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COPOLYMERIZATION OF ETHYLENE INDUCED BY COBALT-60 GAMMA RADIATION

by

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Abstract

The gamma initiated copolymerization of ethylene with a number of different monomers was studied at 20° C and initial pressures to 680 atmospheres. The experiments were conducted statically in two-phase systems with the exception of the ethylene-carbon monoxide system. Isolation of the copolymers was effected by solvent extraction and fractional precipitation techniques. Infrared spectroscopy was used for identification. The composition was determined by elemental analysis. A partial evaluation of some of the reaction products including crystalline melting points, densities, solubility characteristics, and molecular weights are given. Evidence of ethylene copolymerization was established with each of the following monomers: styrene, methyl methacrylate, vinyl acetate, acrylonitrile, allyl acetate, isobutylene, chlorotrifluoroethylene, trans 2-butene, methyl acrylate, isoprene, propylene, vinyl chloride, 1-butene, cis 2-butene, carbon monoxide, vinyl pyrrolidone, methyl vinyl ketone, and divinyl benzene.

The experimental data obtained in the study of the ethylene-carbon monoxide system were found to obey a linear form of the copolymer composition equation. The ratio of specific rate constants for carbon monoxide and ethylene (α) was found to have a value of 22.0, indicating that carbon monoxide as a monomer, is activated to the extent that it adds 22 times as fast as an ethylene monomer to an ethylene free radical chain end.

Explosive decomposition was observed to occur during irradiation of ethylene and chlorotrifluoroethylene under certain irradiation conditions. There is an indication that a threshold radiation intensity exists which induces this violent reaction.

The unique advantage of cobalt-60 gamma radiation is that it can be used to induce and control ethylene copolymerization reactions at low temperatures.

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I. INTRODUCTION

The technical importance of ethylene copolymers and the recent work on the gamma ray induced polymerization of ethylene at high pressures by Steinberg, et al.,(1) and Medvedev, et al.,(2) has led to an investigation of the possibility of the polymerization of ethylene in the presence of other monomers by gamma radiation. The present work was undertaken for the purpose of determining whether a copolymer reaction would occur in an ethylene-base system, and to investigate some of the properties of the resulting polymers. The experimental approach in this study was to make a survey of a number of reactions involving ethylene with other monomers in a radiation field. The identification and characterization of the polymers formed were subsequently attempted in a semi-quantitative manner.

Although radiation induced random-type copolymerization reactions have been reported, particularly with the styrene-methyl methacrylate system,(3,4,5) very little work has been cited in the open literature on the random copolymerization of ethylene by ionizing radiation. Previously published work of this nature exists in some sketchy patent literature.(6,7,8)

In addition to the monomers given in Table I, ethylene was irradiated in the presence of certain additives listed in Table II. The object of the latter work was to determine whether additives, which normally do not polymerize, produced a change in the chemical structure of the resulting polyethylene.

II. EXPERIMENTAL PROCEDURE

1. Monomer Preparation

The inhibitors present in the liquid monomers were removed by distillation under reduced pressure. The distilled monomers were then slowly warmed to room temperature, transferred into storage bottles containing white Drierite, and stored under nitrogen in a refrigerator. The inhibitors present in the gaseous monomers were usually nonvolatile, and except for possible trace amounts entrained during the charge operation, were left behind. The charging operation was performed by condensing the gas into the reaction vessel at low flow rates and pressures. No attempt was made to remove or determine the concentration of any inhibitor that may have been carried over.

The high purity ethylene gas used was supplied by Phillips Petroleum Company and had a concentration of 99.9%, containing about 1,000 ppm of C_1 to C_4 hydrocarbons and less than 5 ppm O_2.

2. Sample Preparation

The reaction vessel used for conducting the copolymerization experiments was of 316 S.S. having an O.D. of 2", an I.D. of 1", and a length of 10", as shown in Figure 1. The vessel was designed to operate at a maximum pressure of 1,000 atmospheres. Both ends of the vessel could be opened to facilitate removal of the polymer. At high conversions, the polymer became compressed and was removed from the vessel in the form of a rod which was easily powdered in a Waring blender. The bottom assembly contained a thermocouple well for measuring reaction temperatures. The upper assembly contained a closure valve and a rupture disc set to burst at 14,000 psi.

Because of the high vapor pressures of the liquid monomers used, a measured amount of freshly distilled monomer was introduced by condensation into the reaction vessel. The monomer was degassed by the freeze-thaw technique through a vacuum system prior to use. Ethylene gas was fed into the vessel through a compressor to a total pressure in the order of 10,000 psi as indicated on a pressure recorder. The reaction temperature and the pressure changes during irradiation could be followed on continuous recorders. A schematic of the equipment is shown in Figure 2.

With this procedure, the concentrations of monomers varied from the bottom to the top of the vessel. The bottom contained a higher concentration of liquid monomer, whereas the top contained a higher concentration of gaseous ethylene. Some estimate of the concentration in each phase is possible, based on vapor pressure and solubility measurements. Weight measurements were used for determination of the monomers introduced and subsequently of the polymer formed.

The exception to the two-phase system was Run #32, Table I, using carbon monoxide, which allowed a homogeneous gas mixture with ethylene.

3. Irradiation Procedure

After charging, Co-60 gamma sources were placed in position in the pool facility and the vessel was irradiated for a given time. Ferrous sulfate dosimetry measurements were made within the heavy walled reaction vessels. All radiations were conducted in the gamma pool facility at Brookhaven National Laboratory at ambient pool temperatures (18° to 20° C).

Because of the complexities involved in determining concentration when homogenizing a two-phase system by stirring, the initial experiments, shown in Table I, were performed in a static unstirred condition.

The mass concentration of monomers used for each system was calculated to minimize the reaction temperature that could be developed during polymerization. This determination was based on reported exotherms observed during the radiation polymerization of the pure monomers.

Substantially high total doses were given each system to allow for the maximum opportunity to react, and in addition, to produce sufficient material for physical and chemical tests.

III. RESULTS

1. Copolymer Isolation

In the synthesis of copolymers, the difficulty invariably encountered exists in the isolation of the copolymer. The difficulties are magnified due to the presence of one or more of the homopolymers of the species used to form the copolymer. Since there is no universal method for the isolation of copolymers from their homopolymer, each system presents problems which have to be treated in a unique manner.

In the copolymer systems, shown in Table I, the majority of the polymerization reaction products were free of homopolymer. The presence of homopolymer was mainly due to the depletion of one of the monomers during the course of the reaction. The object of this work was not to effect an absolute isolation of the copolymer, but to be able to show with some degree of certainty that a copolymer was formed. The two methods used were the preferential solvent extraction method and the fractional precipitation method.

The preferential solvent extraction technique can be applied to a mixture of known polymers which have different solubility properties. The homopolymers are extracted from the mixture stepwise by the use of a preferential solvent for each polymer specie forming the copolymer. This method, alone, is not satisfactory for copolymer isolation, because in most cases the copolymer is soluble in solvent which is preferential for one of the homopolymers. This method was, therefore, modified and used in conjunction with infrared spectrophotometry for qualitative identification of copolymer existence. The scheme, in Figure 3, shows in detail the procedures used for both the solvent extraction and the fractional precipitation methods.

For convenience in describing the procedures, A is ethylene homopolymer, B is the other homopolymer, and AB is the copolymer. In performing these tests, it was assumed that each sample consisted of a polymeric mixture of A, B, and AB.

After removal of the unreacted monomers, the polymer was mixed in a Waring blender. A sample of the mixture was put into a preferential solvent for B. If an insoluble fraction was present, it was dried and pressed into a film for infrared analysis. The presence of characteristic bands for polymer B indicated the copolymer to be present in the insoluble fraction. The soluble fraction containing polymer B was precipitated with a selected precipitant. The polymer was likewise prepared and examined by infrared. The presence of characteristic bands for polymer A indicate the copolymer to be present in the soluble fraction.

Although the preferential solvent method as described is a relatively rapid method for the qualitative identification of a copolymer, it is difficult to resolve the presence of homopolymer in the fraction containing the copolymer. In order to perform chemical and physical tests, any homopolymer present must be separated from the mixture. The method found to be most satisfactory was the fractional precipitation method described by Ceresa(9) for the characterization of block copolymers. The fraction containing the copolymer was dissolved in a solvent and a selected precipitant was slowly added to the solution until precipitation occurred. The precipitate was removed by centrifuging and the precipitant was again added slowly to the solution. This was repeated until all the polymer fractions were isolated. Each fraction was inspected by infrared for the presence of homopolymer.

Only three systems were found to contain homopolymer. These were the ethylene copolymers of vinyl acetate, vinyl chloride, and acrylonitrile. The homopolymer was polyethylene in each case. This was probably due to the overdose received by these systems resulting in the depletion of the comonomer.

2. Solubility

The solubilities of the isolated copolymers were tested in various solvents, as shown in Table III. To determine solubilities, a 1% mixture of polymer with solvent was used. Elevated temperatures, slightly below the boiling point of the solvents, were used when solubility did not occur at room temperature after a period of 24 hours. It can be seen in Table III that most of the copolymers are soluble in solvents for one or the other of its homopolymer species.

It is interesting to note the number of copolymers which dissolved in benzene and carbon tetrachloride, in spite of the fact that polyethylene does not dissolve in either of these solvents. The most interesting effect is that of the solubility of some of these copolymers in solvents for which neither of the homopolymer species is soluble. An example is the ethylene-vinyl chloride copolymer, Run #25-1, Table III. This copolymer was found to be soluble in cold decalin, benzene, tetrahydrofuran, and xylene. Polyethylene is not soluble in these solvents at room temperature and of these, polyvinyl chloride is soluble only in tetrahydrofuran.

The solubility characteristics of the copolymers depend on many factors, such as composition, molecular weight, crystallinity, cross-linkage, etc.; therefore, the solubilities shown in Table III do not necessarily apply to the same copolymers made under different conditions. This difference is apparent in Table III, where the initial concentrations and total doses were varied for some systems.

3. Density

Densities of the copolymers were determined by the density gradient tube technique. This method is rapid and precise for small solid samples. A series of mixtures of two liquids were made up of varying proportions. The more dense solution was poured into a calibrated gradient tube followed by the less dense solutions. Care was taken in layering the solutions in order to preserve the interfaces. The number of solutions used in this manner depends on the density range desired. Diffusion usually occurs in about 24 hours, resulting in a linear gradient over the height of the tube. The gradient was calibrated with glass floats of varying known densities and the density at any point was determined by plotting the density of the floats versus the corresponding height in the tube. Liquids were selected which did not interact with the copolymers studied.

The densities of the copolymers given in Table IV fall between the range of densities for polyethylene and that of the homopolymer specie forming the copolymer. Due to the static nature of the experiments, the varying monomer concentrations affect the composition of the polymers formed at any instant, resulting in a range of densities. The densities reported are, therefore, average densities over the entire range of the experiment.

4. Crystallinity

The presence of crystallites and subsequently the crystalline melting points of the copolymers in Table IV were determined with a hot-stage polarizing microscope. Annealed samples of thin film were placed on the hot-stage and the temperature was slowly raised at the rate of approximately 1° C/min. The crystalline melting point was taken by noting the disappearance of birefringence observed between crossed polarizers. The data in Table IV show that in a number of copolymers the crystalline melting point is extended over a range of temperatures. This effect can be due to the compositional inhomogeneity of the sample, or to the continuous redistribution of polymer chains between the amorphous and crystalline regions as a function of temperature.(10) The presence or absence of crystallinity in a copolymer may depend on many factors.

Of great importance is the geometrical irregularity with which the comonomer enters polymerization, the similarity of the comonomer structures, and the ability of groups such as C=O, CHCl, CF_2, etc., to fit into a crystal lattice. The latter is greatly governed by the size of the group.(11)

Monomers such as methyl methacrylate and vinyl acetate which homopolymerize to form noncrystalline polymers did not inhibit crystallinity in the copolymers shown in Table IV. However, it is probable that crystallinity is greatly reduced with increasing compositional amounts of these polymers.

5. Infrared Spectrophotometric Identification

Powdered samples of the isolated copolymers were hot-pressed into film with a Carver Press. Some difficulties were initially encountered in making satisfactory uniform film for infrared examination. This was due mainly to the unique temperature and pressure requirements for each copolymer system. Conditions were arrived at by trial.

The spectra shown in Figures 4 to 9 are direct traces recorded with a Perkin-Elmer Infra-Cord 137 spectrophotometer, using a slit width of 25 and a scanning time of 12 min. from 2.5 to 15 microns. Film thicknesses of 1 to 5 mils were used depending on the absorption characteristics of the copolymers. Only a few of the spectra in the figures will be discussed, since a complete interpretation of the spectra would require an effort which is outside the scope of this paper. However, a number of distinguishing features of the spectra will be pointed out to show the changes incurred in the basic polyethylene spectrum. To demonstrate these changes, the pure polyethylene spectrum shown in Figure 4a is used as a reference.

The pure polyethylene was produced by gamma radiation at an initial pressure of approximately 10,000 psi and room temperature, as described previously.(1) The simple spectrum of pure polyethylene(12) is easily distinguished by the strong absorption of the C-H stretch band at 3.45 microns, the C-H bending at 6.8 microns, the CH_3 band due to branching at 7.26 microns, and the double peak in the 13.7 to 13.9 micron region due to the vibrations of long chains consisting of four or more $-CH_2-$ units. The doublet is also referred to as the crystalline region, and measurements to determine crystalline content have been made by Tobin and Carrano(11) using the band at 13.7 microns.

The spectrum in Figure 5b shows characteristic bands for both polyethylene and polyvinyl acetate. Characteristic bands for polyvinyl acetate are the carbonyl band at 5.8 microns and the ester bands at 8.1 microns and 9.8 microns. The characteristic bands for polyethylene, shown in Figure 4a, have remained unchanged.

The infrared spectra of the polymers of ethylene with trans 2-butene, cis 2-butene, 1-butene, and propylene, shown in Figures 6b, 6c, 7a, and 7c, are very similar. The differences appear to be mainly in the relative intensity of certain bands. The magnitude of these differences is related to the sample size and composition of the polymer. The presence of peaks other than those for polyethylene demonstrates qualitatively at least, the modification of the polyethylene structure. For example, the band at 7.26 microns, due to the $-CH_3$ bending vibration in each of the above spectra, indicates an increase in the methyl branching.

The spectrum of a film of ethylene-acrylonitrile copolymer in Figure 8a shows the sharp band at 4.45 microns due to the C≡N stretching mode. In spite of the high concentration of acrylonitrile in this sample, the characteristic peaks for ethylene can be easily identified.

The only characteristic polyethylene band remaining unaffected in the ethylene-carbon monoxide copolymer spectrum, Figure 9a, is the carbon-hydrogen stretch band at 3.4 microns. The change in the carbon-hydrogen bending vibration at 6.8 microns has been assigned to a methylene structure adjacent to a carbonyl. The doublet at 13.7 and 13.9 microns indicating four or more carbons in a chain became a singlet and decreased in intensity. The strong carbonyl absorption at 5.8 microns and its harmonic at 2.9 microns indicate a polyketone structure.

6. Molecular Weight.

Several weight average molecular weight measurements(18) were made by the light-scattering method and are given in Table IV. A Phoenix-Brice light-scattering instrument and a Carl Zeiss interferometer were used. The measurements were determined for soluble material obtained at room temperature. The large values for the weight average molecular weights indicate a high degree of polymerization.

7. Ethylene-Carbon Monoxide System

In addition to the initial experiments reported on the ethylene-carbon monoxide system, a number of runs were made in which the initial mole concentration of the two monomers were varied as shown in Table V. Each sample was irradiated for a small total dose of 780,000 rads at a dose rate of 156,000 rads/hr. The chemical composition of the copolymers formed were derived from elemental analyses. The experimental data in Table V were found to obey a simplified form of the copolymer composition equation. The copolymer equation,(13,14,15) as given below, states that a monomer mixture containing the two monomers in the molar ratio (B/A) should yield an initial copolymer with the molar ratio (b/a):

$$\frac{b}{a} = \frac{B}{A} \cdot \alpha \cdot \frac{\beta B+A}{\alpha B+A} \qquad (1)$$

The assumption is made that if monomers A and B undergo reaction, radicals of types A· and B· are formed involving four possible modes of monomer addition as follows:

Reaction	Reaction Rate	Constant
$A\cdot + A \rightarrow A\cdot$	$k_{aa}\,[A\cdot]\,[A]$	$\alpha = \frac{k_{ab}}{k_{aa}}$
$A\cdot + B \rightarrow B\cdot$	$k_{ab}\,[A\cdot]\,[B]$	
$B\cdot + A \rightarrow A\cdot$	$k_{ba}\,[B\cdot]\,[A]$	$\beta = \frac{k_{bb}}{k_{ba}}$
$B\cdot + B \rightarrow B\cdot$	$k_{bb}\,[B\cdot]\,[B]$	

The four reactions are governed by the propagation rate constants k_{aa}, k_{ab}, k_{ba}, and k_{bb}.

The composition of the copolymer can be determined from the ratio of the rate constants α and β.

Since carbon monoxide does not polymerize alone, the number of propagation processes in the ethylene-carbon monoxide system are reduced. If carbon monoxide is designated as component B of the monomer mixture, the rate constant k_{bb} vanishes and $\beta = 0$. In this case, equation (1) reduces to the simple form:

$$\frac{a}{b} = 1 + \frac{A}{\alpha B} \qquad (2)$$

A plot of (a/b) vs (A/B), using the experimental data in Table V, yields a straight line of slope $1/\alpha$ with an intercept of 1, as predicted by equation (2).

The data in Table V are plotted in Figure 10 giving a straight line correlation as indicated by equation (2) and the reciprocal of the slope shows that $\alpha = 22.0$. This means that a carbon monoxide monomer adds 22 times as fast as an ethylene monomer to an ethylene free radical chain end.

In a similar manner, values for α were also calculated from experimental data presented by Brubaker, et al.,(16) and Coffman, et al.,(17) who studied the ethylene-carbon monoxide copolymer system using conventional peroxide initiators. The α value, calculated from Brubaker's data for experiments carried out in cyclohexane at 136 atmospheres and 135° C, was 2.0, while that for Coffman's data performed without solvent at pressures ranging from 850-1,000 atmospheres and temperatures between

120° and 130° C was 6.8. The data reported in Table V are for initial conditions of 650 atmospheres and 20° C. The differences in experimental conditions probably account for, in part, the wide variation in α values; however, it seems significant that in the radiation process the CO is induced to add to an ethylene free radical chain end to a much greater degree than in the conventional free radical initiation process. Further work evaluating α, as a function of temperature and pressure, is needed to support this point of view.

7. Ethylene-Chlorotrifluoroethylene

An interesting observation made during the study of the ethylene-chlorotrifluoroethylene (CTFE) system was the explosive spontaneous decomposition of the components at certain irradiation conditions. The first experiment of the series, shown in Table VI, having an initial ethylene/CTFE mole ratio of 29.1:1, was irradiated at a dose rate of 230,000 rads/hr and room temperature. Polymerization at these conditions proceeded normally to a high polymer conversion at a total dose of 16.2 x 10^6 rads.

A second experiment, prepared in a similar manner, and having a similar ethylene/CTFE mole ratio of 11.9:1, was irradiated at a somewhat higher dose rate of 308,000 rads/hr. After a total dose of approximately 50,000 rads, or 10 minutes of irradiation time, the system exploded violently (the rupture disc was broken) with the formation of a considerable quantity of carbon black. Some white polymer was also found in the bottom of the reaction vessel; the polymer had an ethylene/CTFE mole ratio of 1.69. In an attempt to determine whether the decomposition was due to the concentration of CTFE used, or to the dose rate, several other experiments were performed, as given in Table VI. It is shown that the explosive reaction could be duplicated by increasing the dose rate to 308,000 at two different concentrations (Runs #20-1 and #20-3), and that chlorotrifluoroethylene alone polymerizes without causing a violent explosive reaction (Run #20-2) at a dose rate of 308,000 rads/hr. The indication is that a threshold radiation intensity exists for this system, which initiates a runaway polymerization leading to a thermal decomposition and explosion. Further study, however, is necessary to determine the critical conditions involved in initiating the decomposition of this system in a radiation field.

8. Ethylene and Additives

The series of exploratory experiments in which ethylene gas was irradiated in the presence of various additives is shown in Table II. Sawdust and cotton were used to determine if a reaction could occur between ethylene and the cellulosic materials to form a chemically bonded polymer. Other additives were used to observe possible copolymer reactions or modifications of the resulting polyethylene. Polymerization was inhibited in the presence of benzaldehyde and benzene. The polymer formed in the presence of each of the other additives was extracted and examined by infrared techniques. In every case, the spectra were identical to that of ethylene polymerized in the pure state. It was surprising to find that several experiments involving benzene at high total doses inhibited the production of a polymer. Along these lines, butadiene was also found to inhibit the polymerization of ethylene, under the conditions shown in Table I. It also appeared interesting that materials such as formalin and carbon dioxide had no effect on the chemical structure of polyethylene.

IV. CONCLUSIONS

The following conclusions and generalizations can be made regarding the use of gamma radiation for initiating ethylene copolymer reactions.

1. Ethylene gas can react with a variety of monomeric materials to form copolymers.

2. Ethylene copolymers can be formed at low temperatures and moderate pressures.

3. Monomers which are very sensitive to thermal homopolymerization, such as the acrylates, can be readily directed toward copolymerization with ethylene at low temperatures.

4. Monomers which do not polymerize alone, such as carbon monoxide, can be copolymerized with ethylene.

5. Unsaturated monomers, such as propylene and the butenes, which are known not to polymerize readily in a radiation field or by a free radical mechanism, can be copolymerized with ethylene.

6. In some systems the final composition of the copolymer may be varied depending on the experimental conditions used.

7. In the ethylene-carbon monoxide system, it is possible to vary the initial composition of the monomer concentration without appreciably affecting the final composition of the copolymer.

8. Cobalt-60 gamma radiation can be used to study ethylene copolymer systems for purposes of elucidating the kinetics and mechanisms of other more complex systems, and of systems which cannot be readily copolymerized by conventional catalytic methods.

Of the many advantages offered by gamma radiation as a catalyst for ethylene copolymer reactions, probably the most unique is the ability to induce the reaction to take place at low temperatures. This is particularly true for those systems which have a high rate of homopolymerization at the elevated temperatures required for initiation of copolymerization by conventional free radical catalysts, and also for those systems which do not copolymerize by ionic mechanisms.

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Figure 9 Infrared Spectra of Copolymers.

(a) Ethylene/CO

(b) Ethylene/Vinyl pyrrolidone

(c) Ethylene/Methyl vinyl ketone

Figure 10 Ethylene-Carbon Monoxide System. Final Polymer Mole Ratio vs Initial Monomer Mole Ratio

TABLE I

COBALT-60 GAMMA COPOLYMERIZATION OF ETHYLENE

Irradiation Conditions and Yields at 20° C

Run No.	Comonomer	Intensity Rads/hr	Total Dose 10^6 Rad	Ethylene grams	Comonomer grams	Total Polymer Formed grams	Total Conversion By Wt.%	G_{Total} (1)
1-0	Styrene	132,000	9.0	43.2	21.7	7.8	12.0	-
1-1	Styrene	200,000	19.5	40.5	23.6	15.6	24.3	-
4-0	Methyl methacrylate	205,000	8.8	42.6	23.5	64.1	96.9	2,770
4-1	Methyl methacrylate	111,000	2.9	49.0	10.0	23.3	39.5	3,000
4-2	Methyl methacrylate	308,000	0.92	42.1	23.4	10.4	29.9	3,300
12-0	Vinyl acetate	200,000	18.9	42.8	25.2	60.6	89.1	1,260
12-1	Vinyl acetate	308,000	0.92	41.5	23.3	22.3	34.4	10,200
13-0	Acrylonitrile	200,000	14.0	42.9	19.9	33.2	52.9	935
13-1	Acrylonitrile	230,000	0.92	41.9	20.9	17.2	27.4	5,900
14-0	Allyl alcohol	140,000	9.4	41.4	27.0	- (2)	-	-
15-0	Allyl acetate	200,000	13.5	41.1	22.6	- (2)	-	-
15-1	Allyl acetate	308,000	0.92	41.9	22.9	24.8	38.3	13,800
16-0	Butadiene	135,000	3.2	45.5	0.35	None	-	-
16-1	Butadiene	200,000	4.8	53.8	0.35	None	-	-
16-2	Butadiene	210,000	14.2	43.0	14.0	None	-	-
19-0	Isobutylene	230,000	15.6	41.8	15.0	12.7	22.4	-
19-1	Isobutylene	230,000	0.92	44.5	13.4	1.4	2.4	-
20-0	Chlorotrifluoroethylene	230,000	16.2	49.0	7.0	49.2	87.9	1,430
21-0	trans 2-Butene	200,000	10.0	45.4	10.7	9.9	17.6	-
21-1	trans 2-Butene	230,000	0.9	43.9	13.5	3.0	5.2	-
22-0	Methyl acrylate	200,000	5.5	51.2	5.0	15.3	27.2	1,000
22-1	Methyl acrylate	230,000	0.9	50.0	5.3	7.7	13.9	-
23-0	Isoprene	200,000	2.0	47.4	6.8	1.7	3.1	-
23-1	Isoprene	308,000	0.92	49.3	6.4	1.6	2.9	-
24-0	Propylene	200,000	14.7	43.1	11.8	43.1	78.5	-
24-1	Propylene	111,000	2.1	30.2	28.2	1.4	2.4	-
25-0	Vinyl chloride	230,000	5.3	45.2	14.7	19.4	32.4	1,470
25-1	Vinyl chloride	308,000	0.92	47.4	14.4	5.9	9.5	7,600
25-2	Vinyl chloride	308,000	0.92	40.1	30.0	33.0	47.1	8,800
26-0	1-Butene	200,000	5.5	46.6	6.9	0.7	1.3	-
26-1	1-Butene	230,000	0.92	46.5	8.3	4.5	8.2	-
27-0	cis 2-Butene	200,000	5.5	44.1	11.8	3.2	5.7	-
27-1	cis 2-Butene	308,000	0.9	44.8	13.3	4.2	7.2	-
32-0	Carbon monoxide	230,000	11.0	48.3	6.1	11.2	20.6	644
32-1	Carbon monoxide	308,000	5.5	49.8	4.3	7.7	14.2	890
34-0	Vinyl pyrrolidone	230,000	16.6	45.5	12.5	54.0	93.1	1,750
35-0	Methyl vinyl ketone	230,000	11.0	49.5	9.3	8.8	14.9	-
35-1	Methyl vinyl ketone	308,000	14.4	47.6	10.9	22.4	38.3	890
36-0	Divinyl benzene	230,000	16.0	47.4	10.4	8.4	14.5	-

(1) G-value based on average molecular weight derived from composition.

(2) Weight of polymer formed was not measured.

TABLE II

COBALT-60 GAMMA POLYMERIZATION OF ETHYLENE IN THE PRESENCE OF ADDITIVES

Irradiation Conditions and Yields at 20° C

Run No.	Additive	Intensity Rads/hr	Total Dose 10^6Rad	Additive gms	Ethylene gms	Polymer[1] gms
2-0	Formalin	200,000	14.6	26.6	41.0	39.8
3-0	Sawdust	133,000	5.8	19.0	47.2	11.2
6-0	Benzaldehyde	139,000	13.5	26.3	42.0	None
8-0	Trioxymethylene	20,000	19.3	25.0	45.9	3.1
11-0	Acetone	200,000	9.6	19.0	42.0	33.0
28-0	Cotton	230,000	5.5	13.6	54.6	9.6
29-0	Benzene	135,000	10.7	64.3	16.3	None
29-1	Benzene	920,000	22.1	82.7	9.5	None
30-0	Carbon dioxide	230,000	11.0	9.1	47.7	32.5

(1) Total polymer yield less weight of unreacted additive.

TABLE III

COBALT-60 GAMMA COPOLYMERIZATION OF ETHYLENE

Solubilities of Ethylene Copolymers

Run No.	Ethylene Copolymer	De-calin	Di-oxane	Ben-zene	Carbon Tetra-chloride	Dimethyl-formamide	Ethyl Acetate	Tetra-hydro-furan	Xylene	Cyclo-hexane	Heptane
1-0	Styrene	S	S†	S†	-	-	-	-	-	-	-
1-1	Styrene	S	S	S	-	-	-	-	-	-	-
4-0	Methyl methacrylate	S*	I†	PS*†	PS*	-	I	-	PS	-	-
4-1	Methyl methacrylate	S*	S	PS*	S*	-	I	-	S*	-	-
4-2	Methyl methacrylate	PS*	S	PS*	S	-	-	-	-	-	-
12-0	Vinyl acetate	S*	I	S*†	I	-†	I	-	I	I	I
12-1	Vinyl acetate	S	S*	S†	S	-	PS*	S*	S	-	-
13-0	Acrylonitrile	PS*	-	I	I	I†	I	-	PS	-	-
13-1	Acrylonitrile	I	-	-	-	S	-	I	I	I	-
15-1	Allyl acetate	I	I	I	I	-	I	-	I	-	PS*
19-0	Isobutylene	S*	I	PS*	S*	-	-	-	S	-	-
19-1	Isobutylene	S	-	S†	S†	-	-	-	S	S*	-
20-0	Chlorotrifluoroethylene	S*	I	-	S*	-	-	PS*	S*	S*	-
21-0	trans-2-Butene	S	I	S	S	-	I	-	S	-	-
21-1	trans-2-Butene	S*	-	I	I	-	-	-	-	-	-
22-0	Methyl acrylate	S	-	PS*†	I	-	I	-	S†	-	-
22-1	Methyl acrylate	S*	I	I	-	-	I	-	PS	-	I
23-1	Isoprene	-	-	I†	I	-	-	-	I	-	S*†
24-0	Propylene	S	S	PS	S	-	S*	-	S*	-	S*
24-1	Propylene	S*†	-	S*	S*	-	-	-	S*†	-	S*
25-0	Vinyl chloride	PS	-	-	-	-	-	S†	-	PS	-
25-1	Vinyl chloride	S	PS	S	S*	-	S*	S	S	PS*	I
25-2	Vinyl chloride	I	-	-	-	-	-	S	-	I	-
26-0	1-Butene	I	-	S	S*	-	-	-	-	S*	-
26-1	1-Butene	S*	-	I	S*	-	-	-	S*	S*	-
27-0	cis 2-Butene	-	-	-	I	-	-	-	S*	-	PS*
27-1	cis 2-Butene	S	-	I	S*	S	-	-	S*	I	PS*
32-0	Carbon monoxide	I	I	S	I	I	-	-	S	-	-
32-1	Carbon monoxide	I	I	S	I	I	-	-	S	-	-
34-0	Vinyl pyrrolidone	PS*	I	PS	PS*	-	I	-	S	-	-
35-1	Methyl vinyl ketone	I	-	I	S*	-	I	-	I	I	-
36-0	Divinyl benzene	I	I	I	I	I	I	-	I	-	I
7	Polyethylene	S*†	-	-	-	-	-	-	S*†	-	-

S=soluble, PS=partially soluble, I=insoluble, *=soluble hot, †=solvent for homopolymer.

TABLE IV

COBALT-60 GAMMA COPOLYMERIZATION OF ETHYLENE

Copolymer Characteristics

Run No.	Comonomer	Initial Mole Ratio Ethylene/Comonomer	Final Polymer Mole Ratio Ethylene/Comonomer	Density grams/cc	Crystalline Melting Point °C	Molecular Weight(1) $\bar{M}_w$
1-0	Styrene	7.4	-	1.000	Non cryst.	-
1-1	Styrene	6.4	-	1.000	Non cryst.	-
4-0	Methyl methacrylate	6.5	6.0	1.002	121	-
4-1	Methyl methacrylate	17.5	3.6	0.956	125	530,000
4-2	Methyl methacrylate	6.4	0.1	1.164	Non cryst.	-
12-0	Vinyl acetate	5.2	6.3	0.963	106	-
12-1	Vinyl acetate	5.5	7.1	0.963	105-106.5	-
13-0	Acrylonitrile	4.1	1.3	1.068	118-125	-
13-1	Acrylonitrile	3.8	0.24	1.120	-	-
14-0	Allyl alcohol	3.2	-	0.941	-	-
15-0	Allyl acetate	6.5	-	-	-	-
15-1	Allyl acetate	6.5	93.2	0.939	122.0	-
16-0	Butadiene	250.0	No Polymer Formed			
16-1	Butadiene	295.4	No Polymer Formed			
16-2	Butadiene	5.9	No Polymer Formed			
19-0	Isobutylene	5.6	-	0.895	90.5	-
19-1	Isobutylene	9.0	-	0.908	103-107.5	-
20-0	Chlorotrifluoroethylene	29.2	9.5	1.104	108-119	475,000
21-0	trans 2-Butene	8.2	-	0.954	103-107.5	190,000
21-1	trans 2-Butene	6.3	-	0.963	105-108	-
22-0	Methyl acrylate	31.6	2.2	0.955	123-126.5	-
22-1	Methyl acrylate	28.9	-	0.936	121	-
23-0	Isoprene	16.9	-	-	-	-
23-1	Isoprene	18.7	-	0.956	122	-
24-0	Propylene	5.5	-	0.910	95	67,000
24-1	Propylene	1.6	-	0.908	92	-
25-0	Vinyl chloride	6.9	1.9	-	-	-
25-1	Vinyl chloride	7.3	1.3	-	Non cryst.	-
25-2	Vinyl chloride	3.0	0.15	1.330	-	-
26-0	1-Butene	13.0	-	0.960	104	-
26-1	1-Butene	10.8	-	0.912	102	-
27-0	cis 2-Butene	7.5	-	0.976	117	-
27-1	cis 2-Butene	6.7	-	0.963	125-126	-
32-0	Carbon monoxide	7.9	1.95	1.090	112.5	1,500,000
32-1	Carbon monoxide	11.6	2.3	-	-	-
34-0	Vinyl pyrrolidone	14.4	27.7	1.008	120.5	450,000
35-1	Methyl vinyl ketone	10.9	51.7	0.942	125	-
36-0	Divinyl benzene	21.2	-	-	-	-
8-0	Ethylene	-	-	0.939	122	-

(1) Weight average molecular weight determinations were made by light-scattering method.

TABLE V

COBALT-60 GAMMA COPOLYMERIZATION OF ETHYLENE

Ethylene-Carbon Monoxide System

Dose Rate = 156,000 rads/hr   Total Dose = 780,000 rads

Initial Pressure = 650 atm   Irradiation Temperature = 20° C

Run No.	Initial Monomer(1) Mole Ratio A/B	Final Polymer(2) Mole Ratio a/b
32-15	3.00	1.16
32-8	3.44	1.21
32-12	4.29	1.16
32-10	5.29	1.28
32-17	9.78	1.41
32-7	11.93	1.46

(1) A/B = initial E/CO mole ratio.

(2) a/b = final E/CO mole ratio.

TABLE VI

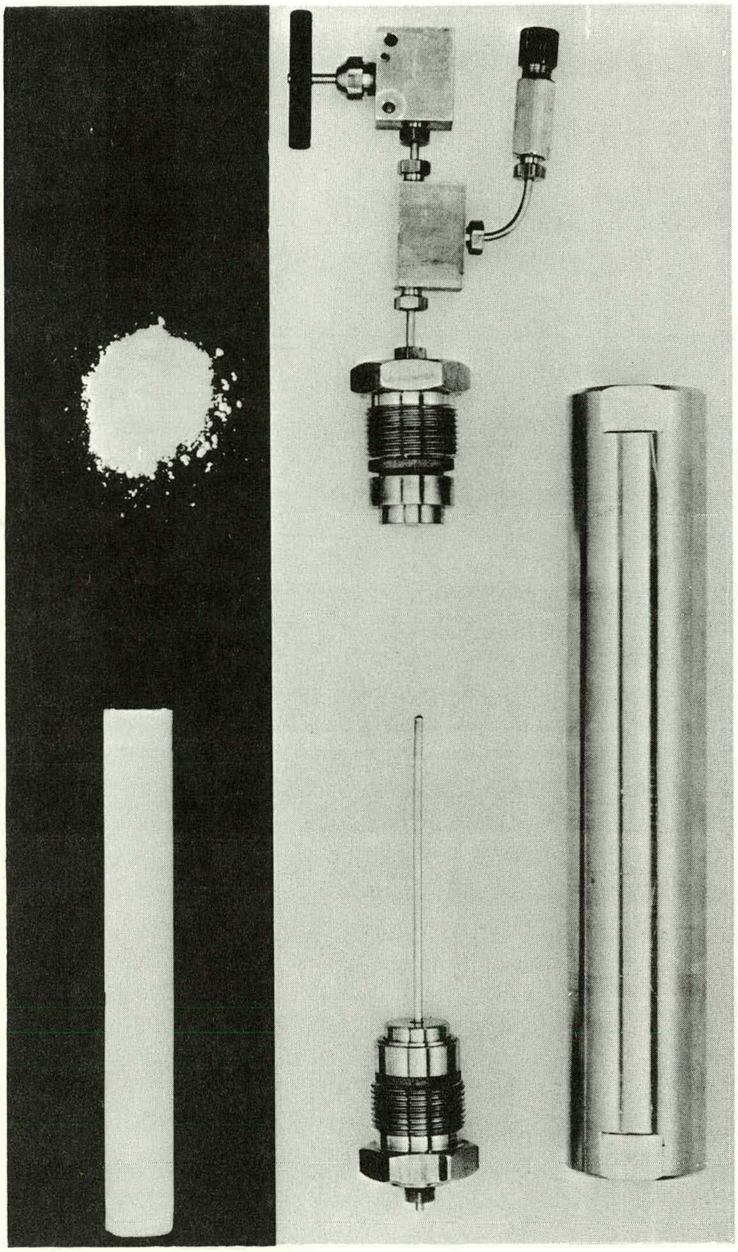
COBALT-60 GAMMA COPOLYMERIZATION OF ETHYLENE

Ethylene-Chlorotrifluoroethylene (CTFE) System

Run No.	Intensity Rads/hr	Dose 10^6 Rads	Ethylene grams	Comonomer grams	Initial Mole Ratio $\frac{\text{Ethylene}}{\text{CTFE}}$	Polymer Formed grams	Final Polymer Mole Ratio $\frac{\text{Ethylene}}{\text{CTFE}}$	Total Conversion By Wt.%	G_{Total}
20-0	230,000	16.2	49.0	7.0	29.1	49.2	9.53	87.9	1,430
20-1	308,000	0.05*	45.0	15.7	11.9	-	1.69	-	-
20-2(1)	308,000	0.92	-	15.4	-	3.0	-	19.5	1,700
20-3	308,000	0.04*	49.0	7.0	29.1	-	1.65	-	-
20-4	216,000	0.5	49.0	7.3	28	20.0	13.18	35.5	20,000

* Total dose at which explosive decomposition occurred.

(1) Pure chlorotrifluoroethylene polymerization.



Co^{60} GAMMA COPOLYMERIZATION OF ETHYLENE. REACTION VESSEL AND ASSEMBLIES

FIGURE 1

RADIATION POLYMERIZATION EXPERIMENTAL EQUIPMENT

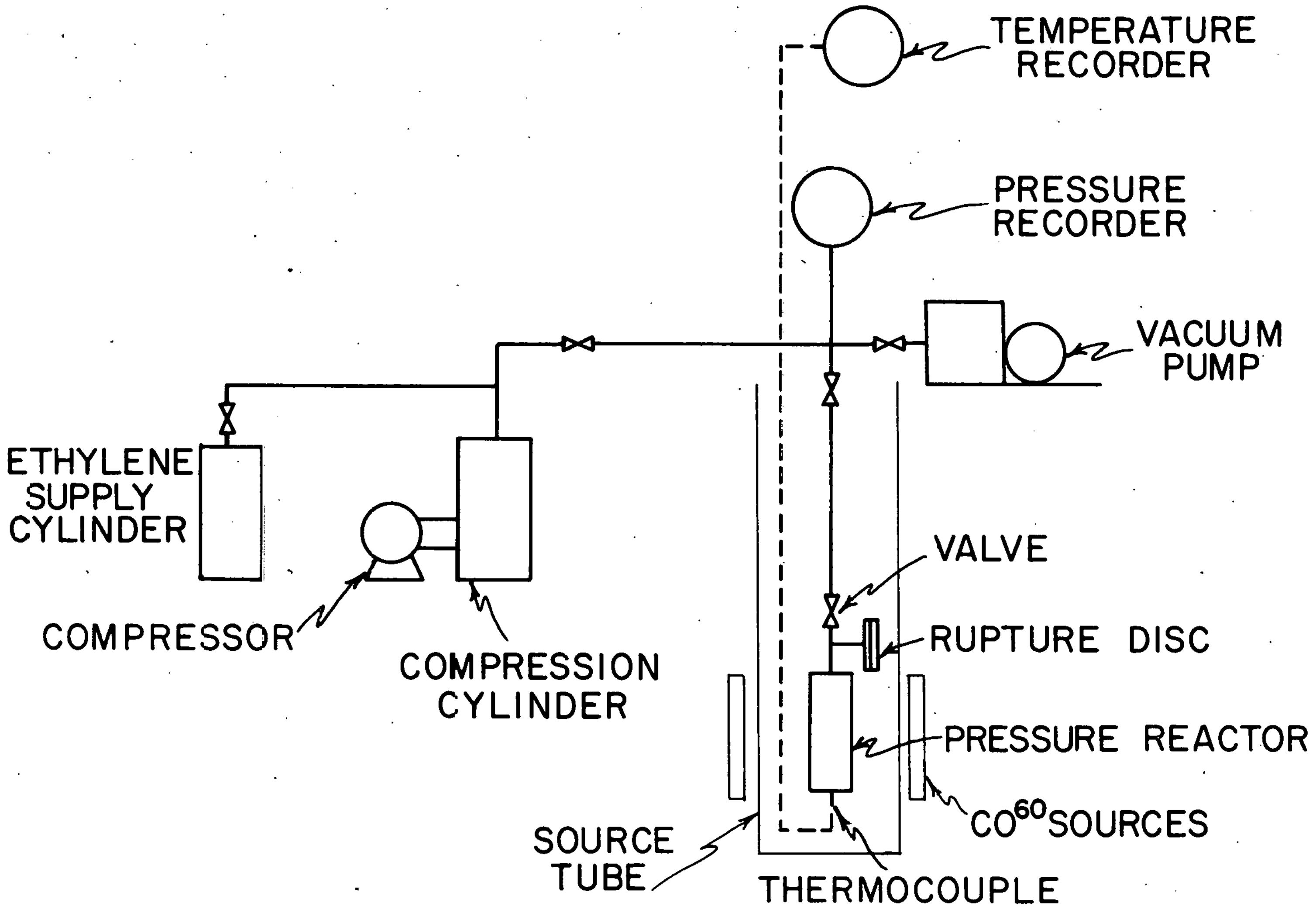


FIGURE 2

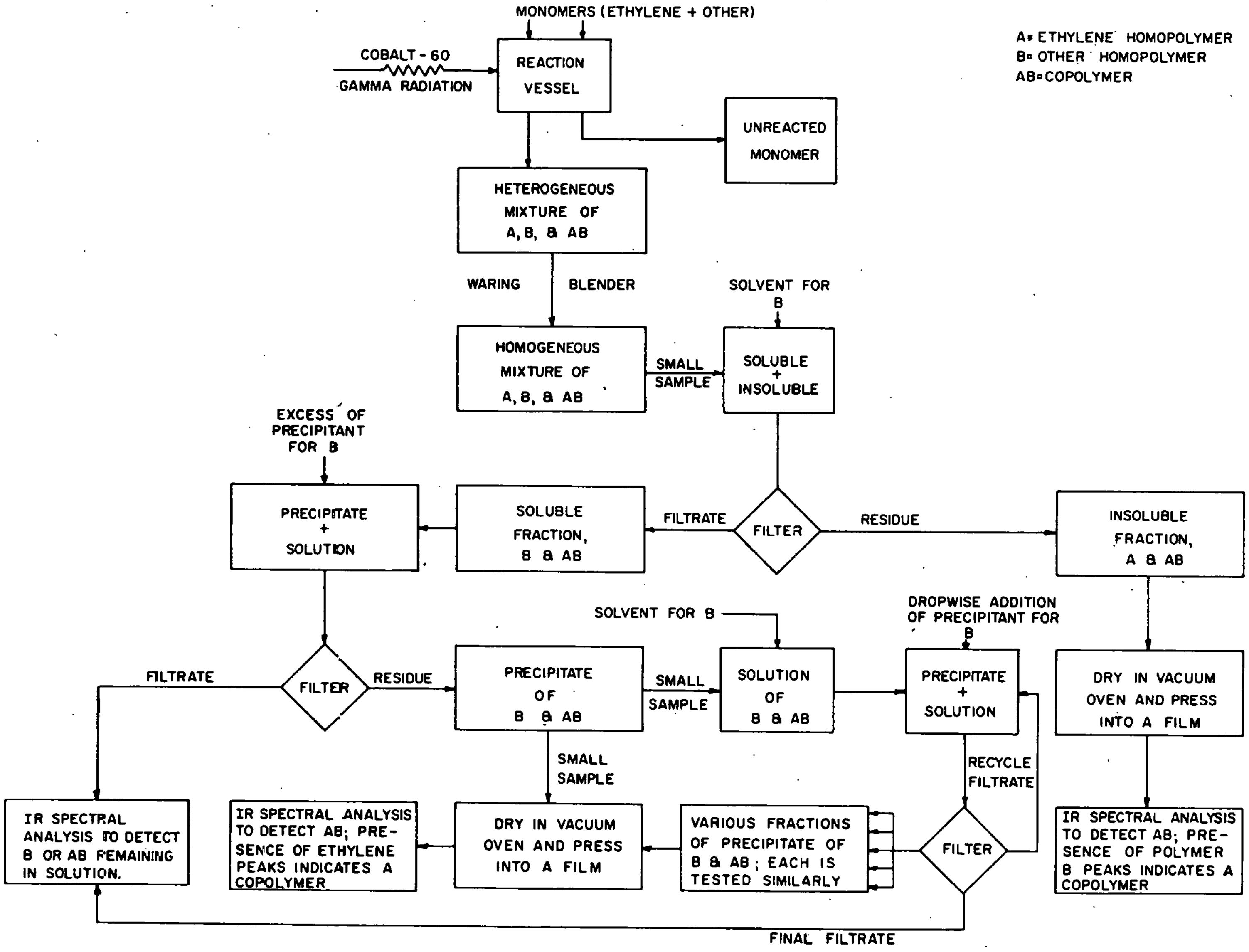


Fig-3 SCHEME FOR IDENTIFICATION AND ISOLATION OF COPOLYMERS

COBALT-60 GAMMA COPOLYMERIZATION OF ETHYLENE
INFRA-RED SPECTRA OF COPOLYMERS

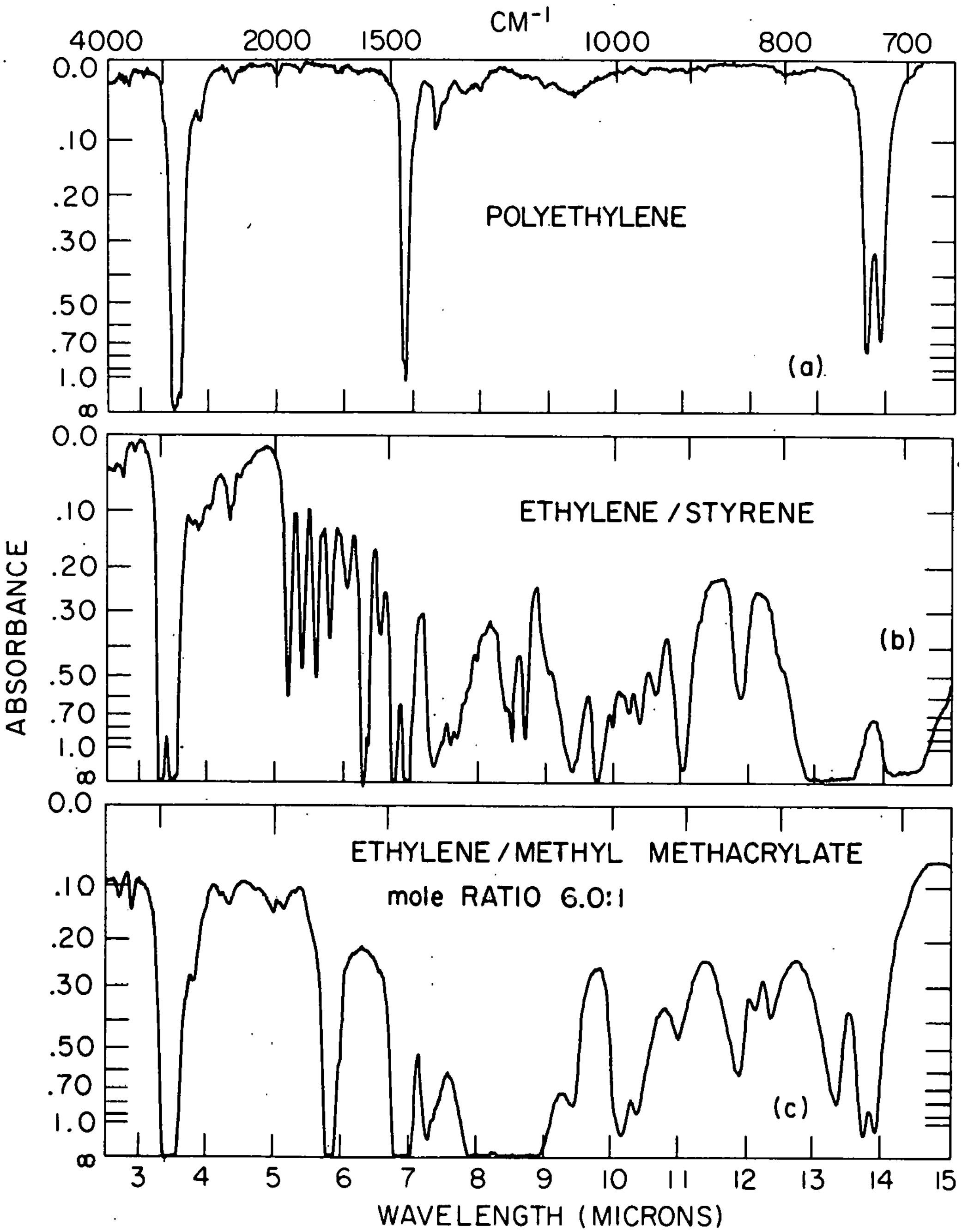


FIGURE 4

COBALT-60 GAMMA COPOLYMERIZATION OF ETHYLENE
INFRA-RED SPECTRA OF COPOLYMERS

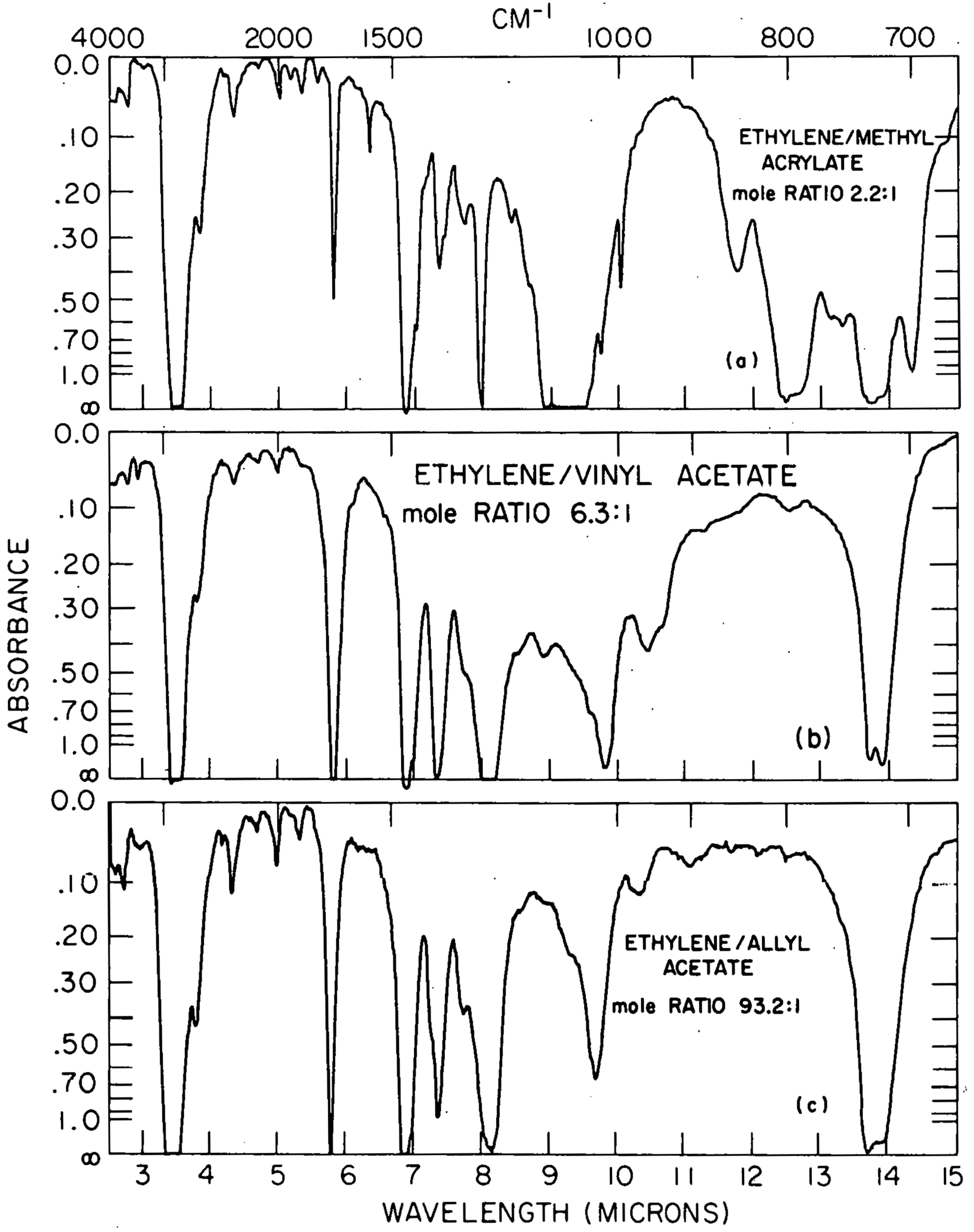


FIGURE 5

COBALT-60 GAMMA COPOLYMERIZATION OF ETHYLENE
INFRA-RED SPECTRA OF COPOLYMERS

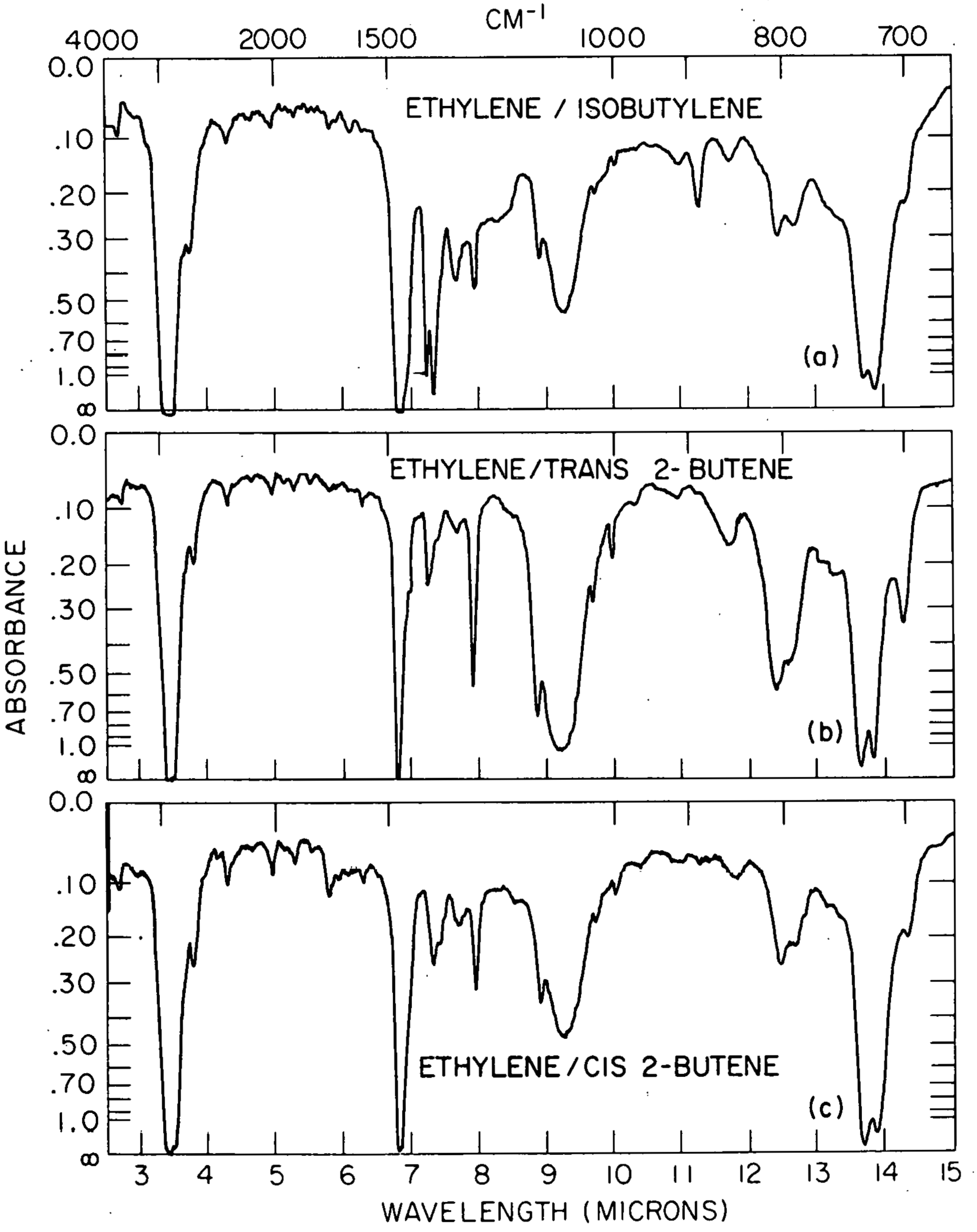


FIGURE 6

COBALT-60 GAMMA COPOLYMERIZATION OF ETHYLENE
INFRA-RED SPECTRA OF COPOLYMERS

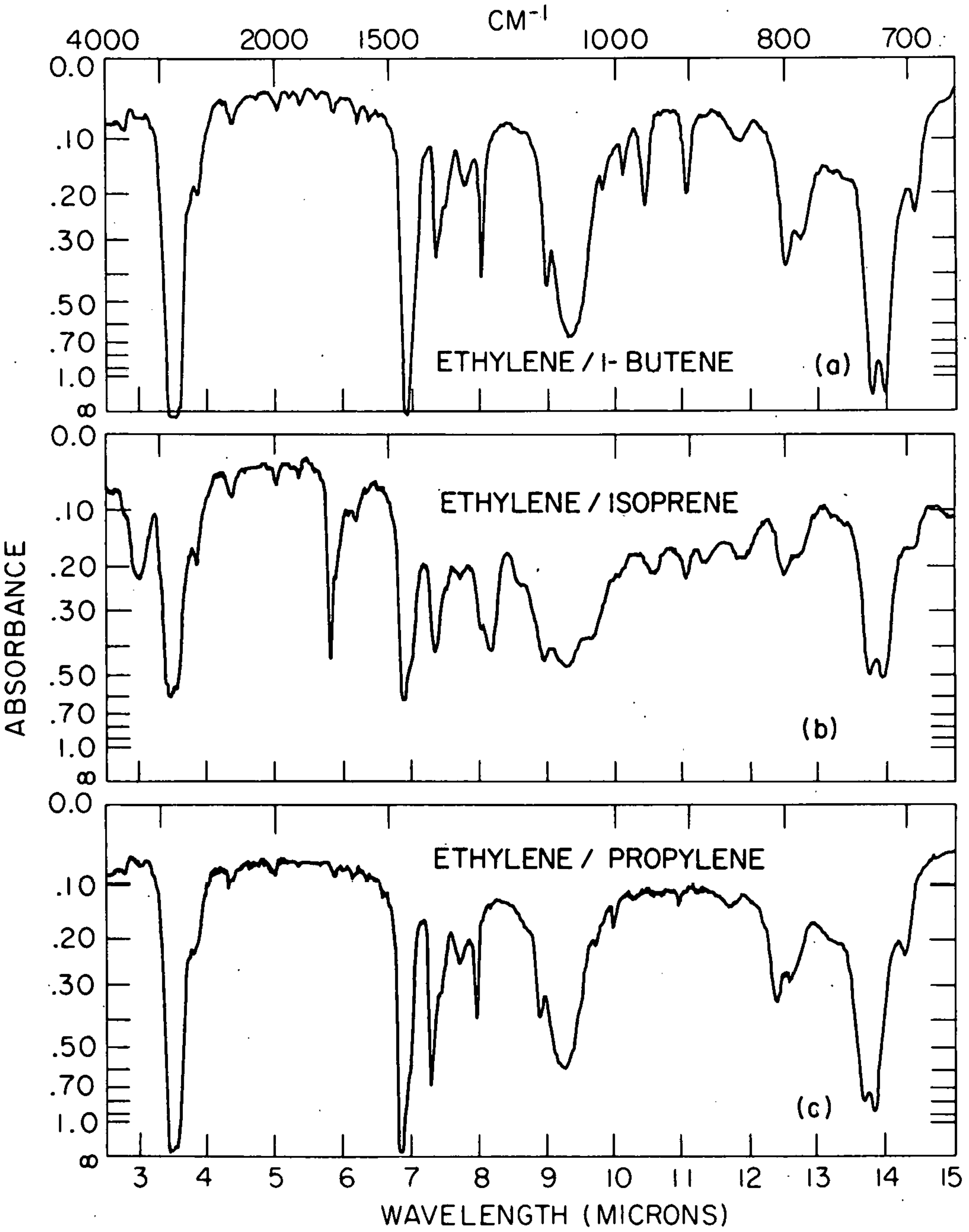


FIGURE 7

COBALT-60 GAMMA COPOLYMERIZATION OF ETHYLENE
INFRA-RED SPECTRA OF COPOLYMERS

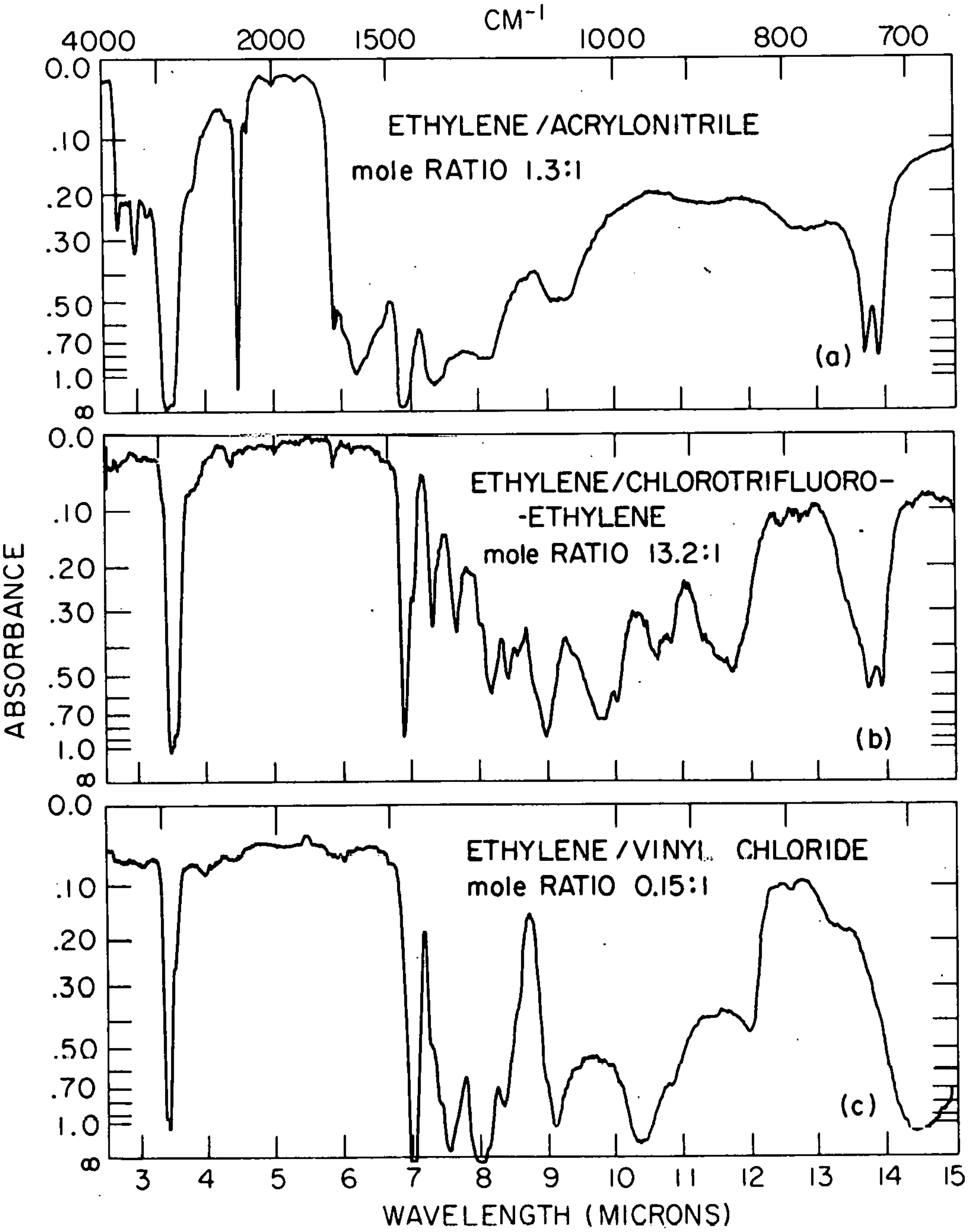


FIGURE 8

COBALT-60 GAMMA COPOLYMERIZATION OF ETHYLENE
INFRA-RED SPECTRA OF COPOLYMERS

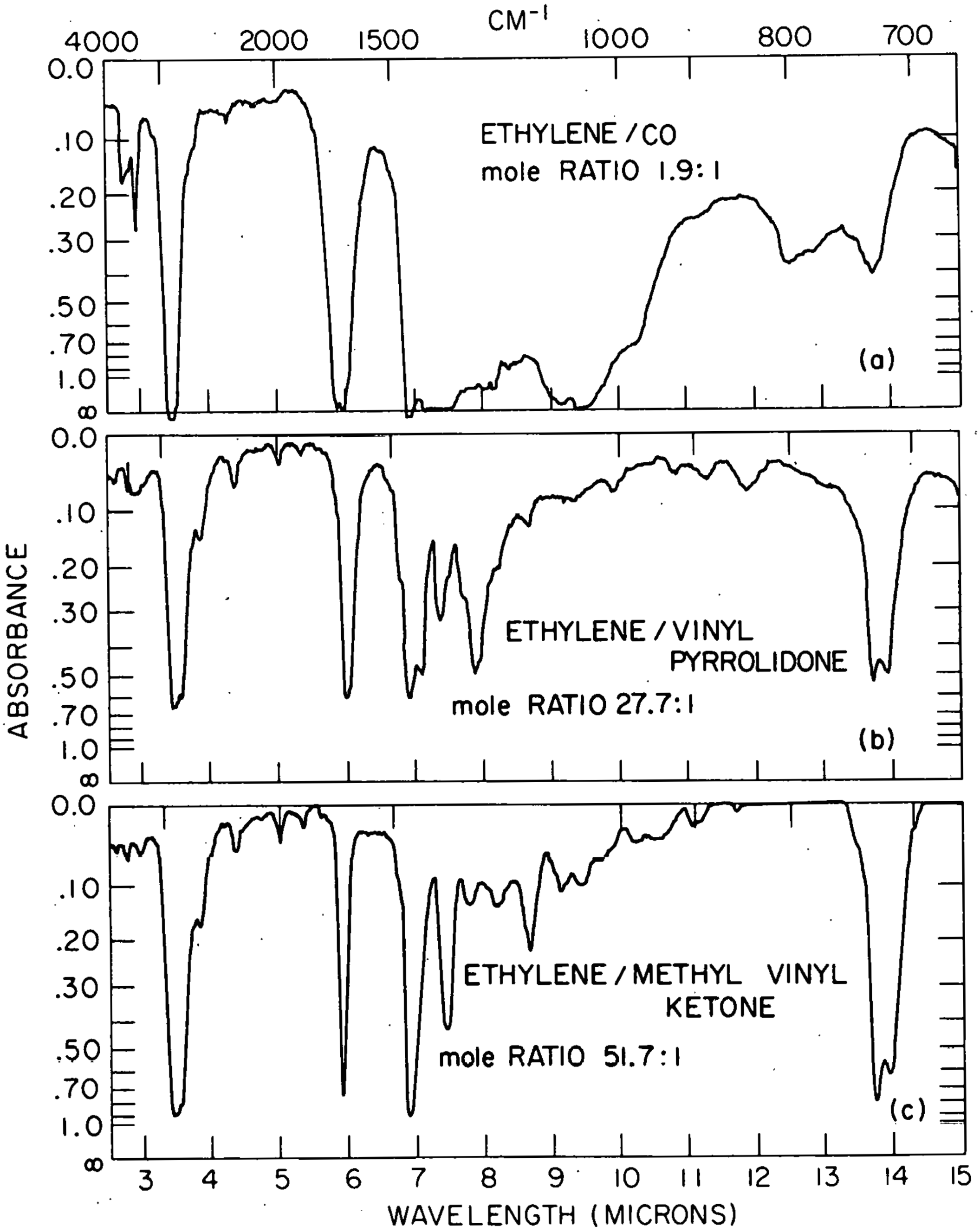


FIGURE 9

COPOLYMERIZATION OF ETHYLENE
ETHYLENE-CARBON MONOXIDE SYSTEM

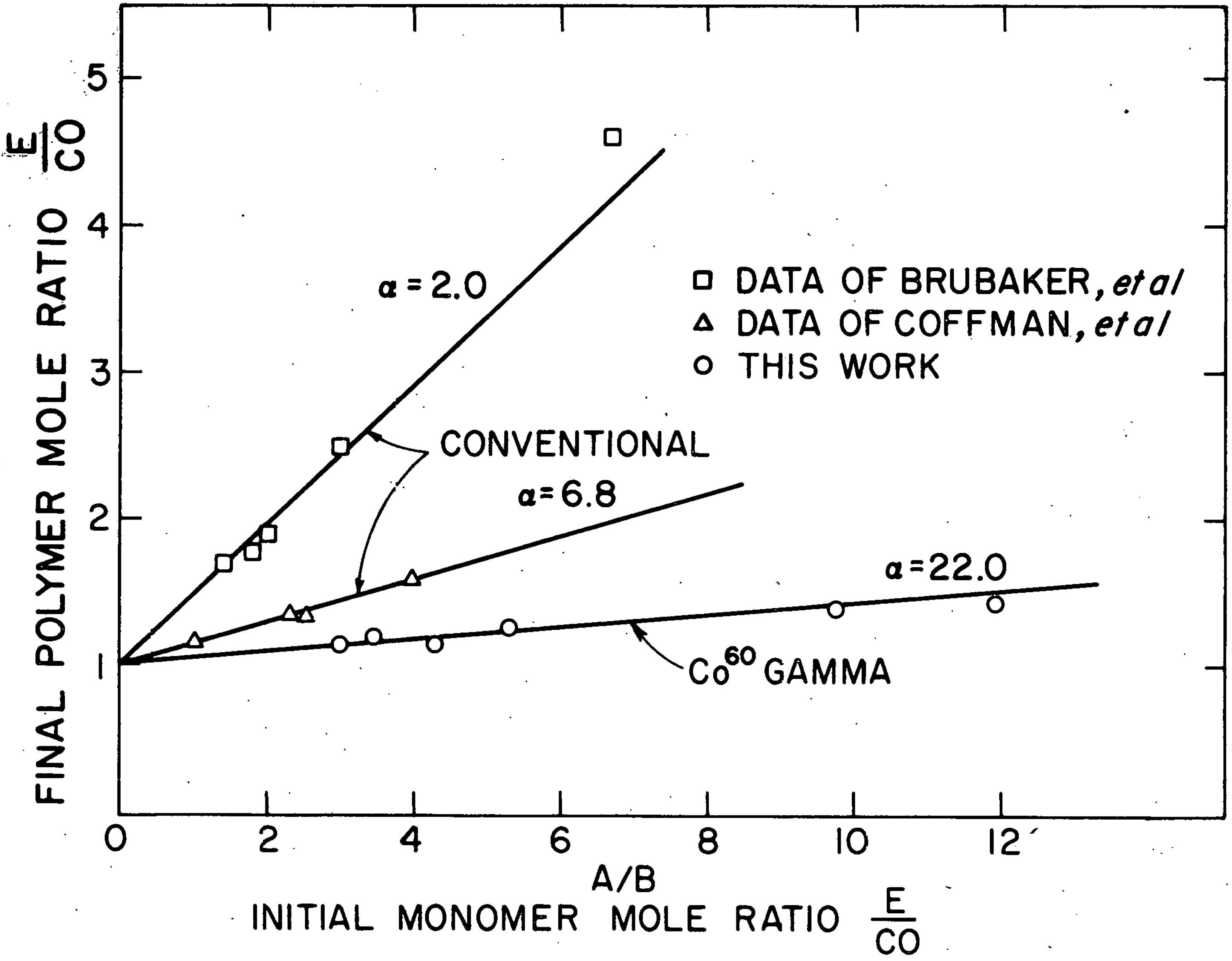


FIGURE 10