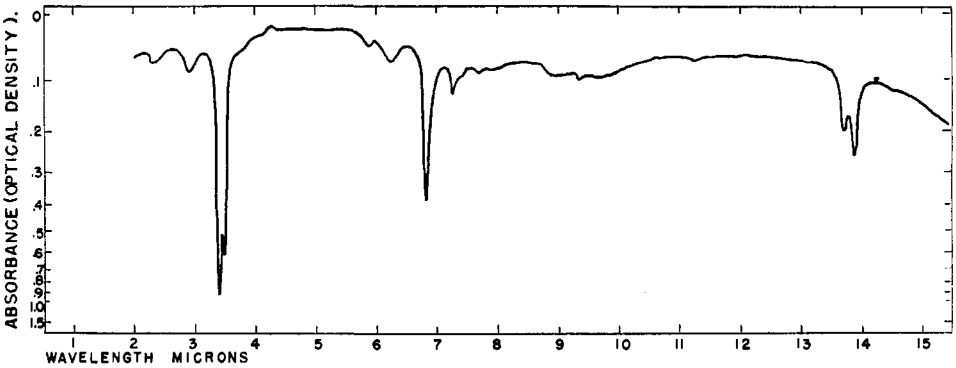

Fig. 5.—Infrared spectrum of a polyalcohol derived from a polyketone of 29.6:1 E/CO mole ratio.

monoxide. The mixed gas was added until the pressure reached 2660 lb./sq. in., and the temperature was brought to 135°. These conditions were maintained for 15 hours, more mixed gas being added to take care of any pressure drop due to reaction. After allowing the reactor to cool, the excess mixed gas was bled off, the tube was opened, and the contents were transferred to a vacuum distillation apparatus fitted with a short column and heating mantle. Removal of the cyclohexane left the copolymer as a residue. In order to ensure removal of small amounts of volatile materials, the copolymer was heated at 100–124° under a pressure of 20 mm., and the molten polymer was purged with a stream of nitrogen for one hour. On cooling, there was obtained 80 g. of a straw-colored wax having a composition corresponding to an ethylene/carbon monoxide mole ratio of 1.5:1. The wax melted at 70–82°.

Anal. Calcd. for $-(CH_2CH_2)_{1.5}CO-$: C, 68.54; H, 8.63. Found: C, 68.61; H, 8.96; inherent viscosity, 0.12; mol. wt., 2427.

The synthesis of polyketones of different composition and molecular weight involved changing the proportions of ethylene and carbon monoxide in the mixed gas, and adjustments in pressure, polymerization medium, and temperature. Procedures II through V illustrate some of these variations. In other respects, the operating procedure was as already described, with the possible exception of the isolation step. When the molecular weight or melting point of the polymer was above that of the foregoing illustration, it was often convenient to employ methods other than solvent stripping for separation of the polyketone. For example, polyketones of higher melting point often separated as fine granules on cooling the reactor. In these cases the polyketones were dried to constant weight in a vacuum oven at 50°. In other instances the copolymers were dissolved in hot benzene or toluene, and this solution was added to methanol with vigorous agitation. The polymer separated as a powder, was filtered, and dried to constant weight.

Procedure II.—This method is identical with Procedure I except that the pressures used for copolymerization ranged from 200 to 14,700 lb./sq. in. as shown in Table I. The polymerization at 14,200 lb./sq. in. was carried out with 0.3 ml. of di-(*t*-butyl)-peroxide since the use of 3 ml. of initiator caused uncontrolled polymerization.

Procedure III.—This method is identical with Procedure I except that (1) monomer mixtures used for copolymerization ranged from 13 to 42% carbon monoxide as shown in Table II, (2) pressure was maintained at 2000 lb./sq. in., and (3) the polymerization was run for 18 hours.

Procedure IV.—This method is identical with Procedure I except that the polymerizations were carried out at temperatures ranging from 120 to 165° as shown in Table VI, and the pressure was maintained at 400 lb./sq. in.

Procedure V.—This method is analogous to Procedure I except for the following differences. The copolymerizations (see Table IV) were carried out in a 1400-ml. reactor containing 1000 ml. of benzene. Ethylene containing 5% carbon monoxide was introduced at 4000 lb./sq. in.

Characterization of Polyketones

Ethylene/Carbon Monoxide Mole Ratio.—The composition of the polyketones is conveniently expressed in terms of the mole ratio in which ethylene and carbon monoxide are combined. This ratio was determined by analyzing the polyketones for carbon and hydrogen. Oxygen values were calculated from these data by difference, and the oxygen values were converted to per cent. carbon monoxide. The remainder of the molecule was assumed to be ethylene.

Recently developed procedures for the direct determination of oxygen have also been used and gave values which agreed with those calculated indirectly from the carbon and hydrogen data.

Molecular Weight.—The molecular weights of the polyketones were determined using an ebulliometric technique. Temperatures were measured using a differential thermometer.[6] The ebulliometer employed was similar to the one described by Kitson and co-workers.[7] Benzene was used as the solvent for most of the polyketones. Polyketones of 3:1 or lower ethylene/carbon monoxide mole ratio were incompletely soluble in benzene, and the molecular weights were determined in dioxane.

Infrared Absorption Spectra.—The infrared absorption spectra were determined using a Perkin–Elmer Model 21 Recording Infrared Spectrophotometer. Specimens were prepared by melting and pressing the polyketone between two flat rock salt plates separated near their edges by metal shims approximately 1 mil thick. The spectra were recorded by Mr. C. F. Hammer of the Polychemicals Department.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra were determined using a Cary Recording Quartz Spectrophotometer and 1-cm. fused quartz cells. Solutions of polyketones in chloroform (1 g. per l.) were irradiated. Chloroform was used as a control blank.

Melting Point.—The melting points were determined by means of a polarizing microscope fitted with an electrically heated stage.[8] The samples were observed with cross-polarized light, and the temperature was noted at which melting was first observed and where all crystalline character disappeared. This range of temperature was taken as the melting point of the polyketone.

Melt Viscosity.—The viscosities of the molten polyketones were determined in capillary viscometers at temperatures of 125 to 225°. Melt viscosities in poises were calculated from calibration factors determined by checking the viscometers with oils of known viscosity.

Inherent Viscosity.—The inherent viscosities of dilute solutions of the polyketones were calculated from relative viscosity values determined at 85 ± 0.05° on xylene solutions containing 0.125% polyketone. When polyketones were insoluble in xylene, the viscosities were determined either in chloroform or in 85% phenol.

Density.—The density of solid polyketones was determined by comparison with solutions of known specific gravity. Water–methanol, water–methanol–potassium iodide mixtures, and water were used. Test solutions were maintained at 23 ± 1°. Samples were dropped into test solutions and the rise or fall of the specimens was noted. The density of the test solutions was then adjusted until the polyketone particles neither rose nor fell.

Fractionation of Polyketones (See Table VI).—Polyketone granules (65 g.) were extracted with 250 ml. of diethyl ether in a soxhlet for 20 hours. Removal of the ether by

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[6] R. E. Kitson, A. N. Oemler and J. Mitchell, Jr., *Anal. Chem.*, **21**, No. 3, 401 (1949).

[7] R. E. Kitson and J. Mitchell, Jr., *ibid.*, **21**, 404 (1949).

[8] L. Kofler and H. Hilbek, *Mikrochemie*, **9**, 38 (1931).

distillation left a soft, grease-like polymer (13 g.). The higher molecular weight fraction was recovered by drying the material left in the soxhlet cup.

A viscous, oil-like polyketone (100 g.) and cyclohexane (100 g.) were shaken in a separatory funnel at room temperature. The cyclohexane-insoluble polyketone separated as a viscous lower layer which was drained off. This material was extracted a second time with cyclohexane (500 g.). The cyclohexane solutions were combined and the solvent removed by distillation. The residue (54 g.) was a mobile oil (see Table VI, Fraction B-I). The cyclohexane-insoluble polyketone was then extracted twice with ethyl ether (250-ml. portions). Removal of the ether left a viscous oil (23 g.) (see Table VI, Fraction B-II). In order to assist in transferring the polyketone, the ether-insoluble fraction was taken up in chloroform. Removal of the chloroform left a soft wax (23 g.) (see Table VI, Fraction B-III).

Derivatives of Polyketones

Hydrogenation to a Polyalcohol.[9]—Into a 400-ml. silver-lined reactor was introduced copper chromite-on-kieselguhr (10 g.) and polyketone (100 g.) having a molecular weight of 1470 and an ethylene/carbon monoxide mole ratio of 29.6:1. The reactor was placed in a mechanical shaker, hydrogen pressure of 1000 atm. was applied, and the reactor was agitated while the temperature and pressure were maintained at 181–188° and 900–1000 atm., respectively, for 15 hours. Excess hydrogen was then bled off, and the residue in the tube was taken up in 800 ml. of hot toluene. The hot solution was filtered through cloth covered with a layer of Super-Cel to remove the catalyst. The toluene was removed from the colorless filtrate by distillation to obtain a white, wax-like polyalcohol (80 g.).

Anal. Calcd. for $-(CH_2CH_2)_{29.6}CHOH-$: C, 84.03; H, 14.11; hydroxyl no., 65.2. Found: C, 83.89; H, 13.98; hydroxyl no., 69.0; mol. wt., 1085.

Preparation of a Polycyanohydrin.[10]—In a three-necked flask equipped with a stirrer and reflux condenser were placed hydrogen cyanide (54 g.) and a polyketone (35 g.) having a molecular weight of 1700 and an ethylene/carbon monoxide mole ratio of 2.4:1. When slurried at 27°, the polyketone dissolved to yield a straw-colored solution. To this solution was added potassium cyanide (0.5 g.), and the mixture was stirred for three hours. Phosphoric acid (1.1 g., 85%) was added to stabilize the cyanohydrin. Excess hydrogen cyanide was removed by distillation. The residue was dissolved in a mixture of benzene (175 g.) and ethyl alcohol (79 g.). Distillation of the solvents removed traces of hydrogen cyanide and left the polycyanohydrin (27 g.) which was a straw-colored, hard, brittle resin. The nitrogen analysis showed that approximately 80% of the ketone groups had been converted to cyanohydrin groups.

Anal. Found: C, 66.99; H, 9.24; N, 9.14; hydroxyl no., 224.

Preparation of a Polyoxime.[11]—A polyketone (100 g.) of ethylene/carbon monoxide mole ratio 1.5:1 and of 3300 molecular weight was dissolved in dioxane (250 ml.) and isopropyl alcohol (250 ml.) by heating the mixture to 90°, and the solution so obtained was cooled to 60°. A cold solution of hydroxylamine obtained by neutralizing hydroxylamine hydrochloride (139 g.) in water (250 ml.) with sodium hydroxide (80 g.) in water (100 ml.) was added, and the mixture was stirred for two hours at 50–60°. The straw-colored reaction mixture was poured into cold water (2 l.) to precipitate the polyoxime which separated as a tacky mass. The aqueous layer was poured off, and the resinous precipitate was agitated with ice-water in a Waring Blendor. This yielded the polyoxime as a white, fibrous polymer (101 g.) which was filtered and then dried over phosphorus pentoxide *in vacuo*. The polyoxime melted at 84–110°. The nitrogen analysis indicated that 78% of the carbonyl groups had been converted to oxime groups.

Anal. Found: C, 58.14; H, 8.75; N, 12.74.

Oxidation to Dibasic Acids.[12]—Into a three-necked, 3-l., round-bottom flask fitted with a reflux condenser, sealed stirrer, heating mantle and steam-heated dropping funnel was introduced 70% nitric acid (2000 g.) and ammonium vanadate (2 g.). The nitric acid was brought to gentle reflux, and molten polyketone (200 g.) was added to the vigorously stirred mixture during four hours. The polyketone had a molecular weight of 900 and contained ethylene and carbon monoxide in the mole ratio of 4.6:1. The addition of polyketone was accompanied by the vigorous evolution of nitrogen oxides and a rise in temperature. The mixture was refluxed for five hours after the last portion of polyketone had been added. Oxides of nitrogen were still being evolved slowly when the reaction was stopped by pouring the mixture onto 2000 g. of cracked ice. The supernatant layer was decanted and distilled at reduced pressure and steam-bath temperature to separate the nitric acid from any oxidation products present. The residue, when combined with the rest of the oxidation product, amounted to 215 g. of crude mixed acids.

The crude mixed acids were refluxed with methanol (640 g.) containing concentrated sulfuric acid (3 ml.). Reflux was adjusted to give a moderate distillation rate. Approximately three-fourths of the methanol was distilled from the mixture during two hours. The sulfuric acid catalyst was then neutralized with calcium oxide, and the distillation was continued until the temperature of the mixture was 120°. A second portion of methanol (240 g.) and sulfuric acid (3 ml.) was then added and the process repeated. Distillation of the residue at 8 mm. yielded 150 g. of mixed esters boiling at 66–170°. The mixed esters were separated into 39 fractions by fractional distillation at 1.2 mm. The boiling range was from 14 to 154°. Refractive indices measured at 25° on the various fractions ranged from 1.4175 to 1.4550, and the molecular weights calculated from saponification numbers ranged from 152 to 263. Comparison of these constants with those reported in the literature for the dimethyl esters of α,ω-dicarboxylic acids indicated that the acids present ranged from succinic through dodecanedioic and possibly higher. The various distilled esters amounted to 69% of the weight of polyketone oxidized and were distributed as indicated in Table VIII.

TABLE VIII

APPROXIMATE COMPOSITION OF ESTERS FROM DIBASIC ACIDS OBTAINED BY POLYKETONE OXIDATION

Esters	%
Dimethyl succinate and glutarate	31
Dimethyl adipate and pimelate	23
Dimethyl suberate and azelate	20
Dimethyl sebacate, 1,11-undecanedioate and 1,12-dodecanedioate	17
Higher esters	9

Selected dimethyl ester fractions were saponified and the melting points of the free acids were determined. The melting points observed, as listed in Table IX, range from that of glutaric to that of azelaic acid, inclusive, and agree with the reported melting points sufficiently well to indicate the formation of the polymethylene dicarboxylic acids by oxidation of the polyketones. Sebacic and undecanedioic acids were not obtained in a pure form.

TABLE IX

ACIDS FORMED BY THE OXIDATION OF POLYKETONES

Acid sought	Molecular weight Calcd. for dimethyl ester	Molecular weight Found for ester fraction (from sapn. no.)	Melting point of acid, °C. Found	Melting point of acid, °C. Liter.
Glutaric	160.17	161–164	93	96[13]
Adipic	174.19	179–182	151–152	152[13]
Pimelic	188.22	184	101–102	103[13]
Suberic	202.24	200–203	138–140	140[13]
Azelaic	216.27	216	104–106	106[13]
Sebacic	230.30	226–231	95–105	133[13]
1,11-Undecane-dioic	244.33	243	95–100	110[14]

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(9) S. L. Scott, U. S. Patent 2,495,292, January 24, 1950.

(10) P. S. Pinkney, U. S. Patent 2,495,284, January 24, 1950.

(11) S. L. Scott, U. S. Patent 2,457,279, December 28, 1948.

(12) S. L. Scott, U. S. Patent 2,436,269, February 17, 1948.

(13) "Handbook of Chemistry and Physics," 31st Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1949.

(14) D. F. Houston and W. A. Van Sandt, *Ind. Eng. Chem., Anal. Ed.*, **18**, 538 (1946).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BROOKLYN COLLEGE]

The Occurrence of Anhydrides in the Pyrolysis of Monocarboxylic Acids[1]

BY DAVID DAVIDSON AND PAUL NEWMAN

A number of monocarboxylic acids have been found to undergo dehydration to the corresponding anhydrides when simply refluxed at 250–350°, a detectable quantity of anhydride being formed within one minute. These results suggest that the known, exothermic hydrolysis of anhydrides is a generally reversible reaction: $(RCO)_2O + H_2O \rightleftarrows 2RCOOH$ + heat.

Although the thermal dehydration of 1,2-dicarboxylic acids to anhydrides has long been a commonplace, only little information concerning a similar dehydration of monocarboxylic acids has previously been available. Thus, in 1929, Hurd[2] stated that while acetic acid is converted to acetic anhydride at elevated temperatures, "no other monobasic acid in organic chemistry behaves in this manner...."

The products of the pyrolysis of monocarboxylic acids which have received frequent mention are hydrocarbons and ketones. These result from the two reactions: (1) $RCOOH \rightarrow RH + CO_2$ and (2) $2RCOOH \rightarrow R_2CO + CO_2 + H_2O$. Each of these reactions is subject to catalysis but both do not necessarily occur under the same conditions. For example, with acetic acid, ketone formation only was noted at 350° in a sealed tube (3% in 50 hours) and the conversion became quantitative when the reaction was catalyzed by sodium acetate.[3] With benzoic acid practically no change was observed at 390° in a sealed glass tube,[4] but with a zinc–copper chromite catalyst,[5] 27% decarboxylation occurred in ten hours at 250°. In quinoline solution with a copper carbonate catalyst, a 94% yield of carbon dioxide was obtained in four hours at the same temperature.[6] In the case of phenylphenylacetic acid, toluene (70% of theory) and dibenzyl ketone (10% of theory) were obtained after 15 hours heating at 340–375° in a sealed tube.[4]

At the time this study was undertaken, acetic acid remained the one case in the literature exclusive of patents in which a pyrolytic dehydration of a monocarboxylic acid to its anhydride had been reported.[7,8] A British patent[9] had also claimed the thermal dehydration of propionic and butyric acids over fireclay at 650° and a number of patents had appeared in which various catalysts, among them phosphoric acid and its salts, were used at 500–1100° for the dehydration of acetic, propionic and butyric acids.[10] Hurd,[2,8] nevertheless, considered acetic acid unique because of the possibility of its dehydration to ketene which could then react with unchanged acetic acid to form the observed anhydride. Since ketene has been obtained by the pyrolysis of acetic anhydride,[11] the assumption that these products appear in the reverse order in the pyrolysis of acetic acid may be open to question.

In the present study it was found that with monocarboxylic acids boiling between 250–350°, anhydrides can be detected[12,13] after refluxing for a minute in a test-tube without added catalysts. This has been verified with a variety of monocarboxylic acids such as benzoic, *p*-chlorobenzoic, anisic, cinnamic, α-amylcinnamic, phenylacetic, capric and myristic acids and with certain dicarboxylic acids which do not form five- or six-membered cyclic anhydrides such as adipic and azelaic acids. It thus appears that the known, exothermic hydrolysis of anhydrides[14] is actually a reversible reaction

$$(RCO)_2O + H_2O \rightleftarrows 2RCOOH + \text{heat}$$

Between room temperature and 300° the equilibrium point in this reaction may generally be so far to the right that the appearance of anhydrides on heating monocarboxylic acids in sealed tubes is likely to be overlooked. Removal of the water formed, however, whether by distillation or by refluxing with an air condenser permits extensive conversion as shown below. One case of a sealed tube experiment which seems to point to anhydride formation is that of trichloroacetic acid.[15] This monocarboxylic acid was smoothly converted to trichloroacetyl chloride in four hours at 300°.

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(1) Abstracted from a thesis by Paul Newman submitted to the Faculty of Brooklyn College in partial fulfillment of the requirements for the degree of Master of Arts, 1951.

(2) C. D. Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., Inc., (Reinhold Publ. Corp.), New York, N. Y., 1929, p. 333.

(3) O. Neunhoffer and P. Paschke, *Ber.*, **72**, 919 (1939).

(4) C. Engler and E. Löw, *ibid.*, **26**, 1439 (1893).

(5) C. R. Kinney and D. P. Langlois, THIS JOURNAL, **53**, 2189 (1931).

(6) M. H. Hubacher, *Anal. Chem.*, **21**, 945 (1949).

(7) E. Peytral, *Bull. soc. chim.*, **31**, 113 (1922).

(8) C. D. Hurd and K. E. Martin, THIS JOURNAL, **51**, 3614 (1929).

(9) R, Meingast and M. Mugdan, British Patent 194,719 (1923).

(10) R. Meingast and M. Mugdan, German Patents 408,715; 410,363; 417,731; 442,256 (1925); 475,885; 488,157 (1929); U. S. patent 1,570,514 (1926); H, Dreyfus, British Patents 462,714 (1937); 478,303; 478,213; 478,325 (1938); French Patents 737,610; 740,912 (1932); U. S. Patents 2,075,889; 2,081,988 (1937); 2,098,334 (1938); 2,160,840; 2,160,841 (1939); 2,202,046 (1940); 2,278,537 (1942); D. C. Hull, U. S. Patent 2,249,527 (1941); J. Maseré and A. Krawezinski, German Patent 742,244 (1943); J. E. Bludworth, M. O. Robeson and H. A. Truby, U. S. Patent 2,439,416 (1948).

(11) N. T. M. Wilsmore, *J. Chem. Soc.*, **91**, 1938 (1907).

(12) α-(*p*-Nitrobenzoyl)-amino-α-toluic acid in pyridine solution gives a blue color with anhydrides (other than five- or six-membered cyclic anhydrides) due to its conversion to the corresponding azlactone.

(13) A. W. Ingersoll and R. Adams, THIS JOURNAL, **44**, 2930 (1922).

(14) J. B. Conn, G. B. Kistiakowsky, R. M. Roberts and E. A, Smith, THIS JOURNAL, **64**, 1747 (1942).

(15) C. Engler and M. Steude, *Ber.*, **26**, 1443 (1893).