ies indicate only the small thermal stability of these complexes.

The hydrolysis–e.m.f. studies, however, prove that the [Ag(trien)]+ ion isolated from alcoholic solution slowly hydrolyzes to the one-to-one complex present in aqueous solution. The most logical explanation for this is to assume a coördination number of four for the Ag+ ion as shown in structures I and II.

The participation of the solvent in the coördination sphere in structure I also explains the high solubility of the aqueous [Ag(trien)]+ form of the complex while the highly blocked nature of struc-

ture II would explain the insolubility in water of the compound from alcoholic solution.

This same symmetrical highly blocked structure would greatly increase cation size and decrease ion pair association in a solvent with a low dielectric constant such as alcohol. This would account for the increase of the molar conductance in alcohol of the complex ion over that of alcoholic silver nitrate.

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Compositional Relationships in the Copolymerization of Ethylene with Carbon Monoxide

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The compositions of polyketones synthesized by the copolymerization of ethylene with carbon monoxide have been found to depend upon the temperature, pressure and composition of the reacting mixture. It has been predicted theoretically and has been confirmed experimentally that a particular mixture of monomers will copolymerize to give a product of the same composition. This "azeotropic" composition has been determined for the system ethylene–carbon monoxide as a function of temperature. In addition, the temperature dependence of copolymer composition has been used to determine the difference between the activation energies of certain polymer chain growth steps.

The synthesis and properties of a new family of linear polyketones obtained by the free radical-initiated copolymerization of ethylene with carbon monoxide under pressure have recently been described.[1] These polyketones are heterogeneous with respect to molecular weight and composition, and the average composition of the polymer formed generally differs considerably from that of the reaction mixture employed. The present paper describes a study of the relationship between the composition of the copolymers and that of the reacting comonomers.

Relationship between Monomer and Polymer Composition

The copolymerization of ethylene with carbon monoxide can be accomplished by introducing the mixed gases under pressure into a reactor containing a peroxide initiator. Since it is observed that the monomers do not combine in the ratio in which they are present, except under special circumstances to be indicated later, it follows that the composition of the monomer mixture, as well as that of the polyketones formed therefrom, must change throughout a batch polymerization. Accordingly, the average composition of the polyketones must depend in part upon the duration of the reaction.

To study these effects quantitatively, the copolymerizations were carried out in a 400-ml. reactor at temperatures ranging from 120 to 130° under pressures of 850–1000 atm. for 16 to 19 hours, employing 0.5 ml. of diethyl peroxide as initiator. Unless otherwise indicated, a solvent was not used. The relationship between the composition of the mixed monomers and the average composition of the copolymers formed during a standard polymerization schedule is shown in Table I. The composition of the monomer mixtures can be read as mole per cent. or weight per cent. since

carbon monoxide and ethylene are of identical molecular weight.

TABLE I

COPOLYMERIZATION OF ETHYLENE WITH CARBON MONOXIDE

Carbon monoxide in monomer mixture, %	Carbon monoxide in polyketone, %	Yield, g.
1[a]	2.2	77
2[a]	3.8	67
4[a]	7.9	49
10	20	69
20.1	38.4[c]	90
28.4	42.6[c]	102
30[a]	42	104
45[b]	45.9	20
47[b]	45.0	58
48	45.7	92
70[b]	47	32

[a] 0.1 ml. of initiator was used. [b] 100 ml. of benzene was present as a medium. [c] Composition of polymer initially formed on reactor wall.

With low percentages of carbon monoxide in the monomer mixture, it was found, under the conditions employed, that carbon monoxide reacted at a relatively higher rate than did ethylene; however, the rate at which carbon monoxide reacted approached that of ethylene when the ratio of ethylene to carbon monoxide in the monomer mixture approximated unity. Copolymers containing more than 50% carbon monoxide were not formed under the conditions discussed here. This implies that under the conditions used, two carbon monoxide units do not add successively in the chain propagation, but must always be separated by one or more ethylene units. (Under these conditions, carbon monoxide resembles maleic anhydride, which heteropolymerizes[2] with many other monomers, but

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

(2) P. D. Ritchie, "A Chemistry of Plastics and High Polymers," Cleaver–Hume Press, Ltd., London, 1949, Chapt. IV, p. 74.

does not form a homopolymer.) It means further that one of the monomer reactivity ratios, namely, that involving the rate constant for the addition of carbon monoxide to a radical ending in carbon monoxide, must be equal to zero. Hence the copolymerization equation[3] becomes simply

$$\frac{d\,M_1}{d\,M_2} = \frac{r_1 M_1 + M_2}{M_2} \tag{1}$$

where subscript "1" refers to ethylene and subscript "2" to carbon monoxide with r_1 equal to the ratio of the specific reaction rate constants (k_3/k_2) for the addition of ethylene and carbon monoxide, respectively, to a radical ending in ethylene.

From equation (1) it is readily seen that if X_2 is the mole fraction of the carbon monoxide in the reaction mixture, then X_2', the corresponding mole fraction for the copolymer formed at any instant will be given by[4]

$$X_2' = \frac{X_2}{(2 - r_1)X_2 + r_1} \tag{2}$$

Approximate values for the composition of the polyketones initially formed were obtained by analysis of the thin layers of polymer first deposited on the walls of the reactor during the copolymerization of mixtures containing 20.1 and 28.4% carbon monoxide in the absence of a solvent (see Table I). From the monomer compositions and the compositions of the polymers formed (38.4 and 42.6% carbon monoxide), it is possible to calculate values for r_1 by use of equation (2). Using the low conversion experimental data, the values calculated for r_1 are 0.142 and 0.155. With 0.15 as an average, it is seen that

$$X_2' = \frac{X_2}{1.85X_2 + 0.15} \tag{3}$$

It is evident from equation (3) that there exists only one mixture of monomers with which the composition of the copolymer will be identical in carbon monoxide content. When calculated from equation (3), this composition is found to be 46% carbon monoxide (or an ethylene/carbon monoxide mole ratio of 1.17). Direct evidence that such an "azeotropic" copolymerization occurs was obtained by analysis of the copolymers formed in four to 18 hours by the copolymerization of ethylene/carbon monoxide mixtures containing 45 to 47% carbon monoxide. The polymerizations were carried out at 130° with 0.5 ml. of diethyl peroxide initiator in the absence of solvent medium. The copolymers so formed contained 44.7 to 45.9% carbon monoxide in comparison with the calculated value of 46% (see Table II).

The foregoing shows that in the polymerization of a monomer mixture having a carbon monoxide content appreciably less than that of the "azeotrope," the monomer mixture will become progressively poorer in carbon monoxide content as the polymerization proceeds, while monomer mixtures containing more than the "azeotropic" proportion of carbon monoxide will become progressively richer in carbon monoxide. As a consequence, the composition of the copolymer formed at any instant will differ from that of copolymers formed at an earlier or later period in the polymerization, and a homogeneous product will not be obtained. However, compositionally homogeneous copolymers of carbon monoxide content lower than that of the "azeotrope" can be obtained by continuously pressuring the reactor during polymerization with a monomer mixture of composition the same as that of the copolymer initially formed. The composition of the initial copolymer can be calculated from equation (3), or can be determined from a plot of that equation.

As an approximate illustration of such a copolymerization, an experiment was carried out in which the reactor was charged at 350 atm. with a monomer mixture containing 20% carbon monoxide, which would be expected to yield a copolymer containing about 38% carbon monoxide. Diethyl peroxide (0.5 ml.) was employed as catalyst at 130°. After polymerization was under way, as indicated by a decrease in pressure, the reactor was repressured at intervals necessary to maintain the pressure at 880–950 atm. with a monomer mixture containing 40% carbon monoxide. The whole polymer formed (110 g. in 17 hours) contained 40–42% carbon monoxide. The compositions of the initial and final polymer layers were 40.1 and 41.7% carbon monoxide, respectively.

Variables Affecting the "Azeotropic" Composition

The "azeotropic" composition can be altered by use of an organic polymerization medium or by carrying the reaction out at different pressures or temperatures. In diethyl peroxide-initiated copolymerizations at 1000 atm. in benzene or cyclohexane, but under conditions otherwise similar to those used in the polymerizations indicated in Table II, the "azeotropic" monomer composition was lowered to 42–45% carbon monoxide. The possible existence of a second phase, when benzene or cyclohexane is present, might account for the difference in composition.

Pressure.—When the pressure was decreased to 136 atm. in copolymerizations in cyclohexane, the "azeotropic" monomer composition appeared to be near 36% carbon monoxide as indicated in Table III.[5] The copolymerizations were carried out in 100 ml. of cyclohexane in a 400-ml. reactor at 135° for 18 hours, employing 3 ml. of di-(t-butyl) peroxide as initiator.

TABLE II
"AZEOTROPIC" COPOLYMERIZATION OF ETHYLENE WITH CARBON MONOXIDE

Carbon monoxide in monomer mixture, %	Carbon monoxide in polyketone, %	Time, hr.	Yield, g.
47[a]	45.0	4	58
45[b]	45.9	8	20
45.5[b]	44.7	18	58
45.5[b]	45.2	18	76

[a] At 850–975 atm. [b] At 700–1000 atm.

TABLE III
COPOLYMERIZATION OF ETHYLENE AND CARBON MONOXIDE AT 136 ATM. IN CYCLOHEXANE

Carbon monoxide in monomer mixture, %	Carbon monoxide in polyketone, %	Yield, g.
42	36.7	78
36	35.7	113
25	28.4	90
13	17.8	61

Temperature.—The effect of temperature on monomer reactivity, composition and molecular weight of the copoly-

(3) F. R. Mayo and F. M. Lewis, THIS JOURNAL, **66**, 1594 (1944).

(4) F. T. Wall, ibid., **66**, 2050 (1944).

(5) We are indebted to Dr. H. H. Hoehn for these data.

mers formed from a given mixture of monomers is illustrated in Table IV. The polymerizations described in that table were carried out in a continuous reactor at 600 atm. with a monomer mixture containing 20% carbon monoxide, which corresponds to an ethylene/carbon monoxide mole ratio of 4:1. The catalyst was a 1:3 mixture of t-butylperoxybutane and di-(t-butyl) peroxide that was introduced into a benzene/water medium of 4:1 weight ratio. The feed rates corresponded to a 1:3 monomer/medium weight ratio. As the temperature increased, relatively greater amounts of ethylene combined, and the copolymers were of progressively lower molecular weight. At 240°, the composition of the polymer formed was identical with that of the monomer mixture, so that "azeotropic" copolymerization evidently occurred.

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TABLE IV

COPOLYMERIZATION OF ETHYLENE AND CARBON MONOXIDE[a]

AT VARIOUS TEMPERATURES
</div>

Temp., °C.	Carbon monoxide, %	Polyketone formed Ethylene/carbon monoxide mole ratio	Molecular weight
200	29	2.4:1	1860
220	25	3.0:1	1090
240	20	4.0:1	790
260	18	4.6:1	650

[a] The mixed monomers contained 20% carbon monoxide.

A simple equation relating copolymer composition to temperature can be readily derived. By rewriting, equation (1) becomes

$$\frac{d\,M_1}{d\,M_2} - 1 = r_1 \frac{M_1}{M_2} \tag{1b}$$

Letting $R = M_1/M_2$ (the ratio of ethylene to carbon monoxide in the monomer mixture), and $R' = d\,M_1/d\,M_2$ (the corresponding ratio in the copolymer), then

$$R' - 1 = r_1 R \tag{4}$$

It is now evident that

$$\frac{d \ln\left(\frac{R'-1}{R}\right)}{dT} = \frac{d \ln r_1}{dT} = \frac{d \ln k_3}{dT} - \frac{d \ln k_2}{dT}$$

or

$$\frac{d \ln\left(\frac{R'-1}{R}\right)}{dT} = \frac{E_3}{1.99T^2} - \frac{E_2}{1.99T^2} \tag{5}$$

where E_2 and E_3 are the activation energies in calories for the corresponding chain growth steps. Upon integration

$$\ln\left(\frac{R'-1}{R}\right) = \frac{-\Delta E}{1.99T} + C \tag{6}$$

where ΔE is the difference between the activation energies (*i.e.*, $E_3 - E_2$) for two of the chain growth steps. Equation (6) is most easily tested by using data for which R is constant and then plotting ln $(R' - 1)$ against $1/T$ (Fig. 1, data from Table IV). From the slope and intercept of the line drawn in Fig. 1, ΔE is found to be 8600 cal. and C is 8.1.
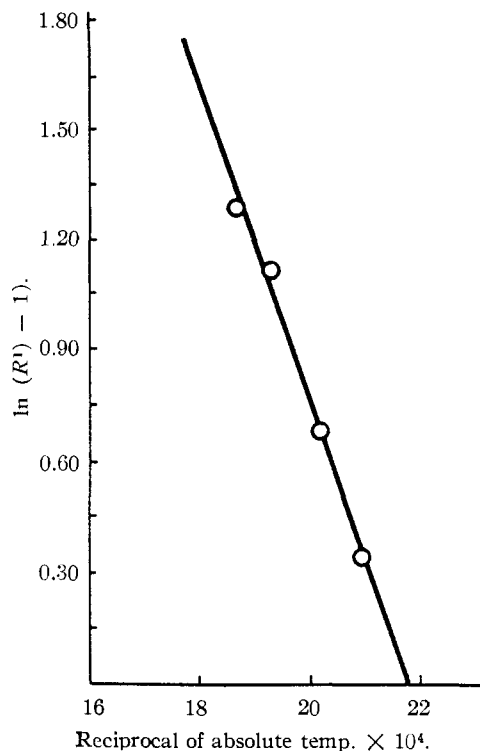

Fig. 1.—Copolymer composition *vs.* polymerization temperature $R = 4$ (equation (6)).

Letting R' equal R, and using the numerical values indicated above, then the temperature (T_A) at which "azeotropic" copolymerization occurs can be related to composition by the equation

$$\ln\left(1 - \frac{1}{R}\right) = -\frac{4300}{T_A} + 8.1 \tag{7}$$

If $R = 4$, then the temperature for the "azeotropic" copolymerization is calculated to be 240° in agreement with observation.

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