FINAL REPORT
PROJECT NO. A-446-10

Physical Properties and Structural Characteristics of Polymers Resulting from "Post-Effect" Polymerization

by L. W. Elston and W. H. Burrows

Covering the Period
1 March 1962 to 31 October 1963
Printed 22 November 1963

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Performed for
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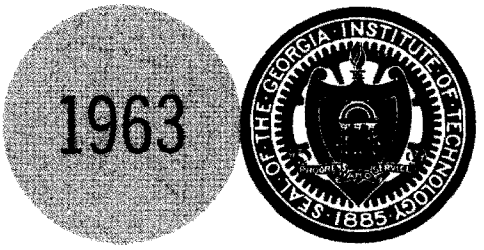
Division of Isotopes Development
Germantown, Maryland



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Atlanta, Georgia

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By

L. W. ELSTON and W. H. BURROWS

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GERMANTOWN, MARYLAND

ABSTRACT

The purpose of this study has been to exploit the peculiar advantages of post-effect polymerization to examine the mechanisms and kinetics of vinyl polymerization. Extent of polymerization and viscosity average molecular weight as functions of initiating dose and post-effect time at room temperature have been observed. Methyl methacrylate has been the monomer used in all experiments. Radiation doses up to 8.73×10^5 rads and post-effect times up to 194 hours have been employed. A low temperature method for quenching and transfer of viscous samples has been developed.

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I. INTRODUCTION

In accordance with AEC Contract AT(38-1)-202, Task No. X, an investigation of "post-effect" polymerization as a method of studying the kinetics of vinyl polymerization was conducted during the period from 1 March 1962 to 31 October 1963. The investigational program under this contract consisted of an extensive survey of applicable literature and an experimental work program divided into four general areas as follows:

(1) Development of apparatus and methods for preparation and study of post-effect polymers.[1]

(2) Systematic exploration of extent of polymerization and molecular weight as functions of initiating dose, post-effect time, and temperature. This phase of the program included preliminary irradiation experiments in laboratory x-ray equipment, although the bulk of the irradiation experiments were performed in the Georgia Tech 12,000 Curie Cesium 137 Research Irradiator.

(3) Detailed examination of the polymers prepared during the exploratory phase of this study. In addition to gravimetric determination of extent of polymerization and viscosimetric molecular weights determined during the exploratory phase, the following quantities were to be examined:

   a. Molecular weight distribution by column chromatography followed by determination of molecular weight of the separated fractions.[3]

   b. Specific volume by direct measurement.[61]

   c. Morphology from infrared.[48,62]

d. Morphology from x-ray diffraction.[61]

e. Degree of branching from infrared.[48,62]

f. Crystalline melting points (if any) by polarized light microscopy.

(4) Analysis of experimental data together with material taken from the literature to throw some additional light on the kinetics and mechanisms of vinyl polymerization in viscous media.

It was anticipated that completion of the proposed work would require one or more renewal periods.

The first phase of this study has received the major portion of the experimental work. The second, or exploratory phase was well under way, and samples for detailed study have been reserved. Data from room temperature ($23^{\circ} \pm 2^{\circ}$ C) experiments with conversions up to 25 per cent have been obtained and planned experiments included higher conversions at room temperature as well as at temperatures of 5° C and 40° C. Only preliminary evaluation of experimental observations has been undertaken.

II. EXPERIMENTAL PROCEDURES

A. Monomer Preparation

1. Extraction

Methyl methacrylate monomer samples were prepared by three extractions with 1 per cent aqueous potassium hydroxide and successive rinsing with distilled water until no further color was observed in the water phase.

2. Distillation

The inhibitor-free sample was then dried for 24 hours over anhydrous potassium carbonate at 5° C, filtered, and distilled at reduced pressure under an inert atmosphere.

Apparatus for distillation of methyl methacrylate monomer at 45° C under an inert atmosphere is presented schematically in Figure 1.

In practice, a gradual flow of nitrogen through the oil bubbler was established and the fine metering valve (A) was adjusted to pass a stream of nitrogen through the inhibitor-free monomer in the still. The filter pump was then turned on and a second metering valve (B) was adjusted to regulate the overall pressure of the system. After approximately 30 minutes purging with dry nitrogen, heat was applied and approximately one-half of the monomer was distilled into an ice chilled receiving flask. The boiling temperature of the monomer was held at 45° C by adjusting the fine metering valve (B) to admit partial atmospheric pressure to the line immediately upstream from the filter pump. Diffusion of water vapor into the receiving flask was prevented by a cold trap. All glass joints in the system were carefully lapped with fine boron carbide, and Teflon sleeves were used rather than lubricant for sealing.

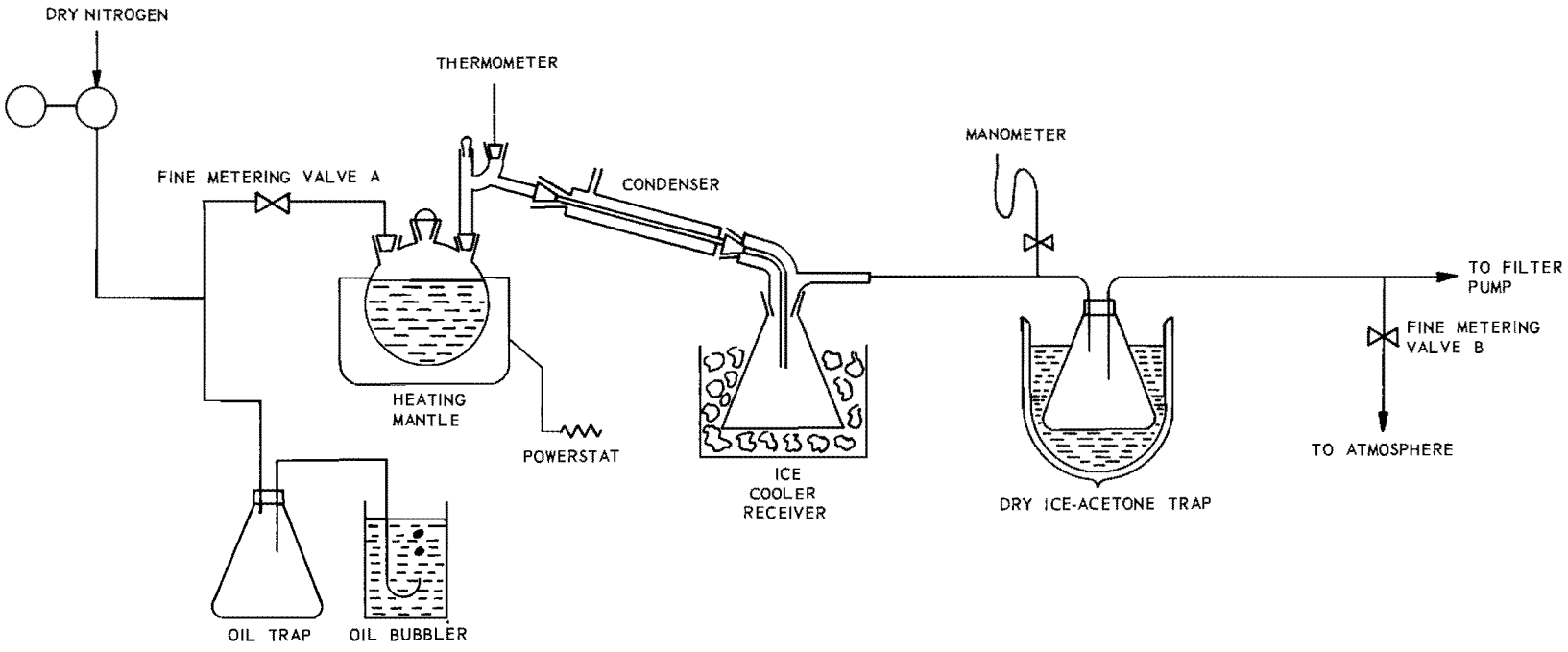


Figure 1. Inert Atmosphere Still.

Immediately after distillation, the monomer was decanted into clean irradiation vessels and tightly closed to exclude light and air. The vessels were slightly overfilled so that some monomer was displaced in closing the containers. After rising to room temperature, the filled vessels were weighed to determine the weight of monomer sample.

B. Irradiation Procedures

1. Irradiation Vessels

a. Stainless Steel Vessels. Twenty-four T-304 stainless steel irradiation vessels were fabricated to suit the outer holes in the Georgia Tech 12,000 Curie Cesium 137 Research Irradiator. The length of these vessels was selected to contain monomer samples in the 2-1/2 inch vertical interval of uniform flux density. To exclude air, these vessels were closed by threaded (1/4 inch NPT) Teflon plugs. There was no evidence of chemically or thermally induced polymerization in methyl methacrylate monomer samples held for 10 days in these vessels. Low level initiation in laboratory x-ray equipment, however, led to rapid polymerization, the gel state being reached in approximately 4 hours after 2 minute irradiations with a tube operated at 50 kv at a plate current of 5 ma. Catalysis by some component of the container wall was suspected. A further bar to use of these vessels was the impracticability of dissolving or transferring a gelled reaction mixture to an inhibitor solution for quenching.

b. Teflon Vessels. Twenty-four irradiation vessels of outside dimensions similar to the stainless steel vessels, and threaded to suit the Teflon plugs on hand, were fabricated from Teflon bar stock.

Figure 2 shows Teflon vessels used for several irradiations. The fragments on the left show brittle fracture and etching of a container used in eight experiments and exposed to a total dose of approximately 6 megarads.

The inner walls of these vessels were straight and of slightly smaller diameter than the threaded top to facilitate transfer of the reaction mass. No measurable polymerization of monomer in these vessels was observed after 10 minute irradiations in laboratory x-ray equipment. Deterioration of these vessels during irradiation in the cesium source was gradual. A brownish, slightly rough appearance on the inside walls, similar to that obtained by etching Teflon with a solution of sodium in anhydrous ammonia, gave evidence of grafting of methyl methacrylate monomer to the inside of the containers. This brownish discoloration became more pronounced after each cycle of filling, irradiation, rinsing with solvent, and cleaning with hot chromic acid. A more obvious form of deterioration was gradual embrittlement of both the container and stopper, which lead to broken stoppers or to splitting of the container during quenching in liquid nitrogen. As this failure had not been observed in containers exposed to less than 6 hours total irradiation, and as their fabrication was easily accomplished, the option of obtaining new vessels as needed seemed preferable to a change in materials or design.

2. Irradiation of Monomers

Monomer irradiation has been performed in laboratory x-ray equipment and in the Georgia Tech Cesium 137 Research Irradiator.

a. Laboratory X-Ray Equipment. Low dose rates and low dose levels were observed using laboratory x-ray equipment. The principal use of this apparatus has been to examine the behavior of monomer and irradiation vessels under mild conditions

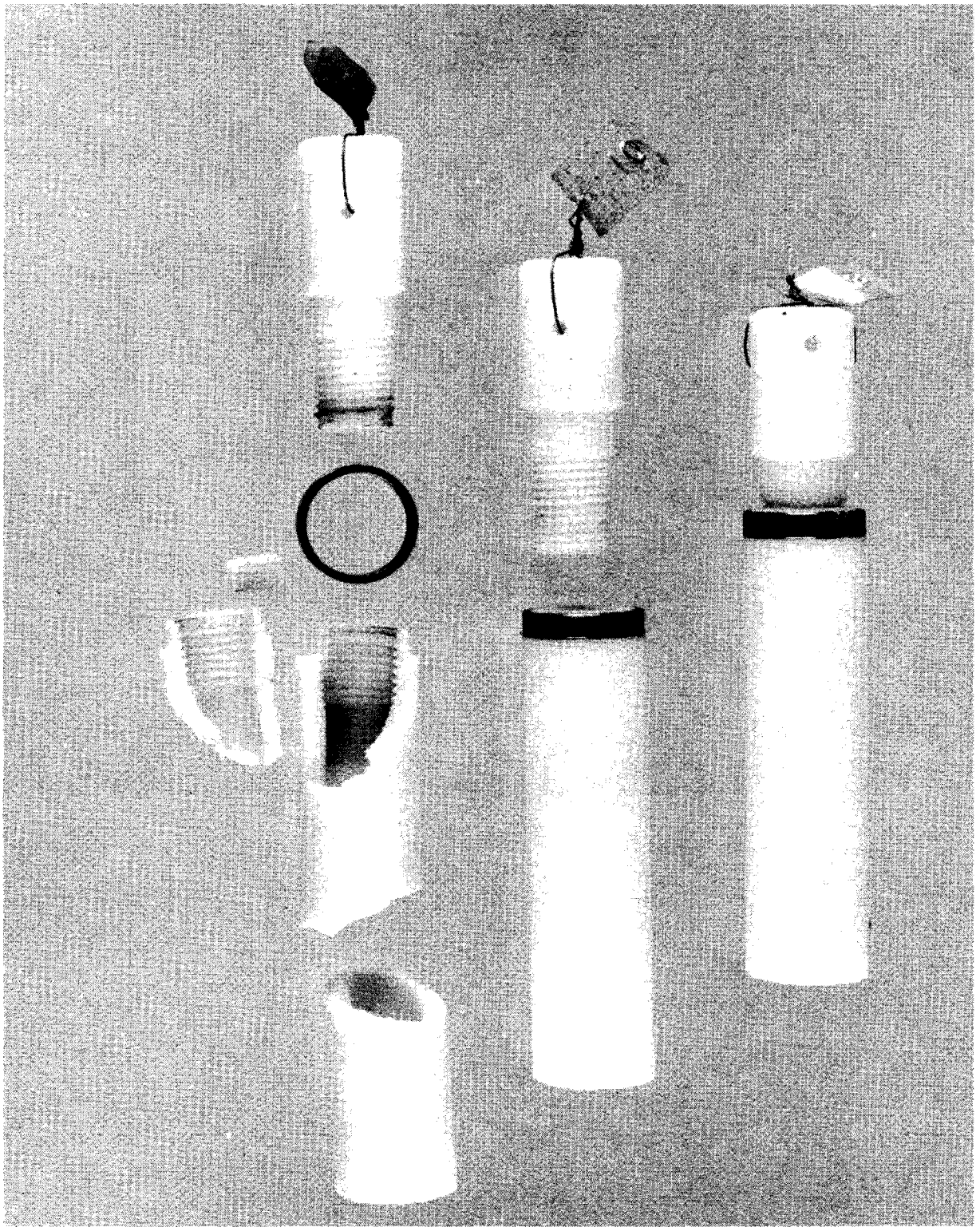


Figure 2. Teflon Vessels Used for Monomer Irradiation.

before exposing them to the more intense radiation flux of the cesium source. This apparatus is shown in Figure 3.

Samples to be irradiated were placed in the lead lined chamber at the right of the apparatus. The tube was operated at 50 kv and at plate currents of 5 and 10 ma. As overheating of the unit restricted continuous operation to 2 minutes at 10 ma, the apparatus was modified to permit cooling oil circulation through the water cooled heat exchangers (West condensers) shown behind the unit. Continuous operation for periods of over 1 hour was then possible.

b. Georgia Tech Research Irradiator. Most of the monomer irradiation experiments have been performed in the Georgia Tech 12,000 Curie Cesium 137 Research Irradiator, using the outer row of holes in a "Notre Dame basket" arrangement. Suitable spacers were employed to locate the monomer samples in the vertical interval of uniform radiation flux. The dose rate in the positions used, as determined by ferrous ion dosimetry, was 4.16×10^{19} ev gm^{-1} hr^{-1}. Application of a factor which relates the electron densities of methyl methacrylate monomer and the ferrous ion dosimetry solution shows the dose absorbed by methyl methacrylate monomer in these positions to be 3.64×10^{19} ev gm^{-1} hr^{-1} or 5.82×10^{5} rads hr^{-1} (these calculations are outlined in the "Calculations" section of this report). Figure 4 illustrates the position of the monomer sample with respect to the radiation intensity curve for these stations.

It will be noted that the center of the reaction mass is located at a radiation intensity higher than that shown by the measured radiation doses. This difference arises from superimposing a scale representation of an irradiation vessel on a plot of dose variance with vertical movement made immediately after installation of the source. The more recent, lower dose rates are valid for these experiments.

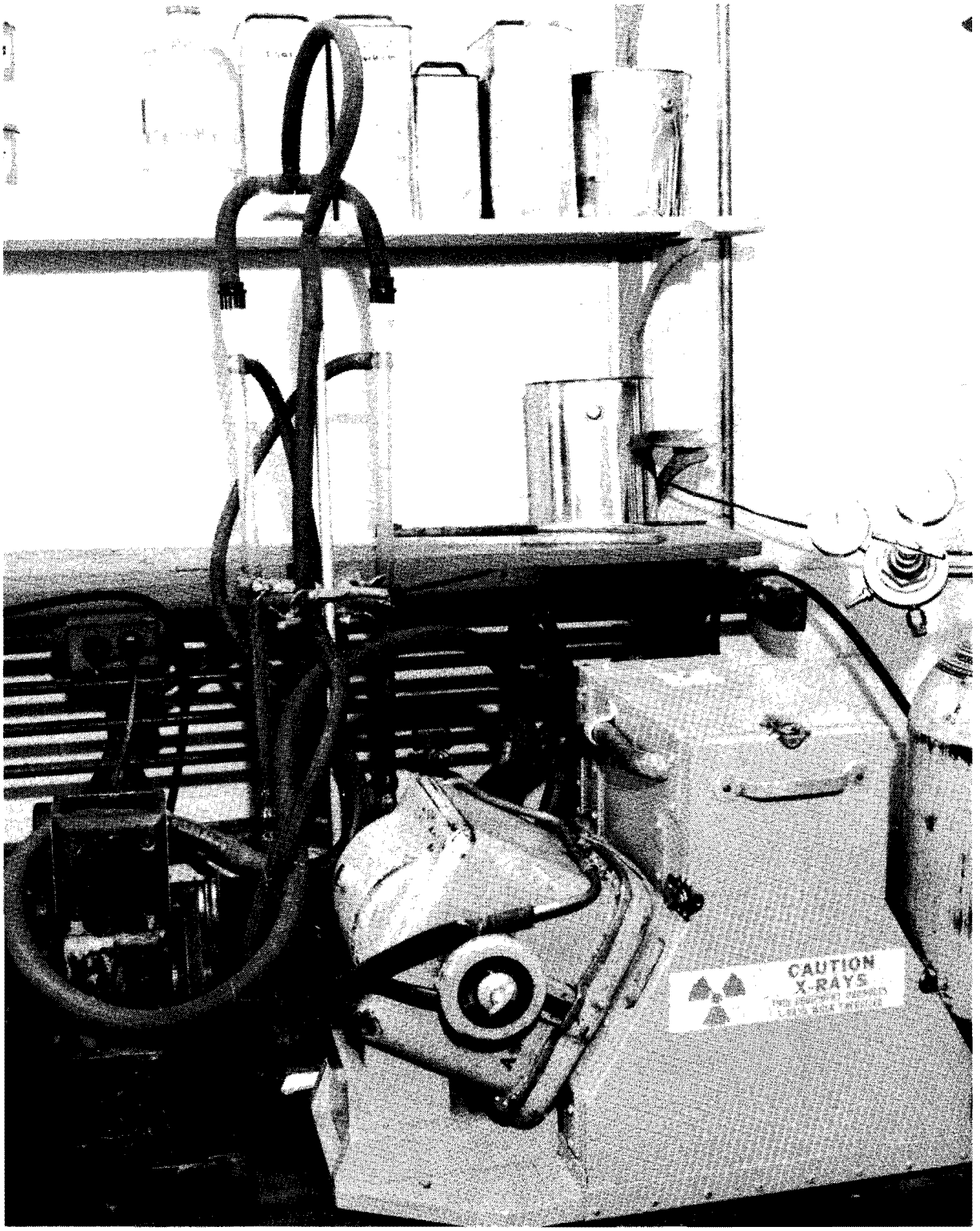
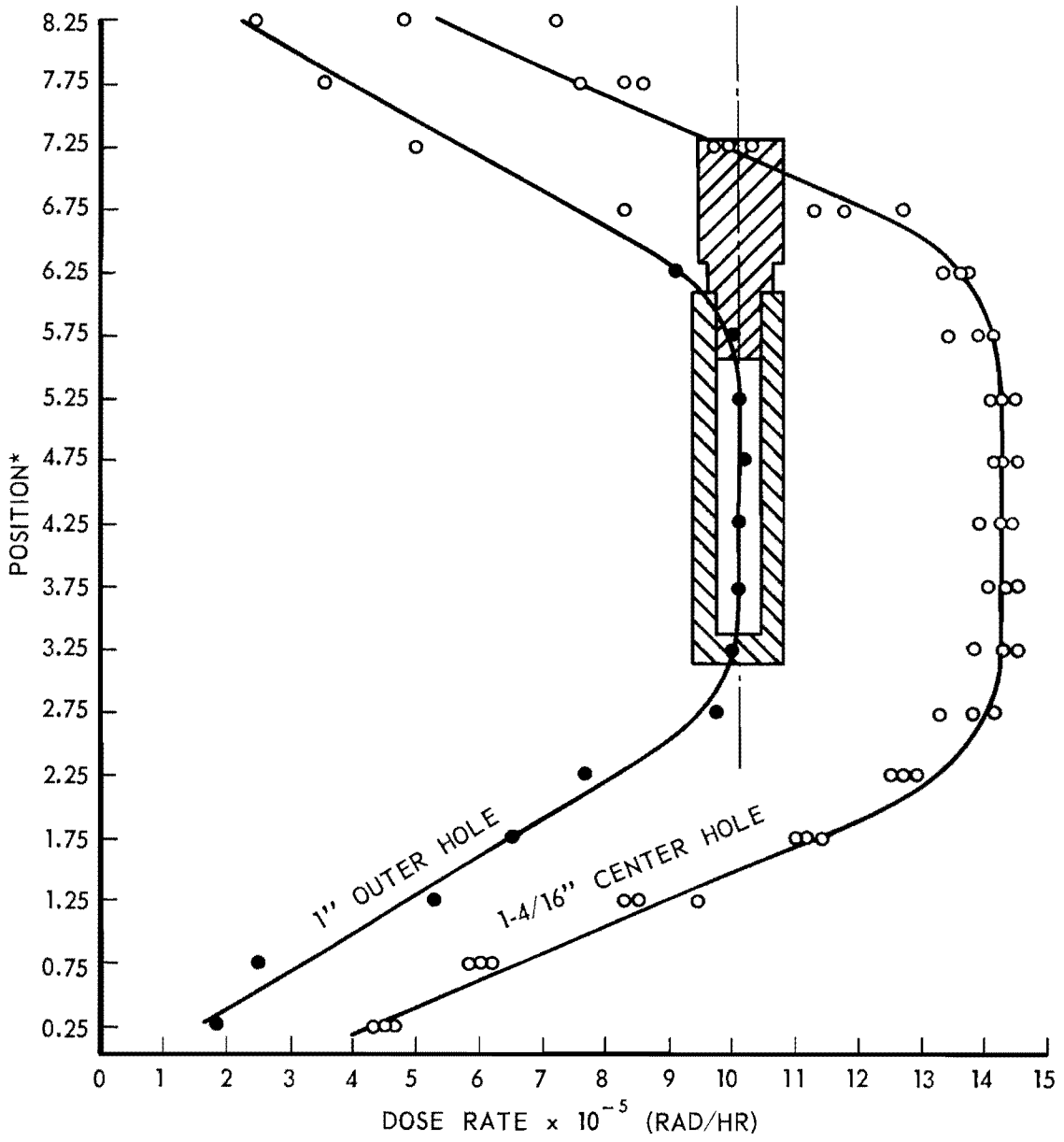


Figure 3. Laboratory X-Ray Equipment.



*The position is measured upward in inches from the bottom of the sample space within the sample carriers.

Figure 4. Location of Monomer Sample in the Cesium Source.

Initial irradiation experiments were conducted cautiously in the order of increasing total dose to establish the dose levels necessary to produce measurable extent of polymerization and post-effect polymerization and to avoid possible contamination of the radiation source by container failure or unexpected exothermic reactions. Irradiation times were increased stepwise from 5 minutes to 1-1/2 hours. The temperature of the samples during irradiation was 35° C in all cases. Extensive post-effect polymerization was observed after irradiation times equal to or greater than 40 minutes, i.e., doses equal to or greater than 3.8×10^5 rads. The dose rate in these experiments is a fixed characteristic of the irradiator.

C. Quenching Procedures

Two methods of quenching the polymerization reaction at any desired time have been in use.

1. Quenching at Room Temperature

The first of these methods consisted of pouring the reaction mixture into 5 ml of a rapidly stirred solution of methyl ether of hydroquinone in benzene. This method has proven satisfactory for radiation doses up to 5.8×10^5 rads and post-effect times up to 1 hour. The sample container was washed several times with methylene chloride, and the washings were added to the flask containing the quenched reaction mixture. (Evaporation of several 5 ml portions of the stock quenching solution showed that each 5 ml portion contained 0.0520 gram of inhibitor.) The flask containing the quenched reaction mixture was then placed on a rotating vacuum evaporator.

Attempts to quench samples irradiated for longer than 1-1/2 hours or after post-effect times greater than 1 hour by the method described above were unsuccessful. On addition of inhibitor solution, the reaction mass gradually imbibed the solvent

with only a brief decrease in viscosity. Attempts to scrape the thickened reaction mass into a flask containing inhibitor solution were also unsuccessful; the product was a viscous liquid or gel which contained both the reaction mass and the imbibed solvent. Addition of more solvent to the mixture led only to absorption of the solvent without decrease in viscosity. It was thus necessary to develop an alternative quenching method to secure reproducible data in the gel (Trömmsdorff) region.

2. Cold Quenching

The alternative method consisted of freezing the reaction mass at the selected time with liquid nitrogen and transferring the solid mass to a test tube containing 10 ml of 1 per cent methyl ether of hydroquinone in methylene chloride and chilled by a bath of dry ice in acetone. The reaction mass was allowed to dissolve in the inhibitor solution from the solid state. The dissolved reaction mass was then poured into a flask suitable for use on a rotating vacuum evaporator and the tube was rinsed several times with methylene chloride, the washings being added to the evaporator flask. A variation of this method is a "cold finger" technique in which liquid nitrogen from a heavy brass cup previously chilled with liquid nitrogen is circulated through a small diameter tube immersed in the reaction mass (Figure 5).

D. Extent of Polymerization

The quenched polymer samples were evaporated to dryness on a rotating vacuum evaporator in tared 100 ml flasks with standard tapered necks. A Teflon sleeve was used to avoid contamination of the sample with sealant or lubricant. Solvent was flashed off at room temperature on the Rinco evaporator. When the disappearance

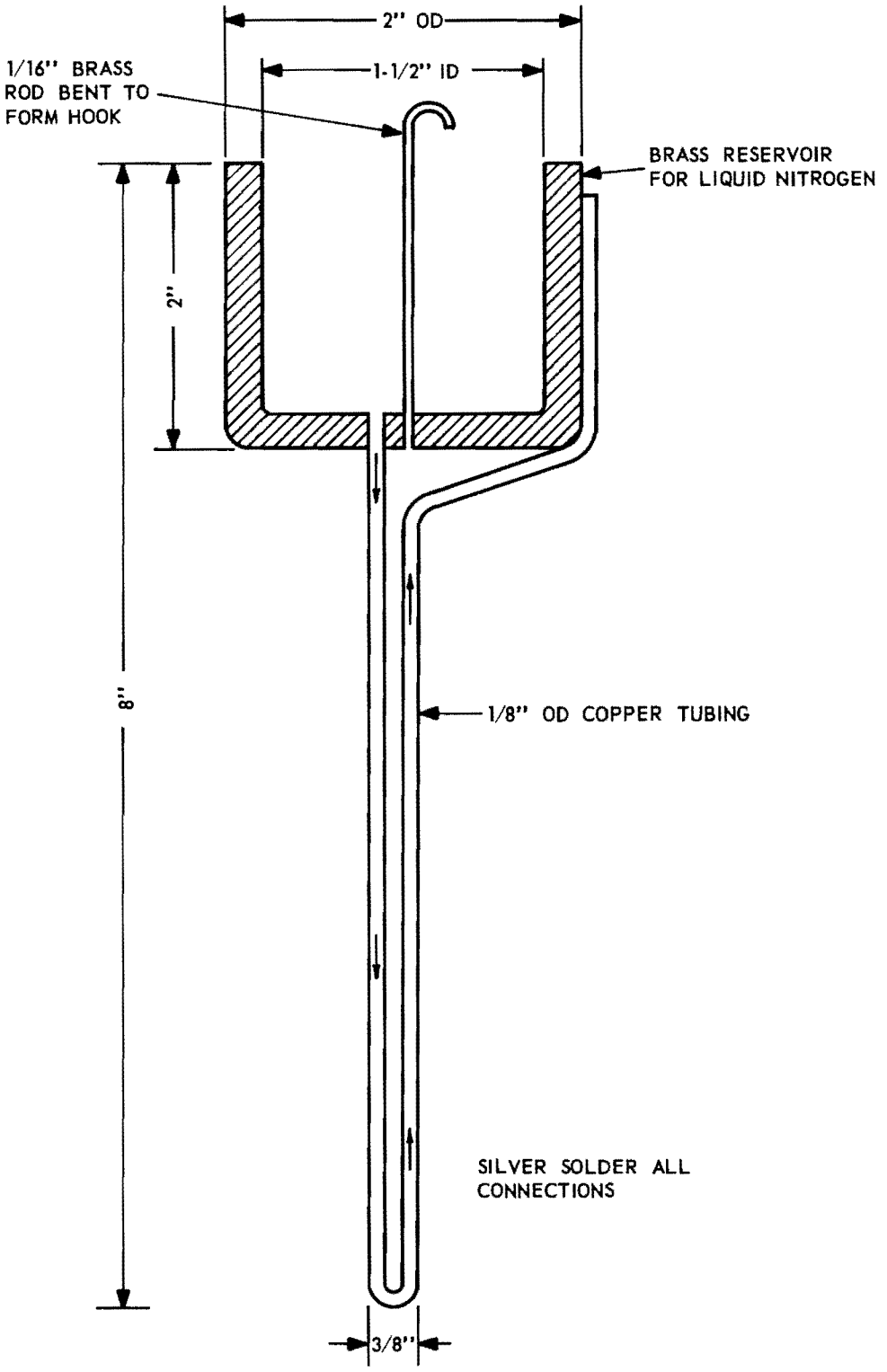


Figure 5. Cold Quenching Device.

of the ice coating on the evaporating flask indicated that volatile solvent had been removed, the flask was transferred to a second rotating evaporator and warmed to 40° C. When the polymer sample appeared to be dry, the flask was placed in a laboratory vacuum oven at 40° C and dried in vacuo for at least 24 hours or until no odor of methyl methacrylate monomer could be detected. The flask was then cooled to room temperature and weighed. Evaporating apparatus is shown in Figure 6 Extent of conversion was calculated from the weight of polymer in the flask (corrected for weight of inhibitor present) and the known weight of monomer in the irradiated sample. To the weighed flask was added 30 ml of methylene chloride. The flask was then fitted with an aluminum foil dust cover and placed on a Burrell wrist action shaker to dissolve. The dissolved sample was placed in a loosely covered Teflon evaporating dish and allowed to evaporate to dryness. When evaporation was apparently complete, the dish containing the sample was held in vacuo at 40° C for 48 hours. This procedure produced a methyl methacrylate film, which was easily stripped from its container and stored for later division into samples for molecular weight determination and other measurements.

E. Fractionation

1. Apparatus Construction

The polymer fractionation apparatus used in this study was adapted from a design described by Weakley, Williams and Wilson.[67]

Figure 7 shows the arrangement of the chromatographic apparatus. At the lower center of the picture is a reduced pressure filtration device used to transfer the contents of the fraction collector tubes to an evaporating vessel. At the lower right is a constant temperature bath for viscosity determination.

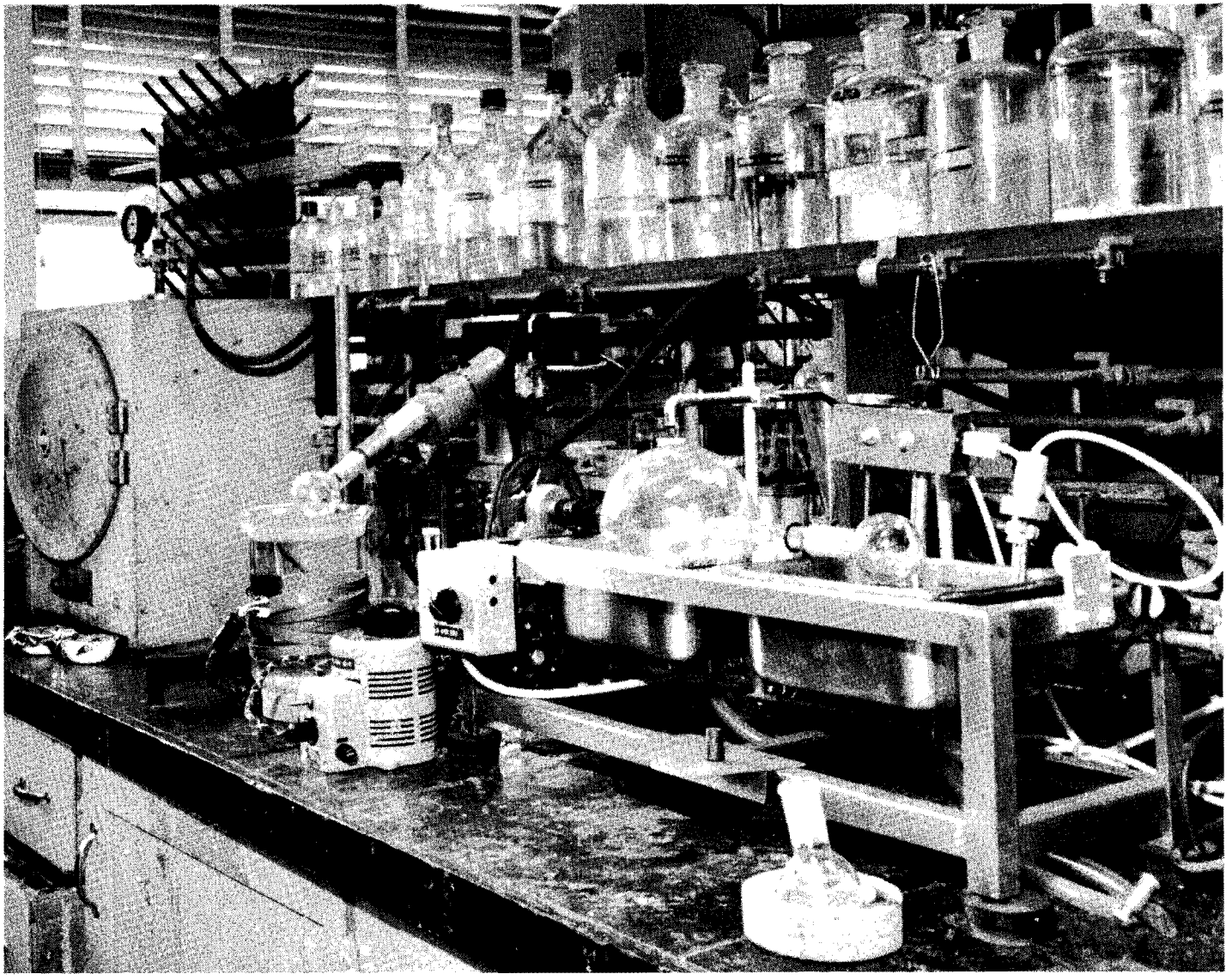


Figure 6. Rotating Vacuum Evaporators and Vacuum Oven.

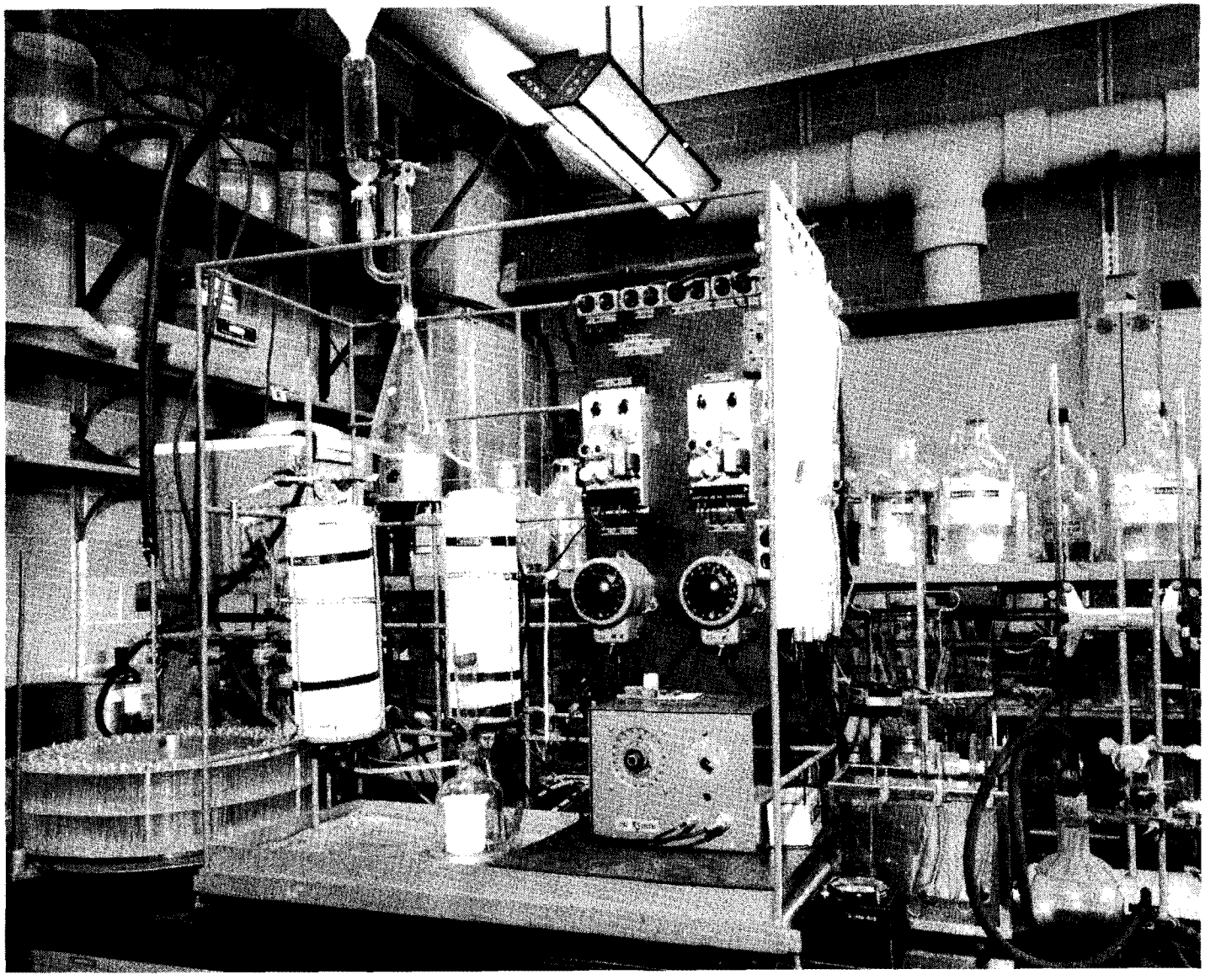


Figure 7. Solvent Temperature Gradient Polymer Fractionator.

The principal parts of the chromatographic apparatus are: (1) reservoir, (2) mixing chamber, (3) magnetic stirrer for generation of a solvent gradient, (4) solvent degassing column, (5) "inverted" chromatographic column, and (6) Rinco automatic fraction collector suitable for either timed or volume control.

Teflon tubing connections between the larger components have replaced the ball and socket joints used in earlier experiments, and pairs of Teflon sleeves have replaced stopcock grease or thickened gylcerol sealant in the ground glass joints. These modifications were made because the thickened glycerol, although resistant to both chloroform and hexane, tended to creep under pressure, frequently leading to leaks and occasionally to sample loss.

The solvent degassing and chromatographic columns are conventional 400 by 20 mm Pyrex glass apparatus, with standard tapered joints at each end and a porous glass disc fused to the plug at the base of each column to support the packing. Packing, which initially consisted of glass beads approximately 0.1 mm in diameter, was replaced by Ottawa sand when the glass packing was found to have migrated into the lower joint during heating cycles, leading to solvent leakage. No apparent change in sample distribution among the test tubes of the fraction collector was observed after this alteration.

The thermal gradient in the degassing column is supplied by tightly wrapped aluminum foil heated by a tightly wrapped nichrome coil at the upper end and cooled by chilled water flowing through copper tubing at its base.

In the chromatographic column, the thermal gradient is supplied by a conductive jacket machined from 3 inch aluminum bar stock. Thermal insulation is provided by a 1 inch thick cylindrical jacket and end caps shaped from "Glassrock," a lightweight, commercially available foamed silica product. This column is heated

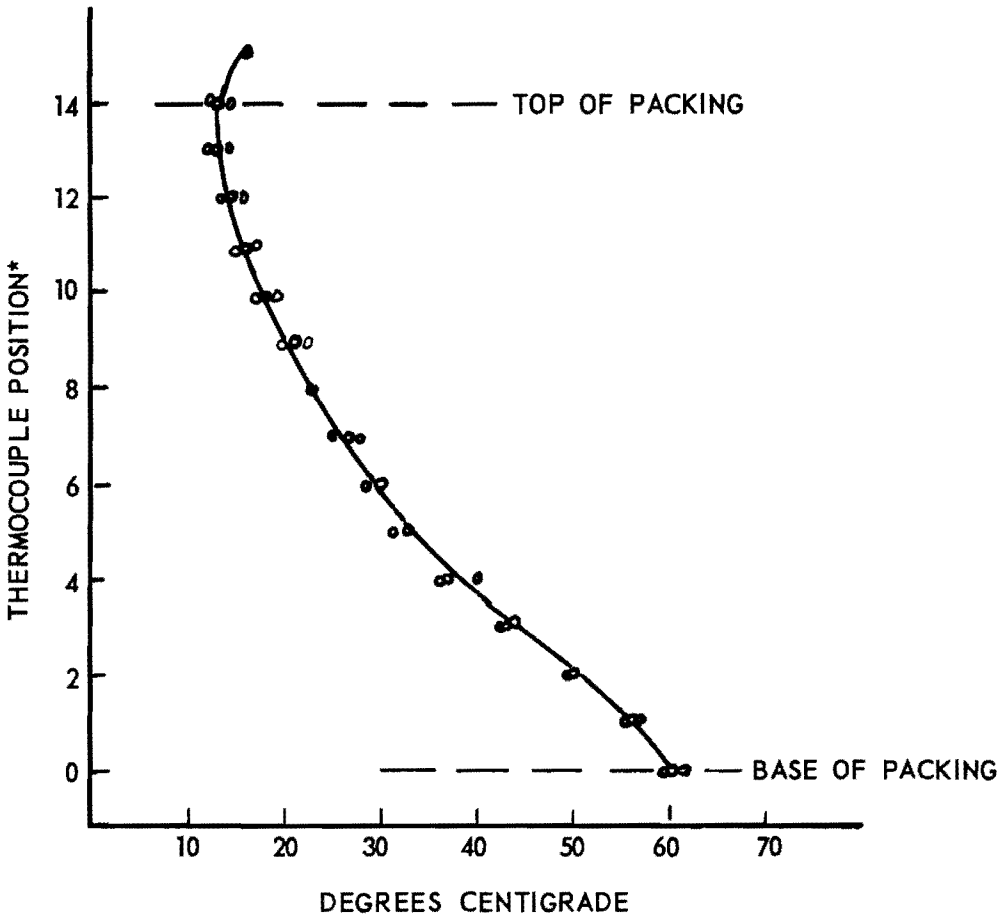
by a tightly wrapped nichrome coil at its base and cooled by chilled water flowing through copper coils extending approximately two-thirds of the way down the column, providing a thermal gradient in the cooling water paralleling that required in the column.

The heating elements are controlled by Thermistemp Model 63 thermoregulators; regulation of voltage to the heaters has proven adequate to maintain fixed temperatures in the columns without need for timed input controllers. Constant temperature cooling water is supplied by a two stage process. Tap water is cooled to approximately 10° C by mechanical refrigeration and passed through a coil in a chest cooled by dry ice immediately before entering the columns. The resulting temperature gradient inside the chromatographic column as measured with a copper-constantan thermocouple in a column packed with glass beads and a typical solvent is shown in Figure 8.

Of the several solvent-nonsolvent systems examined for use in generating a solvent gradient, the most satisfactory was chloroform and hexane. This system appeared to be capable of separating methyl methacrylate polymers in order of increasing molecular weight. A further advantage was that no precipitation of polymer in the volumetric siphon of the fraction collector was observed. It is believed that this advantage arose from preferential evaporation of the more volatile nonsolvent.

2. Preparation of Polymer Samples for Fractionation

Samples of polymer prepared by post-effect polymerization were weighed, dissolved in 50 ml methylene chloride, and placed in a 250 ml Teflon beaker with approximately 50 grams of 20 mesh Ottawa sand and a Teflon coated magnetic stirring bar. Each of the beakers was then placed on a magnetic stirrer and just sufficient hexane to cause a slight increase in viscosity of the solution was added. A loose fitting dust cover of aluminum foil was placed over the beaker, and the sample was



*Thermocouple position in inches from base of column packing.

Figure 8. Chromatographic Column Temperature Gradient.

allowed to precipitate with constant stirring on the sand at room temperature ($23^{\circ} \pm 3^{\circ}$ C). When evaporation of both solvent and hexane was complete, the sand was found to be a brittle, cohesive mass easily ground into 20 mesh particles with an ordinary mortar and pestle. This ground sample was poured on the sintered glass disc of the chromatographic column as the sample to be fractionated.

Similar treatment of polymer samples using chloroform rather than methylene chloride as the solvent component produced a tough, tightly bound mass, which could not easily be ground. This difference in behavior was taken to suggest that the polymer was gradually precipitated from systems where the solvent is more volatile than the nonsolvent, but that it dries from a continuous phase in systems where the nonsolvent is the more volatile component. Samples generally consisted of 0.6000 gram of polymer.

3. Operation of Apparatus

A flow rate through the system of 60 ml per hour was maintained. Best separations were obtained with a 2 liter mixing chamber. Twenty milliliter fractions were separated by means of a volumetric siphon. Complete separation of inhibitor from polymer was achieved. The contents of the fraction collector tubes were filtered under reduced pressure into Teflon beakers and dried at 40° C. Polymer fractions from adjacent tubes were combined to make approximately 0.1 gram samples, which were reserved for examination of molecular weight distribution.

F. Molecular Weight Determination

1. Sample Preparation

The samples used for determination of viscosity average molecular weight were cut from the circular polymer films prepared after the extent of conversion

determination. Radial cuts were made to produce narrow, pie-shaped segments containing proportional amounts of material from both the center and the circumference of the material. The 0.1000 gram samples were placed in 10 ml Class A volumetric flasks, dissolved in 6 ml freshly distilled and dried reagent grade chloroform, and diluted to the mark with additional chloroform. The solutions were thoroughly mixed for 24 hours on a Burrell shaker.

In nine of the samples examined, the inhibitor was extracted from a methylene chloride solution of the methyl methacrylate polymer prior to drying and weighing out the viscosity sample. The extraction was accomplished by shaking the polymer solution with three portions of 1 per cent aqueous potassium hydroxide and decanting off the aqueous phase. The solution was then shaken with successive portions of distilled water until the washings remained clear.

2. Viscosity Determinations

The dissolved samples were filtered through sintered glass funnels into Series 50 Ostwald Cannon Fenske viscosimeters immersed in a constant temperature bath held at 25° C. Successive dilutions with chloroform after each determination of average flow time were made to obtain four or more concentrations for each sample. Observed data and calculated quantities are tabulated in Appendix C.

Table I presents a summary of experimental observations.

G. Miscellaneous Experiments

1. Polarized Light Microscopy

A Bausch and Lamb Dynoptic Model L polarizing microscope was used to examine samples for presence of a crystalline phase. No evidence of crystallinity was detected. This apparatus may also be used for determination of index of refraction by the Becke line method.

TABLE I. SUMMARY OF EXPERIMENTAL DATA

Sample No.	Dose (Rads x 10^{-5})	Post Effect Time (Hours)	Extent of Conversion (%)	Limiting Viscosity No.	Molecular Weight (x 10^{-5})	Remarks
C-1	1.9	0:00	2.1	.850	2.2	a
C-2	1.9	1:00	2.1	.889	2.3	a
C-3	1.9	4:00	3.5	1.470	4.4	a
C-4	1.9	4:00	1.6	--	---	a,g
C-6	1.9	4:00	2.3	1.368	4.1	a
C-5	1.9	24:00	2.1	--	---	a,e,g
C-9	1.9	24:00	2.2	1.392	4.2	a
A-1	3.8	0:00	7.2	.652	1.5	a
D-1	3.8	0:00	6.6	.620	1.4	a
A-2	3.8	0:30	7.7	--	---	a,g
A-3	3.8	1:00	7.4	.813	2.0	a
D-2	3.8	1:00	10.6	.718	1.7	a,f
E-4	3.8	4:00	7.0	1.258	3.8	b
E-6	3.8	4:00	7.5	.751	1.9	b,d
D-12	3.8	18:00	10.7	2.26	7.6	b,f
A-5	3.8	24:00	9.0	1.67	4.6	b
E-7	3.8	48:00	7.3	.720	1.7	b,c
D-13	3.8	24:00	9.5	1.65	5.1	b
D-11	3.8	48:00	6.6	.602	1.4	b,e
E-8	3.8	48:00	9.2	1.87	6.1	b
E-9	3.8	48:00	9.5	1.80	5.8	b
D-4	3.8	48:00	9.6	1.86	6.1	b
G-3	3.8	72:00	9.2	1.15	3.2	b
G-4	3.8	72:00	9.4	1.58	4.9	b
G-1	3.8	96:00	8.6	1.10	3.0	b
G-2	3.8	96:00	8.1	.951	2.5	b
B-1	5.8	0:00	12.9	.613	1.4	a
D-3	5.8	0:00	12.8	.620	1.4	a
F-3	5.8	0:00	11.8	.553	1.3	a,d
B-3	5.8	1:00	---	1.19	3.4	a,c,d
C-11	5.8	1:00	31.1	.690	1.6	a,f
F-4	5.8	1:00	12.3	.621	1.4	a,d
B-5	5.8	3:00	14.6	1.29	3.8	a
E-2	5.8	4:00	11.4	.848	2.1	b,c
E-3	5.8	4:00	13.8	.918	2.5	b
D-8	5.8	4:00	15.0	.710	1.7	b
B-6	5.8	24:00	17.2	1.89	6.3	a,f
D-10	5.8	24:00	12.9	1.34	3.9	a,f
F-1	5.8	48:00	14.0	1.27	3.6	b,d
D-5	5.8	48:00	14.3	1.49	4.4	b

(Continued)

TABLE I. SUMMARY OF EXPERIMENTAL DATA (Continued)

Sample No.	Dose (Rads x 10^{-5})	Post Effect Time (Hours)	Extent of Conversion (%)	Limiting Viscosity No.	Molecular Weight (x 10^{-5})	Remarks
F-2	5.8	48:00	15.0	1.08	3.1	b
F-6	5.8	72:00	15.6	2.09	7.1	b,d
F-9	5.8	72:00	14.0	1.62	5.1	b,d,e
G-16	5.8	96:00	14.6	.695	1.7	b,e
G-17	5.8	96:00	16.1	1.53	4.7	b
G-18	5.8	120:00	14.5	1.13	3.1	b,e
G-5	5.8	194:00	11.9	1.08	3.0	b,e
G-6	5.8	194:00	15.6	1.43	4.1	b
C-13	8.7	0:00	30.1	.610	1.4	a
F-5	8.7	0:00	19.1	.618	1.4	a,d
C-10	8.7	0:00	20.0	.618	1.4	a
C-12	8.7	1:00	18.9	.648	1.4	a
D-6	8.7	4:00	21.9	.722	1.7	b
D-7	8.7	4:00	21.7	.768	1.9	b
C-7	8.7	24:00	23.8	1.98	6.5	b
C-8	8.7	24:00	25.4	1.37	4.2	b
F-7	8.7	72:00	23.5	1.82	5.3	b,d
F-8	8.7	72:00	23.9	1.18	3.2	b,d
F-9	8.7	72:00	14.0	1.62	5.1	b,c,d
G-7	8.7	96:00	25.9	1.13	3.1	b
G-8	8.7	96:00	23.6	1.37	4.1	b
G-10	8.7	96:00	24.7	1.02	2.8	b
G-11	8.7	96:00	25.6	1.57	4.9	b
G-12	8.7	120:00	23.0	1.05	2.0	b,c
G-13	8.7	120:00	23.6	.881	2.3	b
G-14	8.7	168:00	22.7	1.10	3.1	b,c
G-15	8.7	168:00	25.1	1.38	4.1	b
G-9	8.7	194:00	26.9	1.94	6.3	b
E-1	9.6	0:00	23.6	.618	1.4	a

Explanation of remarks:

a. Room temperature quench
b. Cold quench
c. Portion of sample lost during transfer from irradiation vessel
d. Inhibitor extracted from polymer
e. Inhibition of reaction by atmospheric oxygen suspected
f. Chemical catalysis of polymerization suspected
g. Irreproducible reduced viscosity plot

2. X-Ray Diffraction

No evidence of crystallinity was observed in x-ray diffraction studies of several of the polymer films; i.e., no diffraction pattern was observed.

3. Tempering Polymer Films

Samples of polymerized methyl methacrylate representing several initiating doses and post-effect times were dissolved in chloroform, placed on strips of Teflon or aluminum foil, and allowed to dry. The strips bearing the dried samples were covered with hexane containing 2 per cent chloroform or toluene and allowed to swell overnight in tightly closed containers. After drying and stripping, the samples revealed no indication of crystallinity under polarized light microscopy.

H. Outline of Calculations

1. Electron Density Factor for Absorbed Dose

Ferrous ion dosimetry measurements of the exposure cells of the Cesium 137 Irradiator are made periodically by personnel of the Radioisotopes Laboratories. The radiation dose absorbed by the monomer samples is derived from the most recent of these measurements. The calculations are as follows:

Absorbed dose in ferrous ion solution	$= 4.16 \times 10^{19}$ ev $gm^{-1} hr^{-1}$*
Moles electrons $liter^{-1}$ of ferrous ion solution	= 567.52*
Density of methyl methacrylate at 35° C (experimentally)	= 0.9218

* Data furnished by Radioisotopes Laboratory.

Moles MMA monomer liter^{-1}

$$\frac{\text{Weight of liter of MMA}}{\text{Molecular Weight of MMA}} = \frac{921.6}{100.11} = 9.208$$

Moles of electrons liter^{-1} of MMA

$$= 54 \times 9.208 = 497.23$$

$$\frac{\text{Dose absorbed by MMA}}{\text{Dose absorbed by ferrous solution}} = \frac{497.23}{567.52^{*}} = 0.876$$

Conversion to rads is accomplished by the factor:

$$1 \text{ rad} = 6.25 \times 10^{13} \text{ ev gm}^{-1}$$

2. Molecular Weight

Calculation of polymer molecular weights has been based on observation of dilute solutions of the polymer in chloroform at 25° C, using the formula suggested by Weakley, Williams, and Wilson.[67]

$$\eta_{CHCl_3} = 6.6 \times 10^{-5} M_w^{0.77} \qquad (1)$$

where Mw is the viscosity average molecular weight ($\bar{M}v$) and η is the limiting viscosity number of the polymer sample. The quantity η is defined by the relation:

$$\eta_{CHCl_3} = \lim_{C \to 0} \eta r = \lim_{C \to 0} \frac{\eta obs - \eta o}{\eta o C} \qquad (2)$$

where ηr, ηobs, and ηo refer to reduced viscosity, solution viscosity, and solvent viscosity, respectively; and C refers to the concentration of polymer in grams per 100 ml of solution. The quantity η_{CHCl_3} was, of course, obtained graphically. As the measured density of 1 per cent solutions of polymethyl methacrylate in chloroform approached that of the solvent in ten determinations, the ratio of solution density to solvent density was taken to be unity and was not regarded in the calculations. Kinematic corrections were omitted.

Experimentally, the flow time of a 1 per cent solution of methyl ether of hydroquinone in chloroform in a Series 50 Ostwald-Cannon Fenske viscosimeter was found to differ by less than 0.5 second from the flow time of chloroform alone. It was, therefore, possible to define an arithmetical correction factor to be applied to the term C in Equation (2) rather than to attempt physical separation of inhibitor from polymer. The concentration term used in calculating intrinsic viscosity is $C_{corrected} = C_{apparent} \times \frac{\text{Wt. of polymer}}{\text{Wt. of polymer+inhibitor}}$ where $C_{apparent}$ represents grams per 100 ml of unseparated polymer and inhibitor. The weights of polymer and inhibitor are obtained from the gravimetric conversion determination and the known amount of methyl ether of hydroquinone in the quenching solution.

III. DISCUSSION

A. General Considerations

1. Objective

The overall objective of this study has been to apply the technique of "post-effect" polymerization to an examination of the kinetics of vinyl polymerization.

2. Definition of Method

The technique of "post-effect" polymerization consists of exposing a monomer to an initiating dose of ionizing radiation and following the reaction subsequent to irradiation by quenching the samples with a chemical inhibitor after various times and comparing the properties of these samples with those of similar samples quenched immediately after irradiation. As all of the primary radicals are formed during the initiation step, subsequent changes in the nature of the polymer can occur only by growth of polymer chains initiated during the irradiation step or by chain transfer. It is thus impossible to make a physical separation of "post-effect" polymer from that formed during irradiation. In view of the high radiation dose rates and high conversions necessary in this study, appeal must be made to the detailed kinetic scheme rather than the simplified scheme in interpreting observed phenomena. Parts of the detailed kinetic scheme are attached to this report as Appendix B.

3. Evaluation of Method

The use of post-effect polymerization after gamma ray initiation as a method for kinetic study offers several advantages over other means of initiation.

(1) Chemical contamination, stereospecificity, and runaway exotherm associated with chemical catalysis are avoided.

(2) Active sites are uniformly distributed throughout the reaction mass, i.e., surface effects associated with photolysis or thermal initiation do not obscure the bulk reaction.

(3) Polymer degradation associated with full term irradiation is avoided.

The principal disadvantages of the method are:

(1) A portion of the polymer formed during the early part of the initiating step is necessarily degraded during irradiation to a dose level sufficiently high to sustain an appreciable post-effect reaction.

(2) Care is necessary to prevent settling of the more dense polymer, which would destroy the homogeneous distribution of active sites throughout the reaction mass.

It is believed that these disadvantages are tolerable so long as the observed properties of mixtures containing post-effect polymer are compared to those of polymers quenched immediately after similar irradiation and provided that the vessels are turned frequently to avoid extensive settling.

4. Gel Effect

The feasibility of this study rests almost entirely on a gel effect, of which the free radical polymerization of methyl methacrylate is a frequently cited example.[53] This effect has been observed as an acceleration in rate of polymerization at low initiating dose rates and as the appearance of a rise in viscosity accompanying increased reaction rate (Trömmsdorff region) at higher conversions.[14] It has been shown that the destruction of free radicals can be accomplished only by interaction of pairs of free radicals.[5,56] For a given monomer, increasing viscosity with increasing conversion reduces the probability of collision of two active chain ends by reducing the mobility of the growing polymer chains. The controlling factors

are apparently the molecular weight of the polymer formed during the first part of the reaction and the temperature.[4,5,6,14,49,53] With rising viscosity, the rate of reaction passes from activation control to diffusion control with K_t (see Appendix B) decreasing first, but with a drop in K_p at conversions above 50 per cent.[41] At sufficiently high conversions the rate of propagation approaches zero, and both radical chains and the remaining monomer are trapped in the glassy system. This limiting conversion is related to reaction temperature. Above the second order transition temperature complete conversion can be attained. Addition of a good solvent also allows polymerization to approach 100 per cent.[14,49,53]

The principal consequences of this gel effect are:

(1) Increased lifetime of the kinetic chains and a conspicuous post-effect.[14]

(2) Concentration dependence as well as temperature dependence of the "rate-constants."[14]

(3) Change in the reaction order of chain termination from 2 to 1 as viscosity rises with extent of polymerization.[14]

B. Experimental Procedure

1. Selection of Monomer

The choice of methyl methacrylate as the monomer for initial study was based on the abundance of literature on its polymerization by several methods. It was further desired to select a relatively simple system for kinetic study. The following properties of methyl methacrylate were of particular interest:

(1) Chain termination occurs to a large extent by disproportionation.[14]

(2) A marked gel effect is observed, particularly at low temperatures and low conversions.[14,49]

(3) G_r (r = primary free radical) values for polymer and monomer should lie reasonably close to each other, as the double bond in the monomer is not conjugated with the rest of the molecule.[14]

(4) As the polymer is of the degrading type, chain scission on radiolysis rather than cross linking occurs. Some branching does occur from initiation by polymeric free radicals.[6,14,55]

2. Nature of Reaction

Experimental evidence indicates that the gamma ray induced polymerization of methyl methacrylate meets the necessary criterion of being accomplished by a free radical mechanism. The reaction is inhibited by dissolved oxygen, hydroquinone, and methyl ether of hydroquinone. Dissolved oxygen in the monomer is believed to give rise to several of the low conversion rates reported in Table I, and the need for its exclusion is reflected in the design of irradiation vessels as well as in monomer preparation procedures. Lack of evidence of crystalline structure by both x-ray diffraction and polarized light microscopy suggests atactic polymer, which, in turn, suggests free radical mechanism. The duration of the post-effect reaction is also evidence of a free radical mechanism, due to the brief half-life of ionic species.

3. Extent of Polymerization

The low per cent polymerizations suitable for measurement by dilatometry were not followed by an appreciable post-effect reaction. Extent of polymerization for all of the experiments summarized in Table I was estimated gravimetrically. To avoid thermal degradation of the polymer, evaporation and drying were conducted *in vacuo* at temperatures below 40° C. Some increase in extent of polymerization may have resulted from stirring the reaction mass into benzene solutions of inhibitor,

although it is not believed that the observed extent of polymerization was greatly increased in samples quenched immediately after irradiation. Increase in polymerization on addition of solvent to a more viscous mixture, notably reaction mixtures after post-effect times exceeding 4 hours, has been conspicuous. The effect of cold quenching on observed extent of polymerization is not precisely known, as no means to effect quantitative transfer of a gelled reaction mixture from its irradiation vessel into an evaporating flask containing the inhibitor solution without first freezing the reaction mixture has been devised.

Examination of the extent of conversion data in Table I indicates less than satisfactory reproducibility among samples after similar initiating doses and post-effect times. Low results are attributed to the presence of dissolved oxygen in the system, while the anomolously high conversions may arise from settling of the polymer and a resultant active gelled phase in the lower portion of the container. This latter effect has been observed as a viscosity gradient in containers which had not been inverted frequently during long post-effect times.

The duration of the post-effect reaction appears to increase with total initiating dose. While reaction appeared to be complete within 4 hours following a dose of 1.9×10^5 rads, increases in extent of conversion were observed after 24 hours, 48 hours, and 72 hours following doses of 3.8, 5.9, and 8.7×10^5 rads, respectively. The maximum ratio of post-effect polymer to polymer formed during irradiation rose with increasing dose, reaching a ratio of approximately 1:4 seven days after an initiating dose of 8.7×10^5 rads.

The approximate extents of polymerization on samples quenched immediately after irradiation were 6.9, 12.9, 19.9, and 23.6 per cent following doses of 3.8, 5.8, 8.7, and 9.6×10^5 rads, respectively. This nearly linear dependence

of extent of polymerization on total dose suggests that a high concentration of free radicals was achieved during the early stages of irradiation and remained nearly constant. The molecular weights of all of these samples was estimated to be $1.4 \pm 0.1 \times 10^5$; i.e., the molecular weight was within the limits of experimental error, independent of dose.

Application of the detailed kinetic scheme (Appendix B) to these results suggests that a large number of the primary free radicals generated have been consumed in manners other than by initiation of growing polymer chains. As G_r (polymer) is nearly identical to G_r (monomer), it is reasonable to assume that the rate of free radical initiation has remained constant during irradiation. G_r is a symbol for the number of primary free radicals produced by 100 ev of absorbed radiation. Recombination of primary free radicals would contribute least to increasing chain length and increasing extent of polymerization. Termination of growing polymer chains by primary free radicals would also depress both extent of polymerization and molecular weight. A high concentration of primary free radicals would also favor addition of primary radicals to monomer, leading to initiation of a large number of growing chains to compete for available monomer with a consequent tendency toward low molecular weights but with little effect on extent of conversion.[15] A similar effect would arise from chain transfer. Finally, scission of polymer chains during radiolysis would contribute to a decrease in molecular weight, as the chain fragments would favor disproportionation rather than recombination. At a dose rate of 160 rads/sec and at a temperature of 35° C, viscosity average molecular weights of 140,000 can only be attributed to depression of mutual chain termination rate and some enhancement of the ratio of propagation to termination rate by rising viscosity.

4. Molecular Weights

Molecular weights in Table I were estimated by viscosimetry in chloroform solutions at 25° C. The values for the lower molecular weights are believed to be reasonably accurate. For higher molecular weights, the slope of the reduced viscosity vs concentration curve became steep and introduced an element of uncertainty in the intercept or limiting viscosity number from which the $\bar{M}_v$ (viscosity average molecular weight) values were calculated. Use of solvents other than chloroform may be desirable for determining the higher molecular weights.[21,22,34] In contrast to the marked similarity of $\bar{M}_v$ values for polymers quenched immediately after irradiation are the somewhat irregular $\bar{M}_v$ values observed in samples irradiated for identical periods and quenched after several post-effect times. While the possibility of experimental error from dissolved oxygen or polymer settling cannot be ignored, there appear to be trends in the data which suggest kinetic effects. In comparing $\bar{M}_v$ data after 4 hour post-effect times, there was an apparent decrease in $\bar{M}_v$ corresponding to increasing initiating dose. This observation suggests a decrease in rate of propagation with rise of viscosity. Similar molecular weights immediately after irradiation and a negligible concentration of primary free radicals during the post-effect time are assumed. After standing 24 hours, this inverse relation of $\bar{M}_v$ and initiating dose disappears, and $\bar{M}_v$ data, after decay of the post-effect reaction, appears to settle in the vicinity of 5×10^5 with occasional wide deviations which may arise from experimental error or from some unexplained characteristic of the reaction. Detailed study of these samples may throw further light on the cause and nature of these deviations.[27]

5. Fractionation of Polymer

Chromatography rather than fractional precipitation for separation of

fractions was chosen principally for its capability of continuous operation with minimal attention. Corollary benefits are that low molecular weight polymers are not lost through incomplete precipitation and that any number of adjacent fractions can be combined to produce a sample of usable size. The practicability of chromatographic separation of polymer samples in order of increasing molecular weight has been demonstrated by several investigators.[3,25,54,67] While the stereoregularity occurring in poly (methyl methacrylate) prepared by free radical mechanisms is an effective bar to separation of extremely narrow molecular weight fractions, this experimental handicap would be no worse in column chromatography than in fractional precipitation and possibly more tolerable because of the repeated reprecipitations in the solvent and thermal gradient.[3,20,22,23]

IV. CONCLUSIONS

1. Over the range of conditions studied, the molecular weight of polymers resulting from irradiation of bulk methyl methacrylate monomer is independent of total dose.

2. Extent of post-effect polymerization increases with total initiating dose.

3. The molecular weight of polymers after a 4 hour post-effect time decreases with total initiating dose.

4. An increase in the maximum molecular weight attained by the polymer after decay of the post-effect reaction with increasing initiating dose has not been observed.

V. RECOMMENDATIONS

1. Higher irradiation doses than those used in this study followed by longer post-effect times may provide more information on the rates of the several reactions competing in vinyl polymerization in viscous media.

2. Detailed study of the polymers formed, particularly with respect to molecular weight distribution and degree of branching, will provide some estimate of the ratio of chain scission to chain transfer reaction.

3. Study of the polymers formed during post-effect times at temperatures above and below 23° C may throw further light on the effects of viscosity on the competing reactions.

4. Consideration of "post-effect" polymerization as an economic means of manufacturing unique poly (methyl methacrylate) should be abandoned.

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B. Detailed Kinetic Scheme

Step	Rates
(a) Initiation	
$A \xrightarrow{h\nu} 2R^{\cdot}$	$R_i = \phi_A I[A]$
(b) Recombination of primary radicals	
$R^{\cdot} + R^{\cdot} \rightarrow R_2$	$K_{oo}[R^{\cdot}]^2$
(c) Addition to monomer	
$R^{\cdot} + M \rightarrow RM^{\cdot}$	$K_{po}[R\cdot][M]$
(d) Propagation	
$RM_n\cdot + M \rightarrow RM_{n+1}\cdot$	$K_p[RM\cdot][M]$
(e) Mutual termination	
1. Combination	
$RM_n^{\cdot} + RM_n \rightarrow P_{n+m}$	$K_t[RM\cdot]^2$
2. Disproportionation	
$RM_n^{\cdot} + RM_n^{\cdot} \rightarrow P_m + P_n$	$K_t[RM^{\cdot}]^2$
(f) Termination by primary radicals	
$RM_n\cdot + R^{\cdot} \rightarrow P_n$	$K_{to}[RM\cdot][R^{\cdot}]$

In this outline A is any substance in the reaction system, and $R^{\cdot}$ is a primary radical. M is the monomer, RM_n a growing polymer chain, and P_n a "dead" polymer. $\phi_A[A]$ is the rate (in moles per liter per unit radiation dose) of primary free radical production in the system and I is the dose rate. The reaction rate constants K_{oo}, K_{to} and K_t pertain to interaction of free radical pairs. These reactions require very low activation energies of the order of 0 to 2 Kcal/mole, and their rate constants have absolute values of the order of 10^6 to 10^9 liter $mole^{-1}$ sec^{-1}. The constants K_{po} and K_p refer to addition of a free radical to a vinyl double bond. Activation

energies for these reactions approximate 5 to 8 kcal/mole, and the absolute values of the rate constants are of the order of 10 to 10^3 liter $mole^{-1}$ sec^{-1}. Consideration of radical sizes and energies of activation indicates that

$$K_{oo} > K_{to} > K_t > > K_{po} > K_p \ .$$

Applying the usual steady state assumptions leads to an overall reaction rate expression

$$R = K_p[RM\cdot][M\cdot] \ . \qquad (1)$$

At low dose rates the expression

$$R = \frac{K_p}{K_t^{\frac{1}{2}}} R_i^{\frac{1}{2}} [M] \ , \qquad (2)$$

can be derived from Equation (1). The term "acceleration" refers to observed overall reaction rates higher than those predicted by Equation (2).

For higher dose rates, the overall polymerization rate becomes

$$R = \frac{K_{po}}{(2K_{oo})^{\frac{1}{2}}} \cdot \frac{K_p}{K_t^{\frac{1}{2}}} [M]^2 \left[\left(\frac{1 + 4K_{oo}R_i}{KP_o^{\ 2}[M]^2} \right)^{\frac{1}{2}} - 1 \right]^{\frac{1}{2}} \ . \qquad (3)$$

This equation permits the overall reaction rate to rise more slowly than $R_i^{\frac{1}{2}}$. In the limiting case for very high dose rates, the overall reaction rate can be shown to be

$$R = \frac{K_p K_{po}}{K_{to}} [M]^2 \ , \qquad (4)$$

and is independent of rate of initiation (R_i). This limiting case is reached only

where the concentration of primary radicals [R·] is very high, and the molecular weight of polymers formed in this case is extremely low.

The remaining step of importance in the system under investigation is the chain transfer reaction

$$(g) \qquad RM_n\cdot + SX \rightarrow RM_nX + S\cdot \qquad\qquad K_{tr} = [RM\cdot][SX].$$

In this relation SX may be any component of the system and X is the most labile atom in the molecule SX (H in methyl methacrylate).

From the rate equations summarized above, the following expressions for number-average degree of polymerization ($\overline{P}_n$) may be obtained. These expressions assume termination by disproportionation; for termination by combination, $\overline{P}_{n(\text{combination})}$ is equal to $2\overline{P}_n$.

Low dose rate, chain transfer neglected:

$$\overline{P}_n = \frac{R}{R_i} = \frac{K_p}{K_t^{\frac{1}{2}} R_i^{\frac{1}{2}}} [M] .$$

Low dose rate, chain transfer considered:

$$\frac{1}{\overline{P}_n} = \frac{K_t^{\frac{1}{2}}}{K_p} \cdot \frac{R_i^{\frac{1}{2}}}{[M]} + \frac{K_{trm}}{K_p} ,$$

where K_{trm} is the rate constant of transfer by the monomer.

Higher dose rate, chain transfer neglected:

$$\overline{P}_n = \frac{(2K_{oo})^{\frac{1}{2}}}{K_{po}} \cdot \frac{K_p}{K_t^{\frac{1}{2}}} \left[\left(1 + \frac{4K_{oo}R_i}{K_{po}^2 [M]^2} \right)^{\frac{1}{2}} - 1 \right]^{-\frac{1}{2}} .$$

Very high dose rate, terminations involve only free radicals:

$$\overline{P}_n = K_p \frac{K_{oo}^{\frac{1}{2}}}{K_{to}} \frac{[M]}{R_i^{\frac{1}{2}}} .$$

Details of this derivation are found in Chapiro's Radiation Chemistry of Polymeric Systems, pp. 132-138.[14]

C. EXPERIMENTAL DATA

Sample No.	Concentration in g/dl				Observed Flow Time (in seconds)				Observed Viscosity (in centipoise)				Products of Concentration x Solvent Viscosity				Reduced Viscosity			
C-1 (a)	.684	.547	.273	.137	213.2	203.6	163.5	146.2	.887	.847	.681	.608	.371	.296	.148	.074	.930	1.030	.939	.892
C-2 (a)	.639	.511	.256	.133	218.1	201.0	162.1	146.0	.908	.822	.675	.608	.346	.277	.139	.070	1.058	1.011	.957	.943
C-3 (c)	.792	.634	.317	.154	384.8	307.9	206.3	162.9	1.608	1.287	.862	.681	.429	.344	.172	.086	2.485	2.166	1.860	1.616
C-4 (a)	.925	.740	.370	.185	237.4	214.0	175.0	152.1	.988	.891	.728	.633	.501	.401	.201	.101	.890	.870	.925	.901
C-6 (a)	.708	.567	.283	.142	304.5	264.8	188.5	157.7	1.268	1.102	.785	.656	.384	.307	.153	.077	1.891	1.824	1.588	1.481
C-9 (a)	.698	.558	.279	.140	242.6	257.4	187.5	159.3	1.010	1.071	.780	.663	.378	.302	.151	.076	1.238	1.752	1.576	1.592
A-1 (a)	.706	.564	.452	.226	201.9	185.0	173.4	150.8	.840	.770	.722	.628	.383	.306	.245	.122	.778	.745	.735	.705
D-1 (a)b*	.873	.698	.349	.175	214.1	196.4	175.3*	158.5*	.891	.817	.667	.603	.473	.378	.189	.095	.738	.728	.661	.642
A-3 (a)c*	.712	.570	.456	.229	225.0	204.0	186.6	157.1	.937	.849	.777	.654	.389	.309	.247	.124	1.015	.994	.951	.903
D-2 (a)	.923	.739	.369	.185	227.4	207.0	165.7	148.1	.947	.861	.690	.616	.500	.401	.200	.100	.810	.796	.740	.740
E-4 (b)	.810	.405	.324	.162	333.2	226.2	207.3	173.5	1.267	.860	.789	.660	.439	.220	.176	.088	1.651	1.445	1.403	1.341
E-6 (b)	.807	.645	.323	.162	267.7	232.7	184.2	161.6	1.018	.885	.701	.615	.437	.350	.175	.088	1.089	.980	.909	.830
D-12(a)	.840	.672	.336	.168	561.7	440.8	257.7	183.6	2.338	1.835	1.073	.764	.455	.364	.182	.091	3.947	3.552	2.918	2.440
A-5 (a)d**	.900	.720	.576	.128	107.7**	86.7**	73.1**	162.2	1.883	1.516	1.278	.675	.488	.390	.312	.063	2.748	2.497	2.359	2.111
E-7 (a)	.800	.640	.320	.160	213.7	197.6	161.3	145.6	.889	.823	.672	.606	.434	.347	.173	.087	.800	.810	.751	.735
D-13(b)	.841	.673	.337	.169	500.4	407.5	248.5	188.4	1.903	1.550	.945	.716	.456	.365	.183	.092	2.985	2.762	2.202	1.891
D-11(a)	.773	.618	.309	.155	217.7	189.0	158.1	142.9	.906	.787	.658	.595	.419	.335	.167	.084	.869	.731	.695	.631
E-8 (a)	.837	.669	.335	.168	426.0	350.1	228.8	174.9	1.773	1.457	.952	.728	.454	.363	.182	.091	2.711	2.521	2.253	2.044
E-9 (b)	.839	.672	.336	.168	505.8	411.7	252.6	192.5	1.924	1.566	.961	.732	.455	.364	.182	.091	3.037	2.813	2.302	2.088
D-4 (a)	.841	.672	.336	.168	495.2	396.6	237.3	176.7	2.061	1.651	.988	.735	.456	.364	.182	.091	3.331	3.047	2.451	2.121
G-3 (a)	.830	.664	.332	.166	301.1	259.5	187.4	157.6	1.253	1.080	.780	.656	.450	.360	.180	.090	1.580	1.494	1.322	1.267
G-4 (b)	.822	.675	.329	.164	455.1	373.3	239.5	186.8	1.733	1.420	.911	.711	.446	.366	.178	.089	2.670	2.399	2.073	1.899
G-1 (a)	.937	.749	.375	.187	304.6	265.3	189.5	158.8	1.267	1.101	.783	.661	.508	.406	.203	.102	1.427	1.377	1.187	1.167
G-2 (b)	.820	.656	.328	.164	291.0	262.1	195.2	166.7	1.106	.997	.743	.634	.444	.356	.178	.089	1.270	1.278	1.129	1.034
B-1 (a)c*	.934	.467	.233	.117	225.1	172.6	156.2	151.6*	.937	.719	.650	.634	.506	.253	.126	.063	.781	.700	.857	1.270
D-3 (b)	.930	.744	.372	.186	229.7	212.5	176.0	153.6	.874	.808	.669	.584	.504	.403	.202	.101	.659	.660	.629	.416
F-3 (a)	1.00	.800	.400	.200	211.9	194.6	160.5	145.4	.882	.810	.668	.605	.542	.434	.217	.109	.627	.618	.581	.578
B-3 (a)	.747	.478	.381	.095	260.8	213.3	195.4	145.2	1.086	.888	.813	.604	.405	.259	.207	.051	1.343	1.336	1.309	1.216
C-11(a)	.971	.776	.388	.194	232.2	210.1	167.9	148.2	.966	.875	.699	.617	.526	.420	.210	.105	.806	.793	.748	.714
F-4 (b)	1.00	.800	.400	.200	245.7	222.7	180.2	161.0	.934	.847	.686	.612	.542	.434	.217	.109	.723	.703	.664	.642
B-5 (a)	.731	.585	.470	.235	286.7	249.1	224.0	182.2	1.193	1.037	.932	.758	.396	.317	.255	.127	1.644	1.562	1.529	1.701
E-2 (b)	.858	.686	.343	.172	277.0	246.5	189.7	164.2	1.050	.938	.721	.624	.465	.372	.186	.093	1.366	1.065	.962	.882

C. EXPERIMENTAL DATA (Continued)

Sample No.	Concentration in g/dl				Observed Flow Time (in seconds)				Observed Viscosity (in centipoise)				Products of Concentration x Solvent Viscosity				Reduced Viscosity			
E-3 (a)	.877	.702	.351	.176	265.0	234.5	177.1	152.5	1.103	.976	.737	.635	.475	.380	.190	.095	1.181	1.142	1.021	.979
D-8 (b)	.892	.714	.357	.179	257.0	230.6	182.8	161.8	.978	.878	.695	.615	.483	.387	.193	.097	.903	.868	.793	.753
B-6 (d)	.947	.757	.606	.122	136.0	107.1	86.6	39.5	2.378	1.873	1.514	.691	.513	.410	.328	.066	3.579	3.246	2.963	2.258
D-10(b)	.873	.698	.349	.175	401.1	334.2	223.8	179.9	1.525	1.271	.851	.684	.473	.378	.189	.095	2.078	1.929	1.635	1.495
F-1 (a)	1.00	.800	.400	.200	365.3	306.3	207.4	166.1	1.521	1.275	.863	.692	.542	.434	.217	.109	1.806	1.689	1.479	1.376
D-5 (a)	.893	.714	.357	.179	410.5	338.5	215.7	168.8	1.709	1.409	.898	.702	.484	.387	.193	.097	2.411	2.240	1.850	1.649
F-2 (b)	1.00	.800	.400	.200	368.6	304.0	218.0	176.4	1.402	1.156	.829	.671	.542	.434	.217	.109	1.587	1.415	1.323	1.183
F-6 (a)	1.00	.800	.400	.200	671.9	525.4	281.6	195.3	2.797	2.187	1.172	.813	.542	.434	.217	.109	4.161	3.790	2.903	2.486
F-9 (b)	1.00	.800	.400	.200	536.6	439.8	264.1	196.4	2.041	1.672	1.064	.747	.542	.434	.217	.109	2.766	2.604	2.129	1.881
G-16(a)	.887	.709	.355	.177	290.1	199.8	163.4	146.4	1.207	.832	.680	.610	.481	.384	.192	.096	1.383	.755	.719	.708
G-17(b)	.898	.718	.359	.175	439.8	368.4	237.0	186.3	1.673	1.401	.901	.708	.487	.389	.195	.098	2.322	2.208	1.841	1.694
G-18(b)	.894	.715	.357	.179	359.9	307.7	214.8	175.5	1.369	1.170	.817	.668	.485	.388	.194	.097	1.705	1.619	1.418	1.299
G-5 (a)	.858	.686	.343	.172	291.5	254.4	185.3	156.6	1.213	1.059	.771	.652	.465	.372	.186	.093	1.443	1.340	1.231	1.183
G-6 (a)	.888	.710	.355	.178	384.3	316.0	208.7	166.2	1.600	1.315	.869	.691	.481	.385	.192	.096	2.200	2.008	1.703	1.552
C-13(a)b*	.969	.775	.387	.194	216.0	199.2	162.2	160.1*	.899	.829	.675	.609	.525	.420	.210	.105	.680	.683	.633	.638
F-5 (a)	1.00	.800	.400	.200	216.6	198.4	162.5	146.6	.902	.826	.676	.610	.542	.434	.217	.109	.664	.654	.618	.624
C-10(a)	.953	.762	.381	.191	212.5	195.8	180.9	146.0	.885	.815	.753	.608	.517	.413	.207	.104	.663	.661	1.019	.635
C-12(a)	.950	.760	.380	.140	222.7	200.9	163.0	146.2	.927	.836	.679	.609	.515	.412	.206	.103	.748	.714	.665	.650
D-6 (b)	.928	.742	.371	.186	259.1	230.3	183.0	162.5	.985	.876	.696	.618	.503	.402	.201	.101	.881	.831	.766	.752
D-7 (a)	.921	.737	.368	.184	238.3	215.4	169.2	149.6	.992	.896	.705	.623	.499	.399	.199	.100	.902	.887	.819	.810
C-7 (a)b*	.960	.768	.384	.192	662.4	514.9	299.5*	196.3	2.758	2.144	1.139	.817	.520	.416	.208	.104	4.262	3.850	2.870	2.644
C-8 (a)	.964	.771	.386	.193	357.8	305.9	206.4	167.3	1.489	1.273	.859	.696	.522	.418	.209	.105	1.814	1.479	1.517	1.467
F-7 (a)	1.00	.800	.400	.200	568.4	449.7	256.7	185.6	2.366	1.872	1.068	.772	.542	.434	.217	.109	3.365	3.065	2.424	2.110
F-8 (b)	1.00	.800	.400	.200	360.1	308.2	216.2	178.0	1.370	1.172	.822	.677	.542	.434	.217	.109	1.528	1.452	1.290	1.239
F-9 (b)	1.00	.800	.400	.200	536.6	439.8	264.1	196.4	2.041	1.673	1.004	.747	.542	.434	.217	.109	2.766	2.606	2.129	1.881
G-7 (b)	.940	.752	.376	.188	345.3	296.1	214.7	175.3	1.313	1.127	.817	.667	.509	.408	.204	.102	1.515	1.434	1.348	1.225
G-8 (b)	.928	.742	.371	.186	405.7	340.7	227.8	182.0	1.543	1.296	.867	.692	.503	.402	.201	.101	1.990	1.876	1.617	1.485
G-10(b)	.928	.742	.371	.186	313.7	275.2	201.8	170.8	1.193	1.047	.767	.650	.503	.402	.201	.101	1.294	1.256	1.119	1.069
G-11(a)	.934	.747	.373	.187	402.6	335.6	218.9	171.6	1.676	1.397	.911	.714	.506	.405	.202	.101	2.241	2.111	1.826	1.703
G-12(a)	.930	.744	.372	.186	284.1	250.6	184.5	145.7	1.182	1.043	.768	.606	.504	.403	.202	.101	1.270	1.243	1.119	.634
G-13(b)	.925	.740	.370	.195	281.3	252.9	193.5	166.5	1.070	.962	.736	.633	.501	.401	.201	.100	1.054	1.002	.965	.910
G-14(a)	.858	.686	.343	.172	288.3	255.4	185.4	156.5	1.200	1.063	.772	.651	.465	.372	.186	.093	1.415	1.401	1.237	1.172
G-15(b)	.934	.747	.374	.187	420.1	354.6	231.7	184.8	1.598	1.348	.881	.703	.506	.405	.203	.102	2.087	1.990	1.670	1.578
G-9 (a)	.937	.750	.375	.187	534.7	433.0	253.2	185.3	2.263	1.802	1.054	.771	.508	.407	.203	.102	3.388	3.096	2.522	2.216
E-1 (a)	.962	.770	.385	.193	225.5	207.2	165.3	146.4	.939	.862	.688	.609	.521	.417	.209	.105	.762	..767	.699	.638

(a) to = 130.2 sec.
(b) to = 142.5
(c) to = 129.7
(d) to = 31.0

*,** More than one viscosimeter used.