maintains. Equation 1a does not, however, represent the sole course of the reaction, even under

$$C_2(C_6H_5)_6 + O_2 \longrightarrow (C_6H_5)_3COOC(C_6H_5)_3 \quad (1a)$$

limiting conditions, since bis-trityl peroxide is not produced quantitatively. Because of the mildness of the isolation procedure, and in view of the concordance of the experiments with reaction at 25 and 55°, this result cannot be ascribed to decomposition of the relatively stable peroxide[24] subsequent to its formation. The isolation of total oxygenation product, produced under limiting conditions, in excess of the quantity predicted by equation 1a is further evidence of the inadequacy of this equation. Nevertheless, the reaction under limiting conditions appears to constitute a valid procedure for analysis of hexaphenylethane assuming the stoichiometry of equation 1.

If the above conclusion is accepted, it follows that the stoichiometry of the reaction in the presence of pyrogallol, with simultaneous exposure to oxygen and dissolution, is intermediate between those of equations 1 and 2. An alternative conclusion is that the stoichiometry of equation 2 maintains under these conditions but that the ethane employed was highly impure, and further, that, in the absence of pyrogallol, even the limiting consumption of oxygen exceeds that expected from equation 1. This proposal is rendered improbable by the data of Table III which are consistent with the conclusions that, in the absence of pyrogallol, the stoichiometry of equation 1 holds under limiting conditions, whether dissolution of the ethane precedes or is simultaneous with its exposure to oxygen, and that in the presence of pyrogallol the stoichiometry of equation 2 maintains when dissolution of the ethane precedes oxygenation. These conclusions cannot, however, be extended to other hexaarylethanes in the absence of similar experiments.

The present results serve also as a clear warning that prior work, the significance of which depends on establishment of purity of I or a congener by means of quantitative oxygenation, must be approached critically and with close attention to experimental details.

A hypothesis which is consistent with data in the absence of pyrogallol reported here, as well as with the observations of others, involves attack by trityl peroxy radical[12] ($TO_2\cdot$) on the solvent (SH). The formation of TO_2H plus TO_2S under conditions such that little $TO_2\cdot$ is removed by combination with trityl radical ($T\cdot$) would account for the observed consumption of oxygen in excess of Equation (1). When conditions are conducive to combination of $TO_2\cdot$ and $T\cdot$, even to the exclusion of direct reaction of $TO_2\cdot$ with I,[12] attack by $TO_2\cdot$ and $T\cdot$ on SH to yield products such as TO_2H plus TS would account for non-quantitative yields of II accompanied by adherence to the stoichiometry of equation 1. The results in the presence of pyrogallol when oxygenation and dissolution are simultaneous suggest that the reaction may be partially heterogeneous in the sense that $TO_2\cdot$ may attack undissolved as well as dissolved ethane.[12] Solid hexaphenylethane undergoes a rapid surface reaction with atmospheric oxygen yielding a yellow product. A highly reactive radical such as $TO_2\cdot$ would be expected to attack the crystal surface even more rapidly. Further work directed toward the elucidation of these systems is continuing in these laboratories.

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[24] The peroxide can be recrystallized from hot chloroform or carbon disulfide, *cf.* M. Gomberg, *Ber.*, **33**, 3154 (1900).

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Olefin–Carbon Monoxide–Alcohol Copolymers

BY T. L. CAIRNS, D. D. COFFMAN, RICHARD CRAMER, A. W. LARCHAR AND B. C. MCKUSICK

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The radical-initiated copolymerization of ethylene and carbon monoxide in methanol at high pressures gives copolymers containing chemically-bound methanol. Absorption spectra and chemical studies suggest that the methanol is combined in α-hydroxy ester units, $-C(OH)(CO_2CH_3)CH_2CH_2-$. Such units appear to predominate over $-CH_2CH_2-$ and $-C(=O)-$ units in certain copolymers made at 8000 atm. The replacement of ethylene by other olefins or of methanol by other alcohols gives analogous copolymers.

Recent publications from this Laboratory describe a new class of polyketones obtained by the radical-initiated copolymerization of ethylene with carbon monoxide.[1,2] Subsequent study of the effect of polymerization medium on this copolymerization has resulted in the surprising observation that copolymers prepared in alcohols are quite different in character. These new copolymers contain alkoxyl groups due to chemically-bound alcohol molecules. This paper discusses the conditions under which these copolymers are formed and proposes a structure for them.

Copolymers of this new class are obtained when ethylene and carbon monoxide are copolymerized in methanol, ethanol, 2-propanol, *t*-butyl alcohol, benzyl alcohol or 2-(*p*-chlorophenoxy)-ethanol and

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[1] M. M. Brubaker, D. D. Coffman and H. H. Hoehn, THIS JOURNAL, **74**, 1509 (1952).

[2] D. D. Coffman, P. S. Pinkney, F. T. Wall, W. H. Wood and H. S. Young, *ibid.*, **74**, 3391 (1952).

TABLE I

COMPOSITION OF OLEFIN–CO–ALCOHOL COPOLYMERS

Product no.	Procedure[a]	Olefin	Alcohol	Mole % CO in olefin–CO mixt.	Mole ratio, olefin:CO:alcohol, in copolymer	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Alkoxyl, % Calcd.	Alkoxyl, % Found	Sapon. equiv. Calcd.[f]	Sapon. equiv. Found[h]
1	A[b]	Ethylene	Methanol	50	100:104:13	62.0	62.1	7.5	7.7	6.6	7.0	470	309
2	A[c]	Ethylene	Methanol	50	100:110:24	60.3	60.3	7.5	7.5	11.2	11.3	277	316
3	A	Ethylene	Methanol	50	100:96:16	62.4	62.6	7.7	8.3	7.3	7.6	374	279
4	A	Ethylene	Methanol	30	100:90:16	63.0	62.7	8.0	7.9	8.5	7.6		
5	B	Ethylene	Methanol	42	100:138:70	55.0	56.2	7.7	7.3	24.4	26.2	127	159
6	B	Ethylene	Methanol	42	100:140:50	56.2	56.3	7.3	7.2			167	172
7	B	Ethylene	Methanol	59	100:157:58	55.0	55.0	7.0	7.0	19.5	19.8	159	115
8	B	Ethylene	Methanol	82	100:184:96	52.2	51.8	7.2	7.3	27.0	23.1	115	128
9	B	Ethylene	Methanol	63	100:163:76	54.4	54.4	7.1	7.0	21.6	21.8	144	141
10	B	Ethylene	Ethanol	62	100:152:55	57.7	57.8	7.6	7.6	25.8	25.1		
11	B	Ethylene	2-Propanol	56	100:138:43	60.6	60.1	8.1	8.0				
12	B	Ethylene	*t*-Butyl alcohol	56	100:198:79	60.4	60.5	8.5	8.3	40.7	12.1[g]	180	341
13	B	Ethylene	Benzyl alcohol	40	100:125:17	65.4	65.5	6.6	6.6				
14	B	Ethylene	2-(*p*-Chlorophenoxy)-ethanol[i]	40	X:Y:20[d]					7.1[e]	7.1[e]		
15	B	Propylene	Methanol	55	100:164:59	58.8	58.6	7.9	7.8	17.1	19.0		
16	B	Isobutylene	Methanol	80	100:189:59	60.8	61.1	8.2	8.0				
17	B	1-Butene	Methanol	69	100:189:59	60.8	60.9	8.2	8.1				
18	B	Butadiene	Methanol	77	100:89:40	69.2	69.2	8.4	8.3	13.5	12.4		
19	B	1-Butene	*t*-Butyl alcohol	77	100:219:82	63.8	63.8	9.1	9.1	34.1	20.4[g]		

[a] Unless otherwise noted, the pressure used in procedure A was 3000 atm., in procedure B, 8000 atm. [b] Pressure = 1000 atm. [c] Pressure = 2000 atm. [d] $X + Y = 234$. [e] Per cent. chlorine. [f] One ester group per calculated alkoxyl group is assumed. [g] Zeisel determinations of *t*-butoxy groups are known to give very low results. [h] The saponification equivalent of a 1.5:1 E/CO copolymer was 952, showing that little alkali is consumed by E/CO copolymers under the same conditions. [i] C. N. Nair and D. H. Peacock, *J. Indian Chem. Soc.*, 12, 318 (1935).

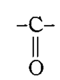
when the ethylene is replaced by propylene, isobutylene, 1-butene or butadiene. The effect of the alcohol in modifying the structure of the copolymer is most marked at very high pressures; thus at a pressure of 8000 atm. in methanol, copolymers have been prepared that contain as much as 26% methoxyl, equivalent to nearly 27% chemically-bound methanol. The effect falls off considerably with decreasing pressure, although copolymers with as much as 7% methoxyl have been prepared at 1000 atm. in methanol. The factors that have an important bearing on the properties of ethylene–carbon monoxide copolymers[1] (or, as they will be called in this paper, E/CO copolymers) are also important here. Probably the most important factor besides pressure is the percentage of carbon monoxide in the olefin–carbon monoxide reaction mixture; in general, the higher the percentage, the lower the yield and the higher the alkoxyl content of the polymer.

E/CO/MeOH copolymers, the type of olefin–CO–alcohol copolymer most studied, are colorless and transparent. They generally soften at 70–90°. Those containing 1–8% methoxyl are orientable and have tensile strengths as high as 4200 lb./sq. in. Those of greater methoxyl content are weaker and are usually unorientable.

E/CO copolymers are composed of ethylene units (I) and carbonyl units (II).[1] It is believed that E/CO/MeOH copolymers contain, in addition to these units, α-hydroxy ester units (III). Other olefin–CO–alcohol copolymers are believed to be composed mainly of carbonyl units and units analogous to I and III. In E/CO/MeOH copolymers containing over 20% methoxyl, III is probably the predominant structural unit.

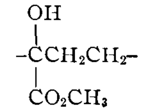
$-CH_2CH_2-$

I



$-\underset{\underset{\displaystyle O}{\|}}{C}-$

II



$-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CO_2CH_3}{|}}{C}}CH_2CH_2-$

III

The evidence that olefin–CO–alcohol copolymers contain α-hydroxy ester units is as follows.

1. **Alcohol Molecules Are Incorporated in the Copolymers.**—More than three hundred olefin–CO–alcohol copolymers have been analyzed for carbon and hydrogen. The data, part of which are shown in Table I, are best explained by this assumption. Moreover, E/CO/benzyl alcohol copolymer contains benzyl groups (shown by infrared analysis) and E/CO/2-(*p*-chlorophenoxy)-ethanol copolymer contains chlorine.

2. **The Alcohol Is Present as Alkoxyl Groups.**—Zeisel analyses of copolymers prepared from methanol, ethanol or *t*-butyl alcohol show that alkoxyl is present (for typical analyses, see Table I). That the alkoxy groups are not ethoxyl groups derived from ethylene, but correspond to the alcohol used, was shown by hydrolyzing in E/CO/MeOH copolymer with alkali and identifying methanol in the hydrolysate.

3. **The Most Highly Methoxylated E/CO/MeOH Copolymers Approach the α-Hydroxy Ester Unit, III, in Composition.**—This unit can be looked on as being composed of one molecule of ethylene, two of carbon monoxide and one of methanol. Several of the samples of Table I approach this composition. The sample coming closest (no. 8) has the mole ratio 1.00 ethylene:1.85 carbon monoxide:0.96 methanol.

4. **Hydroxyl Groups Are Present.**—Infrared absorption spectra of films made from E/CO/

MeOH, E/CO/*t*-butyl alcohol, E/CO/benzyl alcohol and 1-butene–CO–methanol copolymers all show the absorption band at 2.9 μ that is characteristic of O–H.

5. **Carbalkoxyl Groups Are Present.**—Infrared absorption spectra of various olefin–CO–alcohol copolymers show a broad band in the range 5.7–5.9 μ ascribable either to ketone groups, carbalkoxyl groups or both. The ultraviolet absorption spectra of E/CO/MeOH copolymers of 5–10% methoxyl content have well-defined maxima near 275 mμ that indicate the presence of ketone units. In contrast, E/CO/MeOH copolymers of over 20% methoxyl show either no absorption maximum in the 270–280 mμ region or a very slight one, suggesting that for such copolymers the infrared band in the 5.7–5.9 μ range is almost entirely due to carbomethoxyl groups.

Hot, dilute aqueous sodium hydroxide readily dissolves E/CO/MeOH copolymers of 20–26% methoxyl content with loss of most of the methoxyl groups. The infrared absorption spectrum of material left after evaporating a hydrolysate to dryness indicates that carboxylate groups are formed in the process. The amount of alkali consumed in such saponifications (Table I) and the composition of a hydrolyzed polymer isolated after acidification of a saponification mixture are roughly in accord with the equation

$$\text{-CO}_2\text{CH}_3 + \text{OH}^{\ominus} \longrightarrow \text{-CO}_2^{\ominus} + \text{CH}_3\text{OH}$$

An E/CO/MeOH copolymer containing 23.1% methoxyl readily dissolved in cold 29% aqueous ammonia. The product was a polymer containing almost no methoxyl and sufficient nitrogen to be in accord with the equation

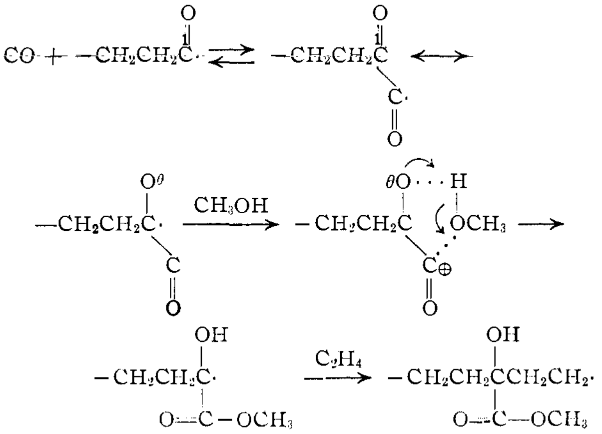
$$\text{-CO}_2\text{CH}_3 + \text{NH}_3 \longrightarrow \text{-CONH}_2 + \text{CH}_3\text{OH}$$

6. **The Hydroxyl Groups Are Probably α to the Carbalkoxyl Groups.**—The ease with which E/CO/MeOH copolymers are saponified and ammonolyzed is indicative of this.[3] Better evidence was obtained by treating E/CO/MeOH copolymers with hot 96% sulfuric acid. This caused 0.23–0.64 mole of carbon monoxide to be evolved per mole of methoxyl group in the copolymers. Under the same conditions, methyl α-hydroxyisobutyrate lost carbon monoxide to the extent of 45–56% of theory, while E/CO copolymers lost almost no carbon monoxide. Bistrzycki and Siemiradzki[4a] have shown that a variety of α-hydroxy acids lose carbon monoxide to the extent of 30–80% of theory under like conditions. Although tertiary acids and α-keto acids (and presumably their esters) are also readily decarbonylated by sulfuric acid,[4] there is little reason to suppose that either type of structure is an important unit in olefin–CO–alcohol copolymers. Accordingly, the decarbonylation of E/CO/MeOH copolymers seems best expressed by the equation

$$\text{-C(OH)(CO}_2\text{CH}_3\text{)CH}_2\text{CH}_2\text{-} \xrightarrow{\text{H}_2\text{SO}_4} \text{-COCH}_2\text{CH}_2\text{-} + \text{CH}_3\text{OH} + \text{CO}$$

Although the presence of α-hydroxy ester units has not been unequivocally established, consideration of the evidence outlined above leaves little doubt that the structure proposed for olefin–CO–methanol copolymers is correct.

It seems unlikely that the α-hydroxy ester units, III, are formed by reaction of E/CO copolymer with methanol and carbon monoxide, for at 130° and a pressure of 8000 atmospheres in the presence of *t*-butyl peroxide, neither 2-butanone, 2,5-hexanedione nor E/CO copolymer gave any evidence of reaction with methanol and carbon monoxide to form α-hydroxy esters. Perhaps they are formed by reaction of carbon monoxide and methanol with acyl radicals at the ends of growing copolymer chains in some such way as the following



Experimental

Preparation of E/CO/MeOH Copolymers.[5] **Procedure A** (Pressure = 1000–3000 atm.).—Most copolymerizations at 1000–3000 atm. were run in equipment and by procedures similar to those of Brubaker, Coffman and Hoehn.[1] For example, a mixture of 50 ml. of methanol and 0.5 ml. of *t*-butyl peroxide was agitated at 130° for 2.3 hours with a gas mixture containing 70% ethylene and 30% carbon monoxide

TABLE II

EFFECT OF GAS COMPOSITION ON YIELD AND COMPOSITION OF E/CO/MeOH COPOLYMER MADE AT 3000 ATM. BY PROCEDURE A

Mole % CO in gas	Yield, g.	Mole ratio, E:CO:CH_3OH, in copolymer	Inherent viscosity, detd. in $CHCl_3$
80	3	100:160:70	0.10
50	8	100:120:40	0.20
30	15	100:90:16	1.12
15	12	100:75:9	1.31
5	37	100:34:1	1.53

TABLE III

EFFECT OF PRESSURE ON YIELD AND COMPOSITION OF E/CO/MeOH COPOLYMER MADE FROM A 70/30 E/CO GAS MIXTURE BY PROCEDURE A

Pressure, atm.	Yield, g.	Mole ratio, E:CO:CH_3OH, in copolymer	Inherent viscosity, detd. in $CHCl_3$
1000	7	100:86:12	0.47
2000	11	100:90:14	0.55
3000	15	100:90:16	1.12
8000[a]		100:110:46	

[a] Procedure B was used.

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(3) M. Gordon, J. G. Miller and A. R. Day, THIS JOURNAL, **70**, 1946 (1948).

(4) (a) A. Bistrzycki and B. Siemiradzki, *Ber.*, **39**, 51 (1906); (b) W. W. Elliott and D. L. Hammick, *J. Chem. Soc.*, 3402 (1951); C. M. Welch and H. A. Smith, THIS JOURNAL, **75**, 1412 (1953).

(5) M. M. Brubaker (to E. I. du Pont de Nemours and Company), U. S. Patent 2,557,256 (1951).

at a pressure of 2900–3000 atm. Removal of solvent as described previously[1] left 14.5 g. of colorless copolymer whose composition is included in Table I (product 4).

Both gas composition and pressure have an important effect on the yield, composition and molecular weight of copolymers prepared by this procedure, as Tables II and III show.

With gas mixtures containing a higher percentage of ethylene than in the example above, less *t*-butyl peroxide must be used or uncontrollable exothermic polymerization that can cause bursting of the safety rupture disk may occur. For example, with a gas containing 95% ethylene, it is best to use only 0.05 ml. of *t*-butyl peroxide. At lower pressures or with gas mixtures high in carbon monoxide, it may be necessary to use more of the peroxide for best results. Thus, if a gas containing only 20% ethylene is used in the procedure above, 2.0 ml. of *t*-butyl peroxide is advisable.

Procedure B (Pressure = 3000–8000 atm.).—A mixture of 1.56 g. of methanol, 0.01 g. of *t*-butyl peroxide, 0.57 g. of ethylene and 0.98 g. of carbon monoxide was put in a stainless-steel cylinder with a movable piston. The cylinder was placed in a Bridgman-type pressure apparatus.[6] The reaction mixture was subjected to a pressure of 8000 atmospheres, heated to 130°, and held at 130° for 17 hours, during which time the pressure gradually fell to 7300 atmospheres. The reaction mixture was cooled to 25° and unreacted gas was vented. The apparent gas absorption was 0.47 g. The reaction mixture was diluted with methanol. The methanol solution was clarified by centrifuging and was then pipetted onto a glass plate. Evaporation of the methanol left a colorless film that was scraped up with a razor blade and dried at 65° (0.5 mm.) for seven hours; weight 0.57 g. The composition of the copolymer (product 9) is shown in Table I, together with those of other similar products. Products 5–8 (Table I) are composites obtained by working up together 3 to 5 reaction mixtures made under identical conditions.

The proportion of carbon monoxide in an ethylene–carbon monoxide gas mixture has a big effect on the yield and composition of the polymer formed. This is illustrated by Table IV.

TABLE IV

EFFECT OF GAS COMPOSITION ON YIELD AND COMPOSITION OF POLYMER MADE AT 8000 ATM. BY PROCEDURE B

Mole % CO in gas	Yield, g.	Mole ratio, E:CO:CH_3OH, in copolymer
25	1.12	100:58:13
40	0.58	100:111:31
45		100:126:41
54	0.59	100:144:53
63	0.57	100:163:76
82	0.32	100:183:83

Preparation of Other Olefin–CO–Alcohol Copolymers.—The copolymers were prepared at 8000 atm. by procedure B above, either the methanol or the ethylene (or both in the case of 1-butene–CO–*t*-butyl alcohol copolymer) being replaced by another substance. Yields were similar when the methanol was replaced by ethanol, 2-propanol, *t*-butyl alcohol, benzyl alcohol or 2-(*p*-chlorophenoxy)-ethanol, or when the ethylene was replaced by propylene or butadiene, but were only 5–25% as great when ethylene was replaced by isobutylene or 1-butene. The product from benzyl alcohol was only partly soluble in the reaction medium. The soluble part was used for infrared analysis and the insoluble part was analyzed after being dried at 65° (0.5 mm.). The products from 2-(*p*-chlorophenoxy)-ethanol and from butadiene were both insoluble in the common solvents and had to be dried and analyzed without purification. The other products were similar in appearance and solubility to the E/CO/MeOH copolymer described above. The compositions of these products are included in Table I.

Physical Properties of E/CO/MeOH Copolymers.—Copolymers prepared at pressures of 2000–3000 atmospheres from gas mixtures with 80 mole % or more ethylene are generally orientable. The ethylene:carbon monoxide:methanol mole ratios of such polymers range from 100:42:1 to 100:90:16 (1–8% methoxyl content). The copolymers soften at 70–90°. Their melting points, observed microscopically with polarized light, lie between 90 and 140°. They are colorless, and films containing over 5% methoxyl are transparent. They are soluble in chloroform or dioxane, sparingly soluble in methanol. Other physical properties are: inherent viscosity, $[\eta]$ (at 25° in chloroform), 0.31–1.5; tensile strength, 2600–4200 lb./sq. in.; elongation at break, 15–540%; Izod impact strength, 0.60–1.30 ft. lb./in.; stiffness, 36,000–56,000 lb./sq. in.; water absorption, 0.44–0.93%.

E/CO/MeOH copolymers other than those described above are generally not orientable. Copolymers containing 20% or more methoxyl, obtainable at pressures of 7000–8000 atm., are more soluble than the copolymers described above. Thus, product 6 readily dissolved in boiling methanol, acetone, dioxane, dimethylformamide, pyridine, acetic acid, phenol and chloroform to the extent of 1% or more and remained in solution at 25°. It showed appreciable but lesser solubility in *t*-butyl alcohol and ethyl acetate and was inappreciably soluble in ether, xylene or water. It readily dissolved in 96% sulfuric acid at 25°. Addition of a small amount of hydrochloric acid to a hot methanol or dioxane solution of product 6 caused insolubilization with partial loss of methoxyl groups; the insolubilization may have been due to transesterification between polymer chains.

Infrared Absorption Spectra.—Spectra were obtained with a Perkin–Elmer Infrared Spectrometer Model 12B having a rock-salt prism. Samples were placed in the spectrometer in the form of films adhering to sodium chloride plates. To prepare a film, a dilute chloroform solution of polymer was cast on a sodium chloride plate. The plate stood at 25° (760 mm.) for 15 hours so that most of the chloroform should evaporate. Last traces of chloroform were removed by holding the plate at 65° (0.5 mm.) for 7 hours. The infrared absorption spectrum of product 5 has strong absorption bands at 2.80 and 5.71 μ, presumably due, respectively, to O–H and C=O groups. Other samples, including those of low methoxyl content such as product 3, have similar spectra. The spectra of films cast from methanol or acetone do not differ significantly from those of films cast from chloroform.

A solution of 25 mg. of product 9 in 0.20 ml. of 10% sodium hydroxide was evaporated to dryness on a salt plate. The infrared absorption spectrum of the residue showed the intense bands at 6.3 and 7.1 μ characteristic of carboxylate ion.

Ultraviolet Absorption Spectra.—Spectra were determined with a Cary Recording Quartz Spectrophotometer, using 1-cm. fused quartz cells. The polymers were generally dissolved in chloroform.

The spectrum of product 3 (λ_{max} 275 mμ; k_{max} = 0.27) is typical of those of products containing 5–10% methoxyl. The spectrum of product 9 is typical of those of highly methoxylated products, showing only low general absorption at 250–350 mμ.

Action of Alkali on E/CO/MeOH Copolymers. (a).—Copolymers containing 20% or more methoxyl dissolve in 5% aqueous sodium hydroxide slowly at 25°, quickly at 100°. They slowly dissolve in 10% sodium carbonate at 100°, but are insoluble in 7% sodium bicarbonate at 100°. They have negligible acidity as determined by direct titration of methanol solutions with phenolphthalein as the indicator; the end-point is reached with two or three drops of 0.1 *N* sodium hydroxide solution, but the phenolphthalein color fades away within a minute or so. Their saponification equivalents (Table I) range from 115 to 172. Copolymers containing less than 20% methoxyl generally swell but are not soluble in 5% aqueous sodium hydroxide.

(b).—A 71-mg. sample of product 2 was dissolved in 2.0 ml. of 10% sodium hydroxide at 25°, and 0.50 ml. of water was then distilled out through a small Vigreux column. The distillate gave a positive xanthate–molybdate test for alcohols,[7] a positive chromotropic acid test for methanol,[8] and a negative chromotropic acid test for formaldehyde. The intensity of color in the first two tests roughly corresponded to the methoxyl content of the copolymer.

(c).—A sample (*ca.* 25 mg.) of product 3 was weighed into a Zeisel bulb, 0.25 ml. of 10% sodium hydroxide and 2 ml.

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[6] P. W. Bridgman, "The Physics of High Pressure," G. Bell and Sons, London, 1949, pp. 30–59.

[7] F. Feigl, "Qualitative Analysis by Spot Tests," Elsevier Press, Houston, Texas, 1946, p. 324.

[8] Reference 7, p. 396.

of water were added, and the mixture was heated on a steam-bath for two hours to effect solution of the polymer. A slow stream of nitrogen was bubbled through the solution while about 75% of the water was boiled off by means of a heated oil-bath. Water (1 ml.) was added and boiled off, and this procedure was repeated five times. Zeisel analysis of the residue showed that it contained 2.8% methoxyl. In a duplicate experiment, the residue contained 2.7% methoxyl. These figures signify a loss of about 86% of the methoxyl of product 3 during the hydrolysis.

(d).—A 201-mg. sample of product 7 was heated with 4 ml. of 0.7 *N* sodium hydroxide at 100° for 4 hours. The resultant solution was filtered and acidified with 2 *N* hydrochloric acid. A viscous resin precipitated. The resin (which was soluble in aqueous sodium bicarbonate) was separated by centrifuging, washed well with water, and dissolved in dioxane containing 10% water. The dioxane solution was clarified by centrifuging and then cast on a glass plate. Evaporation of the dioxane gave a film which, after final drying at 50° (0.5 mm.), weighed 102 mg. Its infrared spectrum had a band at 5.85 μ probably due to $-COOH$.

Anal. Calcd. (assuming $-COOCH_3 \rightarrow -COOH$): C, 52.0; H, 6.3; CH_3O, 0.0. Found: C, 49.0; H, 6.8; OCH_3, 2.9; ash, none.

Similar hydrolysis of product 5 gave a product too soluble in water to be isolated.

Ammonolysis of E/CO/MeOH Copolymer.—A 150-mg. sample of product 4 was dissolved in 5.0 ml. of 29% aqueous ammonia by swirling the mixture at 25° for a few minutes. The solution stood at 25° for 4 days and then was filtered, poured onto a glass plate and evaporated at 90°. The resultant clear, brittle film was transferred to a vial and dried at 65° (0.5 mm.) for 8 hours. It was insoluble in boiling acetone or methanol, partially soluble in water, soluble in 29% ammonia. Its infrared absorption spectrum had bands at 2.9 and 6.0 μ, characteristic of O-H and $-CONH_2$, respectively.

Anal. Calcd. (assuming $-COOCH_3 \rightarrow -CONH_2$): C, 48.4; H, 7.4; N, 11.7; OCH_3, 0.0. Found: C, 43.5; H, 7.6; N, 11.0; OCH_3, 0.6.

Decarbonylation of E/CO/MeOH Copolymers.—Two procedures were used, both based on that of Bistrzycki and Siemiradzki.[4] Table V lists the results, including the results obtained with various substances of known structure.

Procedure A (**macro**).—One hundred milliliters of 96% sulfuric acid was placed in a 150-ml. round-bottomed flask containing a thermometer. A weighed sample (one to five grams) of substance to be analyzed was added, and the flask was attached by means of three feet of rubber tubing of 1/8" wall-thickness to a 500-ml. gas buret filled with water. A tee stopcock was between the reaction vessel and buret so that the system could be opened to the atmosphere. The temperature was raised at a rate of 3° per minute by means of an electric mantle and the contents of the flask were swirled vigorously every two minutes. The gas pressure in the buret was kept near atmospheric by means of a leveling bulb. The temperature was raised until either 500 cc. of gas had collected, gas evolution had ceased, or the flask temperature was 140–170°. Sulfur dioxide was always evolved and sometimes, as in the case of E/CO polymers, 200–300 cc. was collected. Since the rate of sulfur dioxide evolution increased with temperature, a partial sweeping out of the system resulted. The gas was shaken several times with water to remove sulfur dioxide. The volume of the gas was then measured and its carbon monoxide content was determined by Orsat analysis.

TABLE V

DECARBONYLATION OF E/CO/MeOH COPOLYMERS AND OTHER SUBSTANCES BY 96% SULFURIC ACID

Substance decarbonylated	Procedure	Carbon monoxide evolved Calcd., mg./g.	Found, mg./g.	Found, % of calcd.
E/CO/MeOH copolymer, sample 7	B	179[a]	102, 103	57, 58
E/CO/MeOH copolymer, sample 8	B	208[a]	122, 132	59, 64
E/CO/MeOH copolymer, sample 3	A	70[a]	16, 17	23, 24
E/CO/MeOH copolymer, sample 3	B	70[a]	35, 43	50, 61
E/CO copolymer[b]	A	0	1.6	...
E/CO copolymer[c]	A	0	0.3	...
E/CO copolymer[c]	B	0	8	...
Citric acid	A	146	97	67
Triethyl citrate	A	101	104	103
Methyl α-hydroxyisobutyrate	A	238	108, 133	45, 56

[a] It is assumed that one CO per methoxyl group can be evolved. [b] Reference 1; E:CO = 1.8. [c] Reference 1; E:CO = 1.15.

Procedure B (**micro**).[9]—Four milliliters of 96% sulfuric acid was placed in a reaction flask used for microdeterminations of methoxyl by the Zeisel method. A weighed sample (5 to 15 mg.) was added. The reaction flask was connected by glass tubing to a nitrometer containing 50% aqueous potassium hydroxide. Carbon dioxide was passed through the apparatus at 25° until there were microbubbles in the nitrometer. The nitrometer was filled to the top with potassium hydroxide solution and closed. The flask was heated rapidly to 80° and then heated to 140° at a steady rate of 2°/minute by means of an oil-bath. All the while carbon dioxide passed through the apparatus. Heating was stopped, but carbon dioxide passage was continued until there were again microbubbles in the nitrometer. The volume of gas in the nitrometer was measured. Calculations were made on the assumption that all the gas was carbon monoxide.

Attempted Formation of α-Hydroxy Esters by the Action of Carbon Monoxide and Methanol on Ketones.—A mixture of 0.93 g. of 2,5-hexanedione, 0.78 g. of methanol, 0.02 g. of *t*-butyl peroxide and 1.23 g. of carbon monoxide was heated at 130° and 8000–7200 atm. for 16.5 hours. No appreciable amount of carbon monoxide was absorbed. 2,5-Hexanedione was recovered by distillation. No appreciable amount of material boiling above 2,5-hexanedione was formed.

Similar results were obtained when 2-butanone or E/CO copolymer (E:CO = 1.2:1) was substituted for 2,5-hexanedione in the above experiment. The fact that the E/CO copolymer was recovered unchanged is of limited significance because it was only slightly soluble in the methanol.

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(9) This procedure was devised by G. A. Jones, who made the determinations.