

PHYSICAL PROPERTIES AND
STRUCTURAL CHARACTERISTICS OF
POLYMERS RESULTING FROM
"POST-EFFECT" POLYMERIZATION

by

W. H. BURROWS

Project A-446-10

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, 1962-63

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Elston, L. W. and Burrows, W. H.
March 1, 1962--October 31, 1963.

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

April 5, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 1, Project No. A-446-10
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post-Effect' Polymerization"
Contract No. AT (38-1)-202, Task No. X
Covering the Period from March 1 to March 31, 1962.

Gentlemen:

The objectives of this research program are to study the effects of temperature, concentration of monomer, concentration of polymer, dose, etc., on the molecular weights, degree of branching of polymers, and tacticity of the polymer chains resulting from "post-effect" polymerization of monomers such as methyl methacrylate, vinyl pyrrolidone, etc. Monomers will be exposed to brief initiating doses of gamma radiation. At time intervals thereafter, samples will be withdrawn, quenched, and studied as to the following characteristics: extent of polymerization, distribution of molecular weights, determination of molecular weights, branching and cross-linking, crystallinity, specific volume and coefficient of thermal expansion melting point, and morphology.

I. Literature Survey

During the subject period, a survey has been conducted of background material on polymerization, chemical kinetics, and techniques of separating and characterizing polymer fractions. It is intended that this survey will continue throughout the duration of this project, with special attention being given to current literature.

II. Apparatus and Equipment

Vessels for use in exposing the monomer samples to irradiation in the Georgia Tech Cesium 137 Irradiator have been designed, and will be fabricated in the shop of the Engineering Experiment Station. Materials for these vessels are readily available.

April 5, 1962

Apparatus for the chromatographic separation of polymer fractions, utilizing a thermal gradient column, has been designed. This apparatus will be assembled from commercially available glassware, currently on order.

III. Experimental Procedures

Initial experimental work will be directed toward familiarizing project personnel with separation techniques using commercial polymer samples, and toward modification of the apparatus and experimental procedures to secure narrow ranges of molecular weight distributions in the separate chromatographic fractions. An automatic fraction collector will be employed to achieve uniformity of fraction size and to permit freedom of personnel time for concurrent procedures, such as viscosimetry, microscopy, and preparation of samples for infrared spectroscopy.

Preparation and irradiation of samples for "post-effect" studies will begin as soon as the effects of variables in the separation and characterization techniques have been established.


IV. Future Plans


It is expected that the experimental program for the first phases of this project will be under way by the end of the next report period.


V. Personnel

Personnel assigned to this project at present are W. H. Burrows, Project Director, and Lewis W. Elston, Assistant Research Chemist.

Respectfully submitted,


W. H. Burrows
Project Director

Approved: 


Watt C. Whitley, Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

April 30, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 2, Project No. A-446-10
"Physical Properties and Structural Characteristics of Polymers
Resulting from 'Post Effect' Polymerization"
Contract No. AT (38-1)-202, Task No. X
Covering the Period from April 1 to April 30, 1962

Gentlemen:

The research program for the subject period has been largely a continuation of the work of the initial period.

I. Literature Survey

The literature survey has been continued into the subject period, with special attention and study being given to laboratory techniques for sample preparation, separation of polymer fractions, and characterization of the separated fractions.

After experimental work has begun, emphasis on techniques will be reduced, and the literature on chemical kinetics and polymerization mechanisms will be given increased attention. Survey of current literature in all pertinent fields will be a part of the continuing program of research. It is anticipated that a bibliography of reference material pertinent to this problem will be included in a future report.

II. Apparatus and Equipment

A portion of the laboratory equipment and supplies ordered during the first report period has been received. Apparatus for chromatographic separation of polymer fractions is being assembled. This apparatus consists principally of (1) a flask and reservoir for generation of a solvent gradient, (2) a downward flowing solvent degassing column, (3) an upward flowing column for separation of polymer fractions, and (4) a Rinco automatic fraction collector suitable for either timed or volume controlled cycling.

Both the degassing and chromatographic columns will be jacketed with approximately 10 pounds of tightly wrapped aluminum foil, heated at the top by electric heating tapes, and cooled at the bottom by tap water flowing through copper coils.

Each column assembly with its jacket, heater, and cooling coil will be insulated with phenolic foam material and an outer wrapping of aluminum foil. The larger components of the system have been connected by ball and socket joints to permit rapid apparatus setup and to reduce strain between consecutive members.

III. Experimental Procedures

Experimental work has been deferred during the subject period, awaiting arrival of essential equipment. It is hoped that assembly, adjustment, and calibration of equipment will have progressed sufficiently to permit initiation of familiarization experiments during the next report period.

IV. Future Plans

Assembly of apparatus will be carried forward to permit the earliest possible beginning of experimental work.

Respectfully submitted,

A solid black rectangular redaction box covering the signature of the project director.

W. H. Burrows
Project Director

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

June 30, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 3, Project No. A-446-10
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post Effect' Polymerization"
Contract No. AT (38-1)-202, Task No. X
Covering the Period from June 1 to June 30, 1962

Gentlemen:

The research efforts begun in the earlier project periods have been carried forward; however, delay in delivery of key items of apparatus has compelled a temporary reduction in the rate of experimental effort. Every effort is being made to overcome this delay, and it is anticipated that the rate of progress in this study can be accelerated to reach the original planned achievement level within the next two progress periods.

I. Literature Survey

The literature search carried out during the first three project periods has been continued. Of particular interest have been recent papers dealing with polymerization mechanisms, influence of initiating conditions on polymer morphology, and dosimetry. Representative literature is as follows:

- a. Banford, C. H., A. D. Jenkins, and J. C. Ward, "Polymerization in the Solid and Near-Solid States," J. Polymer Sci. 48, 37-51 (1960).
- b. Glusker, D. L., E. Stiles, and B. Yoncoskie, "The Mechanism of the Anionic Polymerization of Methyl Methacrylate. I. Quantitative Determination of Active Chains Using Radioactive Terminators," J. Polymer Sci. 49, 297-313 (1961).
- c. Glusker, D. L., I. Lysloff, and E. Stiles, "The Mechanism of the Anionic Polymerization of Methyl Methacrylate. II. The Use of Molecular Weight Distributions to Establish a Mechanism," J. Polymer Sci. 49, 315-334 (1961).
- d. Johnson, T. R. and J. J. Martin, "Benzene in Water Is Simple, Reliable Gamma Dosimeter," Nucleonics 20, 83-4 (1962).

- e. Küssler, I. and J. Kreisa, "Thermodiffusion Fractionation of Polymethyl Methacrylate and Determination of Molecular Weight Distribution," J. Polymer Sci. 57, 509-515 (1962).
- f. Natta, C., "Stereospecific Polymerizations," J. Polymer Sci. 48, 219-39 (1960).
- g. Magat, M., "Influence des Rayonnements Ionisants sur les Systemes Polymerisables," J. Polymer Sci. 48, 379-91 (1960).
- h. Magat, M., "Sur les Polymerisations Ioniques Amorcees par les Rayonnements Ionisants," Makromolekulare Chemie 35, 159-73 (1960).
- i. Nishioka, A., H. Watanabe, K. Abe, and Y. Sono, "Grignard Reagent-Catalyzed Polymerization of Methyl Methacrylate," J. Polymer Sci. 48, 241-72 (1960).

II. Apparatus and Equipment

Apparatus for chromatographic separation of polymer fractions has been assembled and tested for continuity of solvent flow and operation of the electrical components on hand. Equipment for purification of monomer and solvents has been reconditioned and assembled. On receipt of the thermistor probes required for regulation of the chromatographic columns, calibration of the equipment will quickly be completed.


III. Experimental Procedures

Lack of necessary temperature control equipment for the chromatographic apparatus has restricted experimental effort to examination of fractional precipitation techniques and to the casting and tempering of polymer films on aluminum foil. The scope of these familiarization experiments will be broadened as rapidly as possible.

IV. Future Plans

The literature survey will be continued. It is expected that early delivery of necessary equipment and accelerated experimental effort will permit completion of familiarization experiments and possibly initiation of monomer irradiation during the next report period.

Respectfully submitted,


W. H. Burrows
Project Director

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

July 31, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 4, Project No. A-446-10
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post Effect' Polymerization"
Contract No. AT (38-1)-202, Task No. X
Covering the Period from July 1 through July 31, 1962

Gentlemen:

Research efforts for the subject period have included (1) intensification of literature search, (2) checking and familiarization experiments with the chromatographic equipment, and (3) modification of equipment in the light of preliminary experiments.

I. Literature Survey

The literature search carried out during the earlier project periods has been continued. Effort has been divided about equally between older references giving detailed descriptions of laboratory findings and current literature describing both laboratory arts and theoretical discussions of the chemistry of methyl methacrylate polymerization.

II. Apparatus and Equipment

Examination of the temperature gradient in the chromatographic columns has indicated a need for refrigerated cooling water. A coil immersed in an ice bath is being used to permit column operation until a mechanically refrigerated water line can be installed. Prototype irradiation vessels of stainless steel with Teflon plugs have been fabricated.


III. Experimental Procedures

Familiarization experiments are being carried out to establish a laboratory routine capable of generating meaningful, reproducible data. A high boiling solvent system is being examined to reduce the tendency toward polymer precipitation in the siphon of the fraction collector. Standard techniques of polymer characterization are being explored using commercially available methyl methacrylate polymer.


IV. Future Plans

The literature survey will be continued. It is anticipated that familiarization experiments will be completed and monomer irradiation will be initiated during the next report period.

Respectfully submitted,


W. H. Burrows
Project Director

Approved:


Frederick Bellinger, Chief
Chemical Sciences and Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

September 30, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 5, Project A-446-10,
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post Effect' Polymerization"
Contract No. AT (38-1)-202, Task No. X
Covering Period from September 1 to September 30, 1962.

Gentlemen:

Research efforts for the subject period have included (1) continuation of the literature search, (2) completion and trial runs of the chromatographic equipment, (3) standardization of viscometers, and (4) modification of both equipment and laboratory procedures in the light of preliminary experiments.

I. Literature Survey

The literature search carried out during the earlier project periods has been continued. Several papers containing material of immediate interest in this study were given at the Atlantic City Meeting of the American Chemical Society. Copies of these papers have been requested.

II. Apparatus and Equipment

Construction and temperature calibration of the chromatographic equipment have been completed. A mechanical cooling system has been installed to supply water chilled to 5° C. Further cooling is provided by passing the water through a coil immersed in an ice bath immediately before admission to the coils surrounding the chromatographic column. A flash evaporator is being obtained to reduce the time necessary to remove solvent from the eluted polymer.

III. Experimental Work

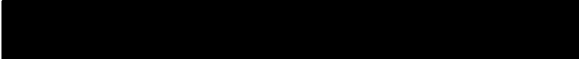
A sample of commercial methyl methacrylate has been separated in the chromatographic apparatus using 3-heptanone as the elution solvent and hexane as a

nonsolvent. Several types of stopcock lubricant have been examined for sealants in the glass system. Satisfactory leak-free glass joints have been obtained with glycerol. Evaporation under reduced pressure has proven necessary to remove the high boiling solvent from the fractionated polymer. A second run using chloroform as the elution solvent is being made to examine the extent of solvent evaporation and the possibility of polymer precipitation in the siphon. Several viscometers calibrated with fluids supplied by the National Bureau of Standards have been used to determine apparent and intrinsic viscosities of commercial polymer samples. Viscometers having extremely fine capillaries are being examined to permit significant readings from solutions containing the small quantities of polymer eluted in chromatographic fractions.


IV. Future Plans

The literature survey will be completed. It is anticipated that familiarization experiments and necessary equipment modifications will be sufficiently advanced to permit initiation of irradiation experiments during the next report period.

Respectfully submitted,


W. H. Burrows
Project Director

Approved:


Frederick Bellinger, Chief
Chemical Sciences and Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

October 31, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 6, Project No. A-446-10
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post Effect' Polymerization"
Contract No. AT (38-1)-202, Task No. X
Covering the Period from October 1 to October 31, 1962

Gentlemen:

Research efforts for the subject period have included (1) review of current literature, (2) further trial runs of the chromatographic equipment, and (3) modification of both apparatus and procedures in the light of preliminary experiments.

I. Literature Survey

Review of the current literature to supplement the initial search is a continuing effort. Detailed study has been given to papers describing polymer characterization.

II. Apparatus and Equipment

A flash evaporator has been received and assembled to reduce the time necessary to remove solvent from the eluted polymer. A standard vacuum oven is also being used to permit simultaneous evaporation of several polymer fractions. A smaller vacuum evaporator is being obtained for use with tared flasks to determine directly the extent of polymerization in irradiated samples. A device for rapid filtration of polymer fractions through sintered glass directly into Teflon evaporating dishes has been constructed.

III. Experimental Work

Several solvent - non-solvent systems have been used to separate commercial polymer samples. A system of chloroform as the elution solvent appears to combine ease of evaporation at moderate temperatures with absence of polymer


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precipitation in the siphon. Substitution of "Teflon" tape for the aluminum foil conventionally used in film casting has improved ease of stripping and permitted a reduction in the thickness of the cast film. Delay in receipt of necessary standard fluids has temporarily interrupted calibration of viscometers capable of handling very dilute polymer solutions.


IV. Future Plans

Calibration of viscometers will be resumed upon delivery of the necessary standard fluids. Dosimetry in the irradiating vessels and irradiation experiments will be begun during the next report period. Familiarization and calibration experiments will be continued.

Respectfully submitted,


W. H. Burrows
Project Director

Approved:


Frederick Bellinger, Chief
Chemical Sciences and Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

November 30, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 7, Project No. A-446-10
"Physical Properties and Structural Characteristics
of Polymers Resulting from 'Post Effect' Polymerization"
Contract No. AT (38-1)-202, Task No. X
Covering the Period from November 1 to November 30, 1962

Gentlemen:

Research for the subject period has included (1) continued survey of current literature, (2) further trial runs and modification of equipment, and (3) development of techniques for characterization of the small polymer samples anticipated from the irradiation study.

I. Literature

Papers to be presented at the International Symposium sponsored jointly by the U. S. Atomic Energy Commission and Battelle Memorial Institute indicate that attendance at this meeting will be valuable to the progress of this study. Review of the current literature has been continued.

II. Apparatus and Equipment

A small rotating vacuum evaporator has been installed in a laboratory fume hood to permit quenching of the irradiated samples in a saturated solution of inhibitor (e.g. hydroquinone) in volatile solvent (e.g. benzene) without exposure of personnel to noxious methyl methacrylate fumes.

Rapid estimation of extent of polymerization is accomplished by use of tared flasks, requiring only a hexane rinse (to remove joint lubricant) and correction for the known weight of inhibitor.

The size of the mixing chamber on the chromatographic apparatus has been increased to improve polymer fractionation. A polarizing microscope is being obtained to permit study of crystalline structure in the separate polymer fractions.

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Godfrey molecular models are being employed to study structural characteristics of polymers.

III. Experimental Work

Calibration of viscometers to be used in this study has been completed.

Trial runs of the chromatographic apparatus have indicated that the entire 0.5 gm polymer sample is being delivered in only fifteen 20 ml fractions. A trial separation using a larger mixing vessel is now underway and is expected to reduce the solvent gradient and permit more precise separation of molecular weight fractions.


Brief (one hour) studies of the mildly acid ferrous ion dosimetry solution have revealed no obvious attack on the stainless steel irradiation vessels. Longer studies are underway.

A joint lubricant consisting of glycerol thickened with pyrogenic silica provides more resistance to solvent extraction and subsequent leakage than conventional stopcock greases or glycerol alone.


IV. Future Plans

Upon satisfactory completion of the chemical compatibility study of ferrous ion solutions in the irradiating vessels, dosimetry in the Georgia Tech 12,000 Curie Cesium 137 Irradiator and in the x-ray source will be initiated.

Respectfully submitted,


W. H. Burrows
Project Director

Approved:


Frederick Bellinger, Chief
Chemical Sciences and Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

December 31, 1962

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 8, Project No. A-446-10,
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post Effect' Polymerization"
Contract No. AT (38-1)-202, Task No. X
Covering the Period from December 1 to December 31, 1962

Gentlemen:

Research for the current period has included (1) continued survey of current literature, (2) further testing and modification of equipment, and (3) continued development of techniques for study of small polymer samples.

I. Literature

Review of the current literature has been continued. Several recent volumes on polymer characterization and polymerization have been acquired by the Price Gilbert Memorial Library. Professor A. Chapiro's Radiation Chemistry of Polymeric Systems, Interscience (1962) has been placed on order. Of particular interest in the volumes on hand are chapters describing microscopy and spectroscopy as means of polymer study.

II. Apparatus and Equipment

A commercially available "Teflon" sleeve has been added to the rotating vacuum evaporator described in Monthly Progress Letter No. 7. This addition permits elimination of the hexane rinse step and improves the precision of estimating the quantity of polymer present in a volatile solvent. Use of "Teflon" sleeves on the standard taper fittings of the chromatographic columns has eliminated "freezing" of joints occasionally encountered with glycerol based lubricants.

Twelve additional irradiation vessels have been fabricated.

A polarizing microscope is on order, and efforts are being made to expedite its delivery.

III. Experimental Work

Trial runs of the chromatographic system using a 2 liter mixing chamber indicate that a 0.5 gm polymer sample is distributed among one hundred and thirty 20 ml fractions. Consecutive tubes may readily be combined to produce five fractions, each containing approximately 0.1 gm of polymer. Dissolution of each of the five combined fractions in a suitable solvent, e.g. acetone, to make 10 ml produces one per cent polymer solutions in volumes compatible with the viscometers available. Successive dilutions of these solutions are expected to permit extrapolation to indicate intrinsic viscosities and to permit an estimate of the molecular weights of the fractions.

Studies of mildly acid ferrous ion dosimetry solutions indicate no apparent attack on the containers after periods of 24 and 72 hours.

No solvent loss was observed from the chromatographic system after standing fully charged for 10 days.

Vacuum dried, separated polymer samples are being stored awaiting delivery of the polarizing microscope.

IV. Future Plans

Ferrous ion solutions in the irradiating vessels and in glass containers will be used for dosimetry studies in the Georgia Tech 12,000 Curie Cesium 137 Irradiator and in the x-ray source.

Separated, dried polymer samples on hand will be dissolved, examined by viscometry, recovered, and cast as films for microscopic and x-ray examination.

Respectfully submitted,



W. H. Burrows
Project Director

Approved:



Frederick Bellinger, Chief
Chemical Sciences and Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

February 8, 1963

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Division of Isotopes Development

Subject: Monthly Progress Letter No. 9, Project No. A-446-010
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post Effect' Polymerization"
Contract No. AT (38-1) - 202, Task No. X
Covering the Period from January 1 to January 31, 1963

Gentlemen:

Research for the current period has included continued survey of the literature, trials and modification of equipment, development of techniques for study of small polymer samples, and compatibility studies of ferrous ion dosimetry solutions in the irradiating vessels.

I. Literature

Review of the current literature has been continued. Detailed study has been given to several recent volumes on polymer characterization and radiation chemistry of polymers, including the following:

1. G. M. Kline, ed., High Polymers, Vol XII, Analytical Chemistry of Polymers, Part I, Interscience, New York, 1959.
2. G. M. Kline, ed., High Polymers, Vol. XII, Analytical Chemistry of Polymers, Part II, John Wiley and Sons, New York, 1962.
3. H. Mark and V. Tobolsky, High Polymers, Vol. II, Physical Chemistry of High Polymeric Systems, 2nd ed., Interscience, New York, 1950.
4. J. C. Robb and F. W. Peaker, eds., Progress in High Polymers, Vol. I, Academic Press, New York, 1961.

II. Apparatus and Equipment

A polarizing microscope and third order quartz wedge has been delivered and placed in service. The "Teflon" sleeves described in Progress Report No. 8, while successful in the vacuum evaporator, have failed to prevent leakage in the chromatographic system on separations lasting more than 72 hours. Use of glycerol based lubricant in addition to these inserts is expected to correct this leakage. Additional "Teflon" inserts for ball joints of the system are being fabricated.

III. Experimental Work


Microscopic examination of previously prepared polymer samples was initiated. Low power (75X) magnification indicates the presence of trapped air and a granular surface matching the texture of the "Teflon" evaporating vessels used to prepare the samples. Passage of a faint beam of polarized light between crossed Nicol prisms suggests the presence of some crystalline material in the films. These experiments will be repeated using higher intensity light sources to permit higher magnification and a sodium lamp for determining refractive index.

Slight deviations in titration of ferrous ion solutions after prolonged standing in the irradiation containers are believed to arise from incomplete removal of soldering flux from a few of the vessels. These vessels are being repeatedly boiled in fresh, distilled water and rechecked until no change is detected in ferrous ion concentration after 72 hours standing.


IV. Future Plans

Crystalline melting points in the polymer films will be determined in the Optics Laboratory of the Engineering Experiment Station. Dosimetry studies and studies of polymer prepared by "post irradiation effect" will constitute a major part of future work.

Respectfully submitted:


W. H. Burrows
Project Director

Approved:


Frederick Bellinger, Chief
Chemical Sciences and Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

March 4, 1963

U. S. Atomic Energy Commission
Division of Isotopes Development
Washington 25, D. C.

Attention: Mr. Martin H. Stein
Radiation and Production Branch

Subject: Monthly Progress Letter No. 10, Project No. A-446-010
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post Effect' Polymerization"
Contract No. AT (38-1) - 202, Task No. X
Covering the Period from February 1 to February 28, 1963

Gentlemen:

Research for the current period has included specialized literature studies, installation of new and improved pieces of equipment, refinement of techniques and initiation of monomer irradiation experiments.

I. Literature

A detailed study has been made of recent volumes on polymer characterization. Information of particular value in experimental planning and evaluation of observed phenomena has been found in the following references:

1. G. M. Kline, ed., High Polymers, Vol. XII, Analytical Chemistry of Polymers Part III, John Wiley and Sons, New York, 1962.
2. J. C. Robb and F. W. Peaker, "A New Method of Fractionating High Polymers," Nature, London, 182, 1591 (1958).
3. J. D. Stroupe and R. E. Hughes, "The Structure of Crystalline Poly-(Methyl Methacrylate) J. Am. Chem. Soc. 80, 2341 (1958).
4. T. G. Fox, B. S. Garrett, W. E. Goode, S. Gratch, J. F. Kincaid, A. Spell, and J. D. Stroupe, "Crystalline Polymers of Methyl Methacrylate," J. Am. Chem. Soc. 80, 1768 (1958).
5. S. R. Caplan, "Fractionation of Polymers by Precipitation Chromatography -- Microtechnique and Theory," J. Polym. Sci. 35, 409 (1959).

II. Apparatus and Equipment

A Burton microscope illuminator and a sodium lamp have been placed in service with the polarizing microscope.

REVIEW

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"Teflon" inserts for ball joints of the chromatographic systems were fabricated in our shop and new, heavy duty, sleeves were procured for all standard taper joints. The packing material of the columns was changed from glass beads to 20-30 mesh Ottawa sand which has far less tendency to adhere to the faces of ground glass joints, causing separation. This combination of measures has eliminated solvent leakage which has been a major problem of this project from the start.

III. Experimental Procedures

Five separations of commercial polymer were attempted in the chromatographic apparatus. The first three fractionations were made prior to the above modifications and were discontinued because of leaks developing after 24 to 72 hours of operation. The two final separations were successful; no solvent or polymer loss was detected after more than 100 hours of operation in each run.


Microscopy performed under improved illumination revealed apparent crystalline structure in one of the commercial polymer fractions examined, although none of the "crystals" appeared to be anisotropic when examined under polarized light. There is some question as to whether the observed regularity of particle shape indicates crystallinity, precipitation of regularly shaped particles of amorphous material prior to complete evaporation of the solvent, or a regular habit of fragmentation of a brittle film. Examination by other techniques will be employed to resolve this question.

Irradiation of methyl methacrylate monomer samples in laboratory x-ray equipment has been initiated. Quenching and examination of the samples at various intervals after initiation is under way.


IV. Future Plans

Irradiation of monomer samples in both laboratory x-ray equipment at recorded power levels and in the Georgia Tech Cesium 137 Research Irradiator will be carried forward concurrently with dosimetry studies in the stainless steel irradiating bottles. Fractionation of polymer samples and studies of the physical properties of these fractions will be conducted concurrently with the radiation experiments.

Respectfully submitted,


W. H. Burrows
Project Director

Approved:


Frederick Bellinger, Chief
Chemical Sciences and Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

April 4, 1963

U. S. Atomic Energy Commission
Division of Isotopes Development
Washington 25, D. C.

Attention: Mr. Martin H. Stein
Radiation and Production Branch

Subject: Monthly Progress Letter No. 11, Project No. A-446-010
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post Effect' Polymerization"
Contract No. AT (38-1)-202, Task No. X
Covering the Period from March 1 to March 31, 1963

Gentlemen:

Research for the subject period included continuation of specialized literature studies, preliminary physical examination of polymers resulting from "post effect" polymerization, and such modifications of apparatus and technique as were necessitated by this study.

I. Literature

Detailed study of the literature on analytical chemistry of polymers cited in Monthly Progress Letters 9 and 10 has been continued. Liquid chemical dosimeter systems other than the ferrous ion system are described by G. V. Taplan in G. J. Hine and G. L. Brownell, eds., Radiation Dosimetry, Academic Press, New York, 1956.

II. Apparatus and Equipment

Fourteen of the stainless steel irradiation vessels have been lined with a polyurethane film. The purpose of this lining is to eliminate catalysis of the polymerization reaction by materials leached from the container walls. As an added benefit, it will permit use of acidified dosimetry solutions.

A microscope illuminator with accessories to permit phase contrast microscopy has been received and is available for use as needed in this study. This technique will expand the information available from polarized light microscopy by permitting rapid identification of isotropic as well as anisotropic crystalline material in polymer films.

III. Experimental Procedures

"Post effect" polymers were formed by brief x-ray treatment of bulk monomer in stainless steel vessels. The reaction was characterized by rapid


rise of viscosity in the irradiated samples and by persistence of a high degree of chemical activity for as much as 25 days after irradiation. During the first 24 hours the sample was changed from a free flowing liquid to an immobile gel. On treatment with inhibitor in solvent (one per cent p-methoxy phenol in benzene) the gel softened momentarily, then returned rapidly to a highly viscous state. It is not certain that this observed phenomenon arose from gel effect (assuming that the methyl methacrylate monomer would be more highly mobile in viscous media than the bulkier p-methoxy phenol molecule) or from chemical catalysts leached from the stainless steel containers. A film cast from the material contained several areas which exhibited optical activity (appearance and extinction) when viewed through crossed Nicol prisms and rotated in a beam of polarized light. Studies of extent of polymerization as a function of time were severely handicapped by the rapid rise in viscosity during the initial period of the reaction. Fractionation of commercial polymer samples has been continued concurrently with initial study of the polymers produced by "post effect" polymerization.

The quantity of inhibitor introduced in removing the gel from the irradiating vessels obscured gravimetric estimates of extent of polymerization. The recovered polymer was divided into two parts, one of which was dried in vacuo at 25° C, while the second was repeatedly extracted with 5 per cent aqueous potassium hydroxide. The first portion produced a brownish film capable of undergoing approximately 25 per cent elongation without breaking. The second (extracted) portion produced a soft, rubbery, deep brown film. It is suspected that this second portion was partially saponified. The brown color and a faint phenol odor in both films indicates that removal of inhibitor was incomplete.


IV. Future Plans

Irradiation of monomer samples in both urethane lined and unlined stainless steel containers will be carried forward in laboratory x-ray equipment and in the Georgia Tech Cesium 137 Research Irradiator. Concurrent activity will include dosimetry studies, fractionation of the "post effect" polymer samples, and study of the physical properties of the separated fractions.

Respectfully submitted,


W. H. Burrows
Project Director

Approved:


Frederick Bellinger, Chief
Chemical Sciences and Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

May 1, 1963

U. S. Atomic Energy Commission
Division of Isotopes Development
Washington 25, D. C.

Attention: Mr. Martin H. Stein
Radiation and Production Branch

Subject: Monthly Progress Letter No. 12, Project No. A-446-010
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post Effect' Polymerization"
Contract No. AT (38-1) - 202, Task No. X
Covering the Period from April 1 to April 30, 1963

Gentlemen:

Research for the subject period included continuation of specialized literature studies, radiation experiments using both laboratory x-ray equipment and the Georgia Tech 12,000 Curie Cesium 137 Research Irradiator, and examination of the "post effect" polymer described in Monthly Progress Letter No. 11.

I. Literature Study

Detailed study of the literature on analytical chemistry of polymers cited in Progress Letters No. 9, 10, and 11 has been continued.

II. Apparatus and Equipment

A precision optical micrometer has been partially successful in estimating the thickness of films cast from separated polymer fractions. The usefulness of this instrument has been restricted by translucency of the cast films and a limit of ± 0.005 mm in the reproducibility of film thickness measurements. The urethane lined irradiation vessels described in Progress Letter No. 11 have proven to be chemically inert and are not affected to any significant extent by radiation in laboratory x-ray equipment or in the cesium source. Similar linings are being applied to the remaining containers to permit experimental designs with 28 samples.

III. Experimental Procedures

Samples of methyl methacrylate monomer were irradiated at 3° and 25° C in urethane lined containers using laboratory x-ray equipment. Within the limits of experimental error, no polymerization was observed immediately after irradiation or in samples quenched at intervals up to 10 days after irradiation.

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Tendency of the x-ray equipment to overheat required that the initiating dose be delivered in 2-minute increments separated by 15-minute cooling periods rather than continuously as in earlier experiments.

Twelve bulk monomer samples were subjected to initiating irradiation in the Cesium 137 Irradiator. Irradiation times were 5 and 10 minutes at dose rates of approximately 6.6×10^5 rads/hr. Extent of polymerization was measured immediately after irradiation and at 24 hour intervals to follow rate of "post effect" polymerization as a function of initiating dose.

The "post effect" polymer described in Progress Letter No. 11 has been separated in the solvent/temperature gradient fractionator. A 0.6 gram sample cut from the original disc yielded 5 per cent inhibitor, approximately 80 per cent polymer whose distribution in the fraction collector coincided with that of a polymer having a known M_w (weight average molecular weight) of 103,000, and 15 per cent of a higher molecular weight fraction. This last fraction exhibited substantially higher tensile strength than films of equal thickness cast from commercial polymers. An x-ray diffraction pattern from this highest molecular weight fraction showed no evidence of crystalline structure. The ability of the brownish polymer film to undergo elongation without fracture, together with its pronounced phenol odor have decreased on storage.

IV. Future Plans

Irradiation experiments will be performed mainly using urethane lined containers in the Georgia Tech Cesium 137 Irradiator. Concurrent activity will include a literature study, dosimetry studies, fractionation of the "post effect" polymer samples, and study of the physical properties of the separated films. Experimental work will be scheduled to exploit the full capacity of the techniques and apparatus assembled during the earlier progress periods.

Respectfully submitted,

[Redacted Signature]

W. H. Burrows,
Project Director

Approved:

[Redacted Signature]

Frederick Bellingher, Chief
Chemical Sciences and Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

May 31, 1963

U. S. Atomic Energy Commission
Division of Isotopes Development
Washington 25, D. C.

Attention: Mr. Martin H. Stein
Radiation and Production Branch

Subject: Monthly Progress Letter No. 13, Project No. A-446-010
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post Effect' Polymerization"
Contract No. AT (38-1)-202, Task No. X
Covering the Period from May 1 to May 31, 1963

Gentlemen:

Research for the subject period included continuation of literature studies, radiation experiments using the Georgia Tech 12,000 Curie Cesium 137 Research Irradiator, and examination of the "post effect" polymers produced in these experiments.

I. Literature Study

A survey of the recent literature has revealed several reports of studies closely related to the objects of this project. The following references are of particular interest:

1. J. P. Berry, "Fracture Processes in Polymeric Materials. IV. Dependence of the Fracture Surface Energy on Temperature and Molecular Structure," J. Polymer Sci., Part A, 1, 993-1003 (1963).

2. M. I. Frolova, L. V. Nevskii, and A. V. Ryabov, "The Light-Aging of Polymethyl Methacrylate. II. A Study of Photodegradation by Means of Radioactive ¹⁴C Carbon," Polymer Science, USSR, 3, 703-708 (1962).

3. J. F. Gernert, M. J. R. Canton, R. F. Porter, and J. F. Johnson, "Column Fractionation of Polymers. II. Instrumentation for Solvent Gradient and Flow Control," J. Polymer Sci., Part C, No. 1, 196-203 (1963).

4. W. R. Moore and R. J. Fort, "Viscosities of Dilute Solutions of Polymethyl Methacrylate," J. Polymer Sci., Part A, 1, 929-942 (1963).

5. A. M. North and G. A. Reed, "Diffusion Controlled Polymerization of

of Some Alkyl Methacrylates," J. Polymer Sci., Part A, 1, 1311-1321 (1963).

6. S. R. Rafikov and G. P. Gladyshev, "Studies in Polymer Synthesis. II. The Photo-Oxidative Activation of Methyl Methacrylate by Ultra-Violet Light," Polymer Science, USSR, 3, 804-812 (1962).

7. N. S. Tsvetkov, "The Polymerization of Methyl Methacrylate by Cathodic Hydrogen," Polymer Science, USSR, 3, 570-576 (1962).

8. V. N. Tsveyskov and M. G. Vitovskaya, "The Photoelastic Effect in Stereoisomers of Polymethylmethacrylate," Polymer Science, USSR, 3, 838-845 (1962).

9. A. V. Tobolsky and D. B. Hartley, "Radical-Anion Polymerization," J. Polymer Science, Part A, 1, 15-22 (1963).

10. L. Utracki and R. Simha, "Corresponding State Relations for the Viscosity of Moderately Concentrated Polymer Solutions," J. Polymer Science, Part A, 1, 1089-1098 (1963).

11. M. P. Vershinia and E. V. Kuvshinskii, "A Study of the Mechanical Degradation of Polymethyl Metacrylate and Polystyrene by Following Molecular Weight Changes," Polymer Science, USSR, 3, 382-90 (1962).

12. V. P. Zubov, V. A. Kabanov, V. A. Kargin, and A. A. Shchetenin, "The Effect of Pressure During the Polymerization Process on the Conformation of the Polymer Chains," Polymer Science, USSR, 3, 468-473 (1962).

The synthesis technique described in reference 6 (above) employs "post effect" polymerization after irradiation with ultraviolet light. There is no obvious reason that activation by gamma irradiation should not be equally successful in a similar polymerization technique.

II. Apparatus and Equipment

Some separation of the urethane lining from the stainless steel reaction vessels after use in several experiments has been observed. The possibilities of applying Teflon liners or of fabricating suitable containers from commercially available Teflon tubing are being explored. Apparatus for distillation of monomers at reduced pressure and in the absence of oxygen has been constructed.

III. Experimental Procedures


Samples of methyl methacrylate monomer have been irradiated for 5, 10, and 20 minutes at a dose rate of 0.6 M rad/hr. Extent of polymerization immediately after irradiation was approximately proportional to absorbed dose. Thermally (or catalytically) initiated polymerization was negligible as determined from duplicate sets of unirradiated samples. Measurement of extent of "post effect"

polymerization, however, failed to show similar per cent polymerization among duplicate samples quenched at identical times after irradiation. The irregularity of extent of polymerization together with low per cent conversion (less than 4 per cent) are tentatively attributed to inhibition by atmospheric oxygen dissolved in the monomer during sample preparation. Polymer distribution among the tubes of the sample collector after chromatographic fractionation was nearly identical for samples drawn from materials quenched immediately after irradiation and 48 hours after irradiation.


IV. Future Plans

Irradiation experiments will be continued using monomer from which oxygen has been carefully excluded. Concurrent activity will include literature study, improvement of irradiation vessels, fractionation of "post effect" polymers, and examination of the properties of the separated fractions.

Respectfully submitted,


W. H. Burrows
Project Director

Approved:


Frederick Bellinger, Chief
Chemical Sciences and Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

July 1, 1963

U. S. Atomic Energy Commission
Division of Isotopes Development
Washington 25, D. C.

Attention: Mr. Martin H. Stein
Radiation and Production Branch

Subject: Monthly Progress Letter No. 14, Project No. A-446-010
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post-Effect' Polymerization."
Contract No. AT (38-1)-202 Task No. X
Covering the Period from June 1 to June 30, 1963

Gentlemen:

The current month's effort has included irradiation experiments in both laboratory x-ray equipment and the Georgia Tech 12,000 Curie Cesium 137 Research Irradiator.

I. Literature Studies

During the subject period detailed study has been given to polymerization kinetics and to the sections of the previously cited literature describing monomer sample preparation.

II. Apparatus and Equipment

Twenty-four irradiation vessels have been fabricated from "Teflon" bar stock to fit the outer array of holes in the Georgia Tech Cesium 137 Research Irradiator. These vessels have replaced the previously used stainless steel vessels. Surface catalysis of polymerization during irradiation had been observed with unlined stainless steel containers. Earlier attempts to remedy this with a polyurethane lining resulted in peeling of the lining from the wall as a result of solvent action by the monomer.

The laboratory x-ray equipment is being modified to permit circulation of cooling oil through a heat exchanger. This arrangement will permit sustained low level irradiation of monomer samples without interruption for tube and transformer cooling.

The glass ball and socket joints in the chromatographic apparatus have been replaced by "Teflon" tubing connections. The system is now leak free under pressures above those required and appears to be capable of sustained operation without attention other than occasional solvent replenishment.

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III. Experimental Procedures

Monomer samples have been irradiated in "Teflon" containers using both laboratory x-ray equipment and the Georgia Tech Cesium 137 Research Irradiator. Ten minutes of total irradiations in the x-ray equipment were performed in five-two minute exposures followed by ten minute intervals for apparatus cooling. No measureable polymerization was detected immediately after irradiation or at intervals up to 96 hours after irradiation.


Similar samples were irradiated to dose levels of 0.11, 0.22, and 0.44 megarads in the Georgia Tech Cesium 137 Research Irradiator. Percentage conversions during irradiation were 0.17, 2.19, and 8.16, respectively. These measurements were made gravimetrically on samples quenched immediately after irradiation, and dried in vacuo. A marked increase in viscosity of a sample irradiated to 4.4×10^5 rads was observed after 24 hours' standing.

Preparation of samples for these experiments consisted of inhibitor removal, washing with distilled water, drying over potassium carbonate, and distillation at 45° C in a closed system under dry nitrogen. These procedures are intended to exclude inhibition of polymerization by the presence of atmospheric oxygen or moisture.


IV. Future Plans

Experimental work for the next report period will be concentrated on irradiation of samples in the Georgia Tech Cesium 137 Research Irradiator. Of immediate interest are extent of polymerization during irradiation to doses up to one megarad and extent of post effect polymerization as a function of time and temperature for several dose levels in this region. Viscometric molecular weights of the polymers formed will be determined. The chromatographic equipment will be operated continuously to permit estimates of molecular weight distribution on as many of these samples as possible. The samples prepared will be reserved for examination of physical properties.

Respectfully submitted,


W. H. Burrows
Project Director

Approved:


Frederick Bellinger, Chief
Chemical Sciences and Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

August 1, 1963

U. S. Atomic Energy Commission
Division of Isotopes Development
Washington 25, D. C.

Attention: Mr. Martin H. Stein
Radiation and Production Branch

Subject: Monthly Progress Letter No. 15, Project No. A-446-010
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post-Effect' Polymerization."
Contract No. AT (38-1)-202 Task No. X
Covering the Period from July 1 to July 31, 1963

Gentlemen:

Research for the subject period has been concentrated on the irradiation of methyl methacrylate monomer samples and on determination of extent of polymerization and molecular weights of these samples immediately after irradiation and at various intervals after irradiation. Literature studies have been temporarily suspended to permit concentration on experimental work.

I. Apparatus and Equipment

Laboratory X-ray equipment has been modified by addition of an oil circulating pump and water cooled heat exchanger. This arrangement permits continuous operation of the apparatus for periods of more than one hour without overheating.

II. Experimental Procedures

Samples of methyl methacrylate monomer have been irradiated to two dose levels in the Georgia Tech 12,000 Curie Cesium 137 Research Irradiator, and have been examined for extent of polymerization immediately after irradiation and at varying intervals after irradiation. Representative results of these experiments are summarized in Table I.

The most conspicuous feature of the data in Table I is the rapid rise of molecular weight on standing after irradiation. The extent of polymerization appears to rise more slowly.

TABLE I
 SUMMARY OF EXPERIMENTAL OBSERVATIONS

| Sample No. | Dose (rads x 10 ⁻⁵) | Post-Effect Time (hours) | Extent of Conversion (%) | Molecular Weight x 10 ⁻⁵ |
|------------|------------------------------------|-----------------------------|-----------------------------|-------------------------------------|
| A-1 | 4.4 | 0:00 | 7.2 | 1.2 |
| A-3 | 4.4 | 1:00 | 7.4 | 1.7 |
| A-5 | 4.4 | 24:00 | 9.0 | 5.4 |
| B-1 | 6.6 | 0:00 | 12.9 | 1.8 |
| B-3 | 6.6 | 1:00 | | 1.9 |
| B-5 | 6.6 | 3:00 | 14.6 | 3.8 |
| B-6 | 6.6 | 24:00 | 17.2 | 5.8 |

The percentage conversions reported in Table I are averages obtained for duplicate samples. This estimate is omitted for Sample B-3 as the duplicate determinations failed to agree within one per cent (based on original monomer). The molecular weights were determined by viscosimetry in chloroform solutions. These values are estimated from the relation:[†]

$$\eta_{\text{CHCl}_3} = 6.6 \times 10^{-5} \text{ MW}^{0.77} ,$$

where η_{CHCl_3} is the limiting viscosity number of the polymer sample in chloroform.

Irradiations were performed in the Georgia Tech Cesium 137 Research Irradiator. Monomer samples were prepared by extraction with dilute potassium hydroxide solution, rinsing with distilled water, distillation under a nitrogen

[†]T. J. R. Weakley, R. J. P. Williams, and J. D. Wilson, "The Molecular-weight Distribution in Some Poly (Methyl) Methacrylates," J. Chem. Soc. London, 1960, 3963-3973.

atmosphere at 45° C, and drying at 3° C over anhydrous potassium carbonate. Samples were decanted into Teflon vessels and tightly closed to exclude air and light before irradiation.


Additional similarly prepared samples have been irradiated in the cesium source to dose levels of 2.2×10^5 , 4.4×10^5 , 6.6×10^5 , and 1.43×10^6 rads and allowed to stand for varying periods before quenching. These quenched samples are being examined for extent of polymerization and molecular weight as a function of "post-effect" time after differing initiating doses.

Fractionation of polymer samples to determine molecular weight distribution is under way.


III. Future Plans

Irradiation experiments will be carried forward as rapidly as the polymers formed can be examined. The duration of "post-effect" reaction at room temperature ($23 \pm 2^\circ \text{C}$) after irradiation to several dose levels will be examined along with the changes in degree of polymerization and molecular weight with extended (36 to 72 hour) times after irradiation. Additional experiments planned include "post-effect" studies at reduced (5°C) and slightly raised (40°C) temperatures. Concurrent experimental work will be devoted to determining an experimental upper limit of conversion at which the gelled reaction mass can be quenched without proceeding to nearly complete polymerization on addition of solvent and inhibitor. While most of the irradiation experiments are planned for the Georgia Tech Cesium Research Irradiator, a few samples will be treated with laboratory X-ray equipment to examine the "post-effect" phenomenon following irradiation at low dose rates. On completion of exploration of the practicable experimental area, detailed study will be given to polymer samples reserved from the exploratory phase of the study.

Respectfully submitted,


W. H. Burrows
Project Director

Approved:


Frederick Bellinger, Chief
Chemical Sciences and Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

September 4, 1963

U. S. Atomic Energy Commission
Division of Isotopes Development
Washington 25, D. C.

Attention: Mr. Martin H. Stein
Radiation and Production Branch

Subject: Monthly Progress Letter No. 16, Project No. A-446-010
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post-Effect' Polymerization"
Contract No. AT (38-1)-202 Task No. X
Covering the Period from August 1 to August 31, 1963

Gentlemen:

Research for the subject period has been concentrated on the irradiation of methyl methacrylate monomer samples and on determination of extent of polymerization and molecular weights of these samples immediately after irradiation and at various intervals after irradiation. Literature studies and modification of apparatus have been temporarily suspended to permit concentration on experimental work.

I. Experimental Procedures

A. Preparation of Monomer

Samples of methyl methacrylate monomer were prepared in the manner described in earlier reports. The procedure involves (1) extraction with dilute potassium hydroxide solution, (2) rinsing with distilled water, (3) distillation under a nitrogen atmosphere at 45° C, and (4) drying at 3° C over anhydrous potassium carbonate. The samples thus prepared were decanted into Teflon irradiation vessels which were then tightly closed to exclude air and light before irradiation.

B. Irradiation

All irradiation procedures were conducted in the Georgia Tech Cesium 137 Research Irradiator. The Teflon tubes containing the monomer were inserted in the outer circle of tubes surrounding the source and kept in those positions for such periods of time as to provide initiating doses of 1.9, 3.8, 5.8 and 8.7×10^5 rads, thus extending both the upper and lower limits of dose level over those reported in Letter Report No. 15. These levels represent absorbed dose, calculated from ferrous ion dosimetry data by means of an electron density factor.

Subsequent to irradiation, the samples were allowed to remain in the Teflon vessels under storage at 23°C, during which time the "post-effect" polymerization reaction proceeded. "Post-effect" times of 1, 4, and 24 hours were permitted.

Experiments currently under way include dose levels from 3.8×10^5 to 1.2×10^6 rads and "post-effect" times from one hour to 96 hours.

C. Quenching

Samples are quenched at the end of the "post-effect" period by dissolving the contents of the Teflon irradiation vessels in a benzene solution of methyl ether of hydroquinone. Until recently, this method has failed in the case of samples which had proceeded to the gel state before quenching. Immediately upon dilution, the polymerization reaction proceeded to the point of producing another gel state, thus interfering with the distribution of the inhibitor and preventing complete quenching.

A technique has been developed in this laboratory for quenching polymerization reactions in viscous media. This technique, which is now in regular use, consists of the following steps: (1) the reaction mixture is rapidly frozen by immersion in liquid nitrogen, (2) the solid reaction mixture is transferred to a solution of methyl ether of hydroquinone in methylene chloride, chilled by a dry ice and acetone bath, and (3) the solid reaction mixture is dissolved in the inhibitor solution at -78°C. This method reduces polymerization in the bulk of the reaction mass, which would occur on warming, and avoids the rapid acceleration of polymerization rate, which has handicapped previous efforts to dissolve a gelled reaction mixture at room temperature.

D. Determination of Extent of Conversion

Following quenching, the polymer samples are separated from excess monomer and solvent in vacuum evaporators, then dried to constant weight at 40°C in a laboratory vacuum oven. The weight of polymer thus obtained is compared to that obtained from samples exposed to equal initiating doses, but with zero "post-effect" period. The result is a measure of the extent of "post-effect" polymerization.

E. Determination of Molecular Weight Distribution

Samples for molecular weight determinations are fractionated in a solvent-temperature gradient column and collected in a series of test tubes on an automatic fraction collector. Molecular weight determinations are made from viscosimetric measurements in chloroform solutions (see Progress Letter No. 15).

Fractionation of polymer samples has proceeded continuously. Determination of molecular weight distribution from the separated fractions has been deferred, however, as all of the available molecular weight capacity is being used in the current systematic exploration of "post-effect" phenomena.

II. Results and Conclusions

Table I presents a summary of the measurements of extent of conversion and viscosity average molecular weight of the polymer samples obtained by "post-effect" polymerization in these experiments. The increase of molecular weight and extent of conversion with both increasing initiating dose and extended "post-effect" time appears to persevere as previously observed. There are, however, some irregularities in the pattern of experimental observations; e.g., samples C-7 and C-8. Reasonable causes for these irregularities have been identified, and duplicate experiments to resolve these discrepancies are under way.

TABLE I
 SUMMARY OF EXPERIMENTAL OBSERVATIONS


| <u>Sample No.</u> | <u>Dose</u> (rads x 10 ⁻⁵) | <u>Post-Effect Time</u> (hours) | <u>Extent of Conversion</u> (%) | <u>Molecular Weight x 10⁻⁵</u> |
|-------------------|---|------------------------------------|------------------------------------|---|
| C-2 | 1.9 | 1:00 | 2.0 | 1.3 |
| C-3 | 1.9 | 4:00 | 2.3 | 2.6 |
| C-4 | 5.8 | 4:00 | 11.6 | 2.0 |
| C-5 | 1.9 | 24:00 | 2.1 | † |
| C-6 | 1.9 | 4:00 | 2.3 | 2.6 |
| C-7 | 8.7 | 24:00 | 23.8 | 7.1 |
| C-8 | 8.7 | 24:00 | 25.4 | 5.6 |
| C-9 | 1.9 | 24:00 | 2.2 | 3.1 |
| C-10 | 8.7 | 0:00 | 20.0 | 1.3 |
| C-12 | 8.7 | 1:00 | 19.9 | 1.4 |
| D-2 | 3.8 | 0:00 | 6.6 | 1.4 |
| D-3 | 3.8 | 1:00 | 10.6 | 1.2 |

† Defective viscosimeter. Duplicate determination under way.


III. Future Plans

Irradiation experiments will be carried forward as rapidly as extent of conversion and molecular weight can be determined on the polymers formed. The low temperature quenching method will be used to extend the area of exploration into the high conversion (Trömsdorff) region where large "post-effect" yields may be expected. Initiating dose level and "post-effect" times will be increased. Although the temperature of the Georgia Tech Cesium 137 Research Irradiator is fixed at 35° C, "post-effects" will be examined in samples held at 5° C, 23° C, and 40° C. A few samples will be treated with laboratory x-ray equipment to examine the "post-effect" phenomenon following irradiation at low dose rates. The bulk of experimental effort in the near future, however, will be directed toward systematic exploration of extent of conversion and viscosity average molecular weights in the practicable experimental area, which has been greatly expanded by development of the cold quenching technique.

Respectfully submitted,


W. H. Burrows
Project Director

Approved:


Frederick Bellinger, Chief
Chemical Sciences and Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

October 9, 1963

U. S. Atomic Energy Commission
Division of Isotopes Development
Washington 25, D. C.

Attention: Mr. Martin H. Stein
Radiation and Production Branch

Subject: Monthly Progress Letter No. 17, Project No. A-446-010
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post-Effect' Polymerization"
Contract No. AT (38-1)-202 Task No. X
Covering the Period from September 1 to September 30, 1963

Gentlemen:

Research for the subject period has been concentrated almost entirely on the irradiation of methyl methacrylate monomer samples and on determination of extent of polymerization and molecular weights of these samples at various intervals after irradiation. Literature studies have been temporarily suspended to permit concentration on experimental work.

I. Experimental Procedures

A. Preparation of Monomer

Samples of methyl methacrylate monomer were prepared by extraction, rinsing, and distillation according to the method described in Monthly Progress Letter No. 16. To prevent contamination of the monomer by stopcock lubricant and leakage of air into the system the ground glass joints were lapped with fine boron carbide, and Teflon sleeves were used instead of stopcock grease.



B. Irradiation

Irradiation procedures were identical to those described in Monthly Progress Letter No. 16. Initiating dose levels were 3.8, 5.8, and 8.7×10^5 rads.

Subsequent to irradiation, the samples were allowed to remain in the Teflon vessels under storage at 23° C, during which time the "post-effect" polymerization proceeded. Post effect times from 1 to 194 hours were permitted.

C. Quenching

Samples were quenched at the end of the post-effect period by dissolving the contents of the Teflon irradiation vessels in a benzene solution of methyl

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ether of hydroquinone for non-viscous samples or by the cold quenching technique described in Report No. 16 for viscous samples, generally those arising from post effect times longer than one hour.

A handicap to the cold quenching technique has been a tendency of the Teflon vessels to crack during immersion in liquid nitrogen. A "cold finger" technique is being explored to permit transfer of the frozen reaction mass without need for freezing the irradiation vessel.

D. Determination of Extent of Conversion

The gravimetric procedure for determination of extent of conversion as described in Report No. 16 has been continued.

E. Determination of Molecular Weight

Molecular weight determinations have been made from viscosimetric measurements in chloroform solutions. As measurements of the flow time of a one per cent solution of methyl ether of hydroquinone in chloroform in an Ostwald Cannon Fenske viscosimeter differed only slightly from the flow time of chloroform alone, it appears that the dilutions of solutions of polymethyl methacrylate and inhibitor may be corrected arithmetically rather than by physical removal of the inhibitor prior to viscosimetric molecular weight determination. Attempts to remove inhibitor from chloroform or methylene chloride solutions of polymer and inhibitor by liquid-liquid extraction with dilute potassium hydroxide solutions followed by rinsing with distilled water have led to slightly higher apparent molecular weights than those calculated for similar polymer samples using an arithmetic correction factor. It is suspected that some of the lower polymer has been saponified and rendered water soluble by the dilute potassium hydroxide.

II. Results and Conclusions

Table I presents a summary of the measurements of extent of conversion and viscosity average molecular weight of the polymer samples obtained by post-effect polymerization in these experiments.

Examination of the data summarized in Table I indicates that reproducibility of results of similar experiments is still unsatisfactory. There is, however, a surprising similarity in molecular weight immediately after irradiation to several dose levels, e.g., samples D-1, D-3, F-5, and E-1 represent polymers quenched immediately after initiating doses of 3.8, 5.8, 8.7, and 9.6×10^5 rads, respectively. The apparent molecular weight of all four samples is 1.4×10^5 . Extent of post-effect polymerization continues to rise with level of initiating dose and post-effect time.

III. Future Plans

Irradiation experiments will be carried forward as rapidly as extent of conversion and molecular weight can be determined on the polymers formed. The

February 27, 1963

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Mr. Martin H. Stein, Chief
Process Radiation Section
Radiation Development Branch
Division of Isotopes Development

Subject: Special Progress Report, Project No. -446-010
"Physical Properties and Structural Characteristics of
Polymers Resulting from 'Post effect' Polymerization"
Contract No. AT (35-1) - 202, Task No. 4

Gentlemen:

1. Background

The technique of "post effect" polymerization consists of exposing a monomer sample to brief initiating doses of ionizing radiation, following which further polymerization proceeds spontaneously in the absence of light, air, or further radiation. This technique has been adapted by several investigators to permit grafting of monomers to previously irradiated polymeric materials.

2. Justification

"Post effect" polymerization, by avoiding contamination of the reaction mixture by chemical catalysts and polymer degradation from continuing radiation, offers an exceptional opportunity for the study of polymerization reaction kinetics. The use of x-ray and gamma irradiation assures uniform dose distribution throughout the sample and avoids the surface effects inherent in initiation by heat or ultra-violet radiation. A further benefit from this technique may be the isolation of polymers with unusual physical or chemical properties.

3. Experimental Approach

Initiating irradiation of monomer samples is performed in laboratory x-ray equipment and in the Georgia Tech Cassius 137 Research Irradiator using stainless steel bottles with "Teflon" screw plugs. Irradiated samples are quenched and examined at various intervals after exposure to several known radiation doses. Treatment of these samples consists of evaporation in vacuo to measure extent of polymerization followed by chromatographic separation into fractions of relatively narrow molecular weight range. Among the techniques used for characterization of the polymer fractions obtained are viscosimetric molecular weight determination, infrared absorption spectroscopy, casting and tearing of films on foil, x-ray methods, and examination of the physical properties of films cast from the separated fractions.

chemical activity, physical properties, and a wealth of background literature available led to the choice of methyl methacrylate as the first monomer to be studied. Initial studies are designed for bulk polymerization, although the study may be extended to emulsion polymerization should a suitable technique be devised.

It has become necessary to combine the separately planned activities of apparatus construction and familiarization experiments using conventional polymers. This consolidation, while briefly delaying the initiation of irradiation experiments, has permitted modification of equipment and techniques to produce consistent results, which will be necessary in comparisons to be drawn between the properties of "post effect" polymers and the properties of conventional polymers as measured in these laboratories and as reported in the literature.

2. Results

1. Chromatographic apparatus. A satisfactory system capable of operating for 100 hours with only occasional additions of solvent has been assembled.

Initial experimental procedures concentrated on construction and modification of apparatus and selection and modification of laboratory techniques. A fitted jacket was machined from an aluminum bar to provide the chromatographic column with a nearly linear temperature gradient from 10° C to 60° C. This replaced the compressed aluminum foil wrapping originally planned for this purpose. Increase in mixing vessel volume from 250 ml to 2000 ml decreased the solvent gradient and broadened the sample distribution from nine tubes to over 100 20 ml fractions on the automatic fraction collector. Eight non-solvent-solvent systems (e.g., hexane-alcohol, hexane-3-hexanone, hexane-aromatic hydrocarbon, and hexane-chlorinated solvent) were examined for ability to fractionate a polymer sample, ease of evaporation in vacuo at moderate (less than 40° C) temperatures, and ability to be retained in the system. Glass bead packing materials of several diameters were examined. The present system employs hexane and chloroform dried over calcium chloride, "Teflon" sleeves lubricated with thickened glycerol at all glass joints, and 20-30 mesh Ottawa sand as column packing. Recovery of a 0.6 gram sample was 100 ± 0.2 per cent from 40 tubes of the fraction collector.

2. Rotating vacuum evaporator. Dissolved samples of commercial polyethyl methacrylate in several solvents were recovered quantitatively at temperatures less than 30° C.

3. Dosimetry solutions. Ferrous ion solutions, sufficiently acid to permit reproducible titrations with permanganate, attacked the stainless steel irradiating vessels and resulted in an increased ferrous ion concentration. A ferrous ion solution containing only 5 ml concentrated sulfuric acid per liter was stable on standing and did not attack the irradiation bottles. Reproducible end points were obtained by adding 1 part of 1:10 sulfuric acid to each 4 parts of ferrous ion solution immediately before titration.

4. Viscosimetry. Twelve Ostwald-Lannon-Fenske viscosimeters covering a range from 0.5 to 640 centistokes and requiring 5 to 10 ml samples have been calibrated with National Bureau of Standards oils. Measurement of viscosity vs concentration of methyl methacrylate solutions in several solvents have been made and extrapolated to obtain intrinsic viscosity values resembling those reported in the literature.

5. Film Preparation. Thin polymer films have been prepared by dipping aluminum foil or "Teflon" strips into a polymer solution and drying and by evaporation of a polymer solution covering aluminum foil and "Teflon" strips in a "Teflon" container. The most uniform and easily stripped films were obtained on "Teflon" substrates by the latter method.

6. Conclusions

Because of the preliminary nature of this work, it is not possible to draw significant conclusions at the present time.

7. Future Plans

Samples of methyl methacrylate polymer will be prepared by "post effect" polymerization and their characteristic properties will be measured. The data obtained from these experiments will be compared with corresponding data taken from the literature. Where possible, it will be useful to accompany each measurement of a "post effect" polymer property with a parallel "control" measurement performed on a conventional polymer sample. This "control" measurement will be valuable in determining whether deviations from literature values result from laboratory error or from unique characteristics of the "post effect" polymer. It is hoped that some elucidation of the reaction mechanism will result. Polymer fractions possessing unusual properties (if any) will be noted.

Respectfully submitted,

[REDACTED]
A. H. Burrows
Project Director

Approved:

[REDACTED]
Frederick Bellinger, Chief
Chemical Sciences and Materials Division

QUARTERLY TECHNICAL STATUS REPORT NO. 1

PROJECT NO. A-446-10

PHYSICAL PROPERTIES AND STRUCTURAL CHARACTERISTICS
OF POLYMERS RESULTING FROM "POST-EFFECT" POLYMERIZATION

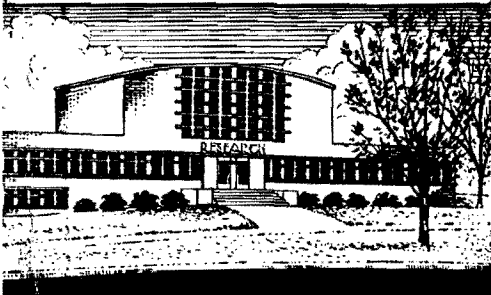
by

L. W. ELSTON and W. H. BURROWS

COVERING THE PERIOD
1 MARCH 1962 to 31 MAY 1962
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DIVISION OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND



Engineering Experiment Station
Georgia Institute of Technology

Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
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ABSTRACT

Activities have included survey and review of literature pertinent to the various aspects of this project, formulation of the details of a plan of procedure, procurement of equipment, materials and supplies required for the laboratory work, and assembly and construction of the apparatus for polymer fractionation. Methyl methacrylate has been chosen as the monomer for initial study. Calibration of equipment will be followed by familiarization experiments utilizing commercially available polymers.

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This report contains 12 pages.

I. INTRODUCTION

The broad objectives of the proposed research are to study the effects of temperature, concentration of monomer, concentration of polymer, dose, etc., on the molecular weights, degree of branching of polymers, and tecticity of the polymer chains resulting from "post-effect" polymerization of monomers such as methyl methacrylate, vinyl pyrrolidone, etc. "Post-effect" polymerization minimizes the undesirable effects resulting from continued ionizing radiation or associated with the use of chemical catalysts.

Monomers such as methyl methacrylate will be exposed to brief initiating doses of gamma radiation in the Georgia Tech Cesium 137 Irradiator. At time intervals thereafter, samples will be withdrawn, quenched, and studied as to the following characteristics (1): extent of polymerization, distribution of molecular weights, determination of molecular weights, branching and cross-linking, crystallinity, specific volume and coefficient of thermal expansion, melting point, morphology from x-ray, and morphology from infrared.

II. DISCUSSION

Previous studies of molecular weight distributions and classification of molecular structures of polymers of methyl methacrylate, vinyl pyrrolidone, etc., have been made on polymer masses obtained by initiation involving heat, catalysts, or continued ionizing irradiation (5). Each of these methods produces side effects which tend to obscure the mechanism of the polymerization reaction. The principal objections to each may be summarized as follows:

| <u>Method of Initiation</u> | <u>Objectionable Features</u> |
|-----------------------------|--|
| 1. Thermal | a. Lack of uniformity resulting from poor heat transfer b. Heat degradation of polymer molecules |
| 2. Catalytic | a. High temperature coefficient of reaction rate, tending to cause "run-away" reactions b. Specificity of catalysts, promoting branching or linearity, atacticism or isotacticism |
| 3. Continued Ionization | a. Polymer degradation b. Cross-linking resulting from creation of reactive sites. |

"Post-effect" polymerization, or continued polymerization after removal from the initiating source, and in the absence of light or catalysts, has long been recognized (21). Rate studies made indicate that the rate of post-effect polymerization is dependent upon the concentrations of both monomer and polymer present in solution after irradiation (12). These studies do not seem to have included such factors as time dependence of the post-effect, distribution of polymer molecular weights, degrees of branching and cross-linking, or tacticity. Studies of these factors are included in the present research program to throw light on the theoretical aspects of polymerization reactions. If the polymerization involves only the reaction of free radicals, one would expect an atactic product. Isotacticism would be a strong indication that polymerization was proceeding through operation of an ionic mechanism.

III. EXPERIMENTAL

A. Tentative Project Plan

The following tentative project plan was prepared before initiation

of work on this project:

| Project Activity | Monthly Report Period | | | | | | | |
|---------------------------------------|-----------------------|-----|-----|-----|-----|-----|-----|-----|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct |
| Preliminary literature search | X | | | | | | | |
| Continuing literature search | | X | X | X | X | X | X | X |
| Procurement of equipment and supplies | X | | | | | | | |
| Organization of laboratory program | X | | | | | | | |
| Assembly of apparatus | | X | X | | | | | |
| Familiarization experiments | | | X | X | | | | |
| Irradiation studies | | | | | X | X | X | X |
| Application for renewal | | | | | | X | | |
| Final report, first contract period | | | | | | | | X |

Changes in availability of project personnel and unavoidable delays in obtaining necessary equipment have caused the project to lag approximately 2 weeks behind the planned achievement level. It is hoped that increased effort will permit completion of the proposed study within its allotted period without sacrifice of any of the planned investigations.

B. Discussion of Experimental Plan

A number of the experiments necessary to characterize a polymer require extended lengths of time for completion. The experimental program was therefore designed to include automatic equipment capable of continuous operation for several days with little or no operator attention and to permit conducting as

many as possible of the time consuming operations, e.g. tempering of films for crystal formation, concurrently. The personnel effort saved from routine operation could be usefully employed for a larger number of measurement operations such as viscosimetry and infrared spectra of polymer fractions than would otherwise be possible and to extend the scope and intensity of the literature search.

As the techniques of polymer treatment require certain laboratory skills not universally required in ordinary chemical manipulation, a significant benefit could be anticipated by including a brief training period for project personnel using commercially available polymers. Comparison of results obtained during this training period with the literature data obtained by other investigators using similar materials is expected to serve the purposes of building confidence of project personnel, pointing up deficiencies in technique and apparatus design, and improving comprehension in the assigned literature search.

C. Method of Attack

1. Selection of Monomers

The selection of monomers for this study will depend upon a number of properties of the monomer and corresponding polymer, such as vapor pressure, solubility, stability of emulsion, etc. It will be desirable to employ monomers of simple chemical structure, but to avoid problems arising from high vapor pressures, high energies of activation, etc. Monomers such as methyl acrylate, methyl methacrylate, vinyl pyrrolidone, etc., would appear to be the most likely candidates. Methyl methacrylate has been chosen for initial studies, as it has the further advantage that its polymerization by full period irradiation with gamma rays from cobalt-60 and cesium-137 has been extensively studied (19, 22). Hence, data derived from the proposed research will provide a broad

basis for comparison of the results obtained by full period and by post-effect irradiation.

2. Irradiation

The monomer may be exposed to the brief irradiation period in bulk, in solution, or in emulsion form. Initial experiments will be performed with bulk monomer (methyl methacrylate) in which the polymer is readily soluble. The Georgia Tech Cesium-137 Research Irradiator will be used to provide brief but accurately measured exposure periods of various lengths to the monomer systems. This reaction mixture, free of chemical catalysts and protected from light, will then be able to undergo further polymerization only through operation of the post-effect. The doses of radiation, which will be much lower than those normally used where maximum polymerization is desired, will be accurately measured by ferrous ion, benzene, or other standard dosimeter. Uniformity throughout the reaction mixture is anticipated, as gamma radiation is not subject to the "surface effects" characteristic of irradiation by ultraviolet or other lower energy sources.

3. Quenching and Examination

Immediately after exposure, and at definite time intervals thereafter, samples will be withdrawn from the reaction vessel and quenched with an inhibitor, such as methyl ether of hydroquinone. The optimum frequency of sample withdrawal and duration of each experiment will be determined at an early date. The quenched samples will be examined according to the following program:

a. Extent of polymerization will be estimated gravimetrically from the weight of polymer remaining after removal of the monomer by reduced pressure distillation, followed by coagulation, filtration and drying (15).

b. Distribution of molecular weight will be obtained by fractional

precipitation from varying solvent systems (15). This property will also be studied using a column method of separation by molecular weight fraction. The thermal gradient column described by Schneider (24) has been successfully used for polymethyl methacrylate. A combination of thermal and solvent gradient (an extension of this principle (27,28)) will be used in the present program.

c. Determination of molecular weights within each fraction may be obtained by viscosimetric techniques; however, a micro-molecular weight technique has been developed in the laboratories of Dr. J. A. Knight in the Engineering Experiment Station and is available for use on this project. This technique employs a thermistor measurement of freezing point lowering and is accurate to within 1 to 2 per cent.

d. Degree of branching and cross-linking will be estimated through infrared examination of the polymeric products (25).

e. Crystallinity will be indicated by x-ray diffraction studies. For those polymers showing some degree of crystallinity, the weight fraction of amorphous material will be estimated by obtaining the integral of x-ray scattering intensity as a function of the scattering angle for the amorphous halo, omitting the peaks, and comparing the results with the integral obtained from similar measurements of the material slightly above its melting point (11, 26).

f. Specific volume and coefficient of thermal expansion of the amorphous phase can be determined by measuring these properties directly at temperatures above the melting point. For the crystalline phase, these properties may be determined from the lattice distances estimated from the spacings of the diffraction rings (26).

g. The melting point of the crystalline phase is most easily measured by examining a thin film of the material with a hot stage microscope

between crossed polaroids. The crystalline phase, by rotating the plane of polarization, allows some light to be transmitted through the viewing polaroid. When the melting point is reached, this light disappears (25).

h. Morphology will be determined by x-ray and infrared studies. Measurements of the foregoing properties provide a direct means of determining the volume fraction of crystalline material present at any temperature. Crystallinity is associated with structural features of the polymer molecules tending to favor geometrical packing arrangements, and is thus a feature of isotactic polymers of short side chains. Bulkiness of side chains, atacticism of the polymer chain and, in some cases, syndiotacticism tend to give rise to amorphous bodies. Natta and Corradina (23) have made an extensive study of the relationships of crystallinity to these structural features and it is anticipated that results of the proposed research will be interpreted in the light of their work.

Infrared analysis has been used (18 a,b) to determine the relative quantities of atactic and isotactic phase in polypropylene. Its applicability to that purpose in the present research will be investigated. The method has been applied to methyl methacrylate (17).

D. Apparatus

1. Sample Irradiation

Irradiation of monomer samples will be performed in the Georgia Tech 12,000 Curie Cesium-137 Research Irradiator. A plan view of the sample holder is shown in Figure 1.

The monomer will be contained in stainless steel bottles equipped with "Teflon" screw plugs to exclude air. Each bottle will be numbered to correspond to one of the 12 sample holders and will be marked so that orientation of the

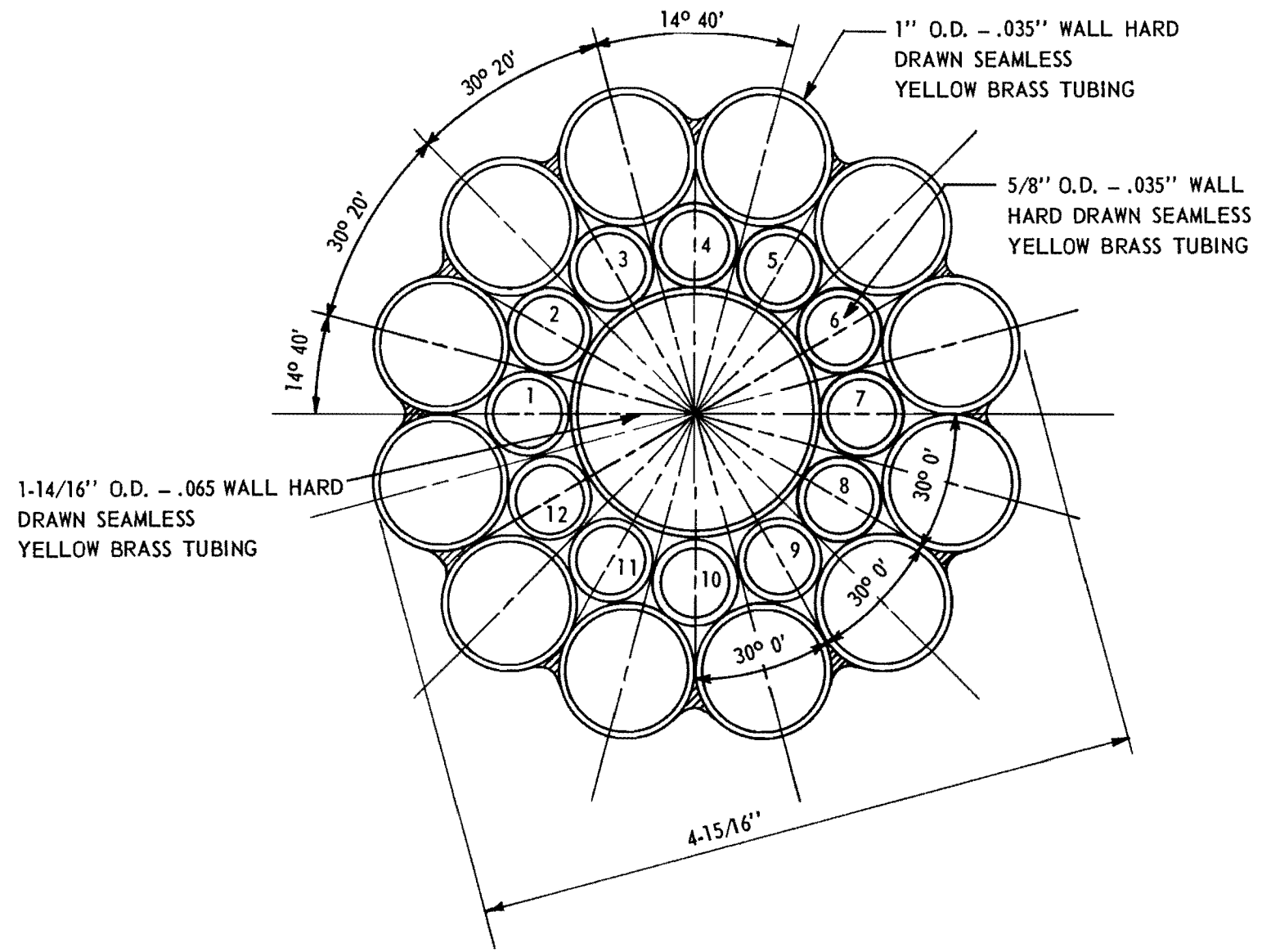


Figure 1. Horizontal Cross-Section of Tube Nest.

bottle in its holder with respect to the source material will be reproducible in successive experiments. Conventional ferrous ion or other standard dosimetry will be used to measure the dose rate in each of the sample bottles. Dose variance of the irradiator with vertical movement is displayed in Figure 2.

In the outer row of the tube nest the dose is uniform for a vertical distance of approximately 2-3/4 inches, although there is some variation in the horizontal plane. Use of a sample length of 2-1/2 inches and proper spacers will assure uniform irradiation of each sample over its entire length.

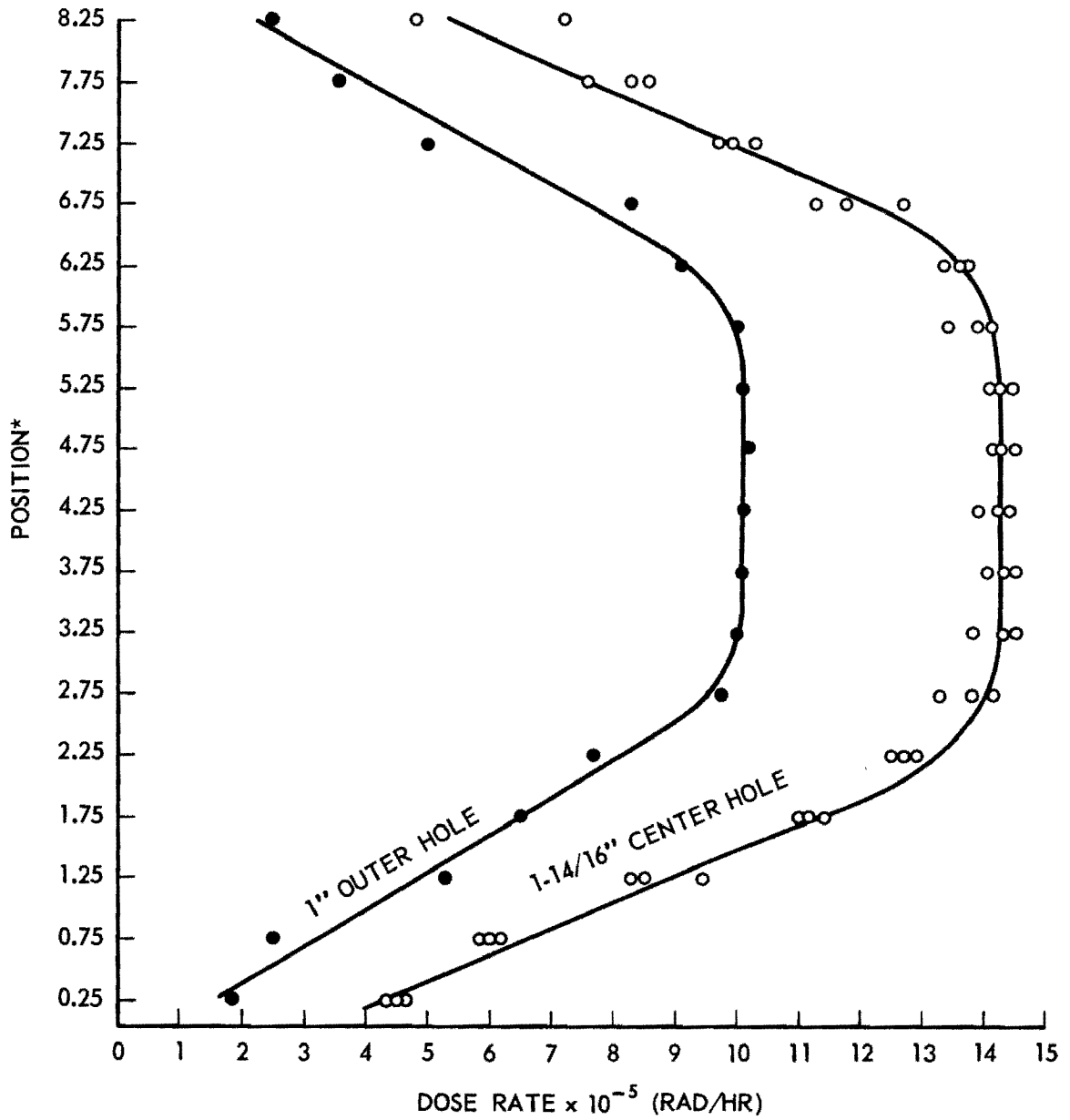
2. Separation of Polymer Fractions

Chromatographic apparatus for separation of polymer fractions is adapted from a design described by Weakley, Williams and Wilson (27). A schematic diagram of this equipment is presented in Figure 3.

The principal parts of this apparatus are a reservoir, mixing chamber, and magnetic stirrer for generation of a solvent gradient, a solvent degassing column, and "inverted" chromatographic column, and a Rinco automatic fraction collector suitable for either timed or volume control. Ball and socket joints are included between the larger components to facilitate apparatus setup and to reduce the danger of strain induced breakage.

Solvent mixer flasks of several sizes have been chosen to permit variation of solvent independently of rate of flow through the system.

The solvent degassing and chromatographic columns are conventional 400 mm x 20 mm. Pyrex glass apparatus with standard tapered joints at each end and a porous glass disc fused into the plug at the base of each column to support the packing. Packing, initially, will consist of glass beads approximately 0.1 mm in diameter. Beads 0.05 mm and 0.20 mm in diameter are on hand, should their use be justified. The thermal gradient in these columns is supplied by tightly



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

Figure 2. Dose Variance with Vertical Movement.

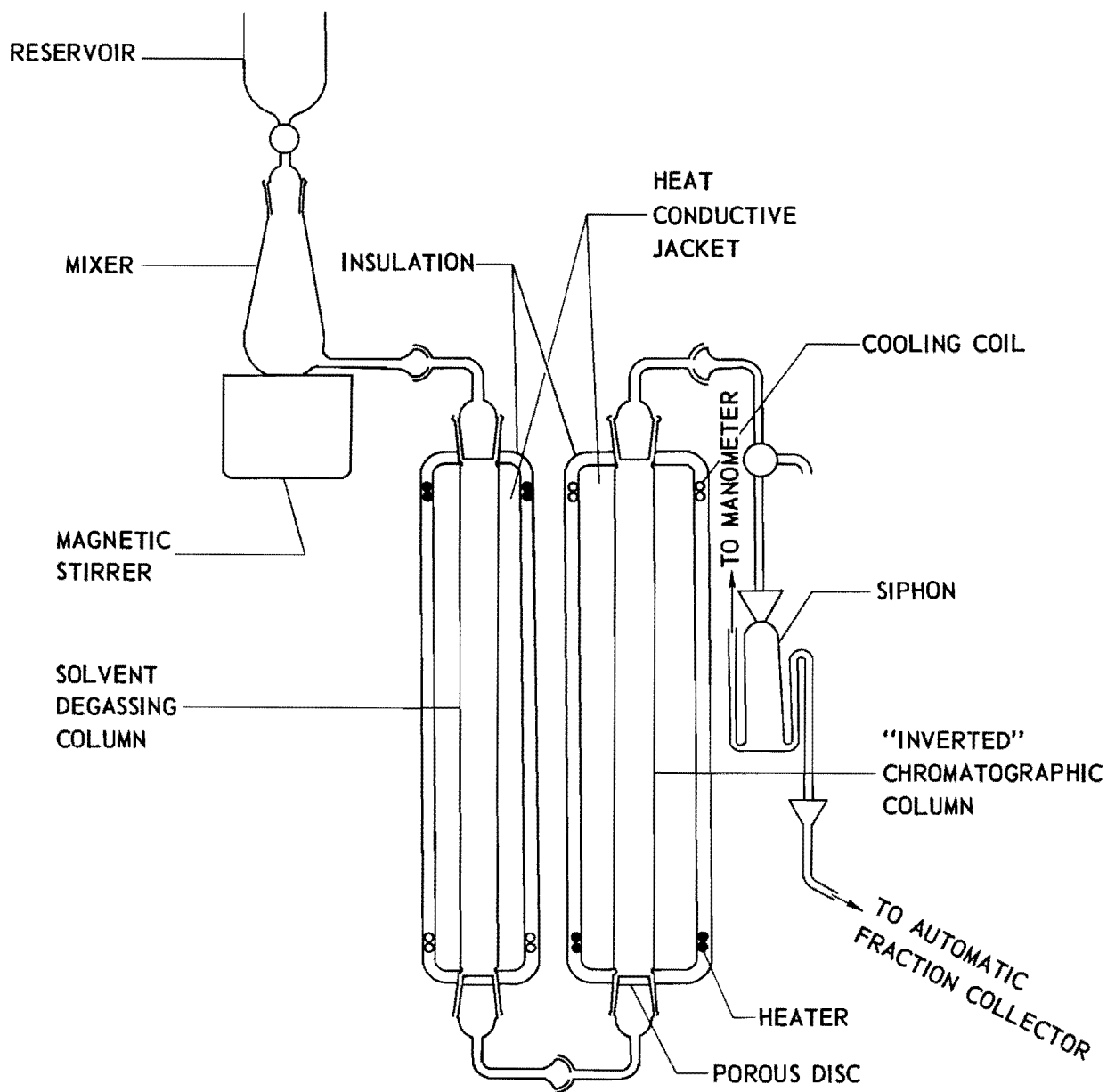


Figure 3. Apparatus for Chromatographic Separation of Polymer Fractions.

wrapped aluminum foil heated by a tightly wrapped nichrome coil at one end and cooled by chilled water flowing through copper tubing at the opposite end. After wrapping, the aluminum foil was further compressed by a closely wrapped spiral of nylon tire cord over its entire length. Thermal insulation is provided by a one inch thick cylindrical jacket and end caps shaped from "Glasrock," a lightweight, commercially available, foamed silica product. A thin wrapping of glass wool prevents damage to the insulating shell by thermal expansion of the aluminum jacket. The heating elements will be controlled by Thermistemp, Model 63 thermoregulators. Regulation of voltage applied to the heaters will be used in early experiments, although the controls are suitable for use with timed input controllers, should their use become necessary.

Construction of this apparatus is complete except for installation of the thermoregulators. Every effort is being made to expedite their delivery.

3. Smaller Apparatus

Standard laboratory glassware, stills for solvent and monomer purification, laboratory balances, including a Mettler microanalytical balance, viscosimeters, and constant temperature baths are on hand.

IV. FUTURE PLANS

Upon completion of the familiarization period, irradiation of monomer samples and systematic study of polymers produced will be initiated. Early investigation will be concentrated on methyl methacrylate, a choice suggested by the wealth of literature on conventionally produced polymer available for comparison with experimental data obtained from "post-effect" polymerization. It is thus anticipated that the initial phase of this project will provide

both training and useful experimental results. Studies of other monomers and/or more detailed study of methyl methacrylate "post-effect" polymers will be proposed for future investigation, should this project warrant renewal.

V. LITERATURE REVIEW

The literature reviewed during the first three project periods has been divided between material necessary for overall project planning and information required for early laboratory manipulation. Of long range interest have been discussions of the morphology of polymers resulting from specific preparative methods (17, 22), postulated reaction mechanisms leading to formation of the observed products (4, 10), kinetics of polymerization reactions under various experimental conditions (4, 19), and application of thermodynamic techniques to treatment of observed data (8). Of immediate use are experimental techniques such as the use of infrared spectrophotometry to indicate polymer morphology and chain branching (17, 18, 25), viscosity of polymer solutions as a function of molecular weight (1, 13, 14), separation of polymer fractions (1, 3, 24, 27), light and x-ray scattering phenomena (16, 17, 23), and rate of polymerization as a function of radiation dose rate (22). It is believed that this approach will furnish specific laboratory information as it is required and will simultaneously lead to the accumulation of sufficient theoretical background to permit rational treatment of experimental data.

Respectfully submitted:



W. H. Burrows
Project Director

Approval:



Fred Bellinger
Chief, Chemical Science and Materials Division

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QUARTERLY TECHNICAL STATUS REPORT NO. 2

PROJECT NO. A-446-10

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By

L. W. ELSTON and W. H. BURROWS

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ABSTRACT

Activities during the period included survey and review of literature pertinent to the various aspects of this project, studies of laboratory polymer characterization procedures using commercially available polymer samples, and modification of both equipment and experimental procedures. Calibration of equipment and preliminary experiments is nearly complete. Irradiation studies will be initiated during the next report period.

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I. INTRODUCTION

The broad objectives of this research are to study the effects of various experimental parameters upon the molecular characteristics of polymers resulting from "post-effect" polymerization of certain monomers. Quarterly Technical Status Report No. 1 discussed the experimental parameters, specific methods to be employed, and relationships between observations anticipated from these methods and molecular characteristics of the polymer products obtained.

The molecular characteristics of the products are determined by the mechanism of the polymerization reaction; a free-radical mechanism tends to produce atacticism, and an ionic mechanism operates to produce an isotactic product. The research is thus a kinetics study of the polymerization reaction in which the undesirable effects resulting from continued ionizing radiation or associated with the use of chemical catalysts are minimized through use of "post-effect" polymerization.

It has been suggested that temperature and physical state of the monomer during irradiation and polymerization influence the choice of free radical or ionic reaction mechanism (1,2). There are, however, reports of abundant evidence for the presence of trapped free radicals in the solid and near-solid states (3).

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 3. C. H. Bamford, A. D. Jenkins and J. C. Ward, "Polymerization in the Solid and Near-solid States," J. Polymer Sci. 48, 37-51 (1960)

II. EXPERIMENTAL

A. Tentative Project Plan

Results obtained during the preliminary experiments indicate the need for more extensive modification of both apparatus and proposed techniques than was anticipated in the original tentative plan. As a consequence, actual polymerization studies have been delayed. It is expected, however, that irradiation experiments will be initiated during the next month.

B. Experimental Procedures

Experimental work has been directed principally toward assembly and modification of apparatus and development of techniques necessary for polymer characterization, as outlined in succeeding paragraphs. Plexiglas lathe turnings, rendered oil-free by extraction with hexane, have been used for preliminary experiments and for trial operation of the apparatus fabricated in our laboratory, shop, and glass blowing facility. Methyl methacrylate samples of known molecular weight and inherent viscosity are being used as controls and for comparison of measurements made by project personnel with those obtained in other laboratories.

1. Sample Irradiation

Stainless steel bottles have been fabricated to fit into the 12 outer sample positions of the Georgia Tech Cesium 137 Research Irradiator. These bottles are equipped with Teflon screw plugs to exclude air. Chemical dosimetry will be used to assay the gamma-ray dose in each of these vessels in its assigned position and orientation. Two of these bottles are shown in Figure 1.

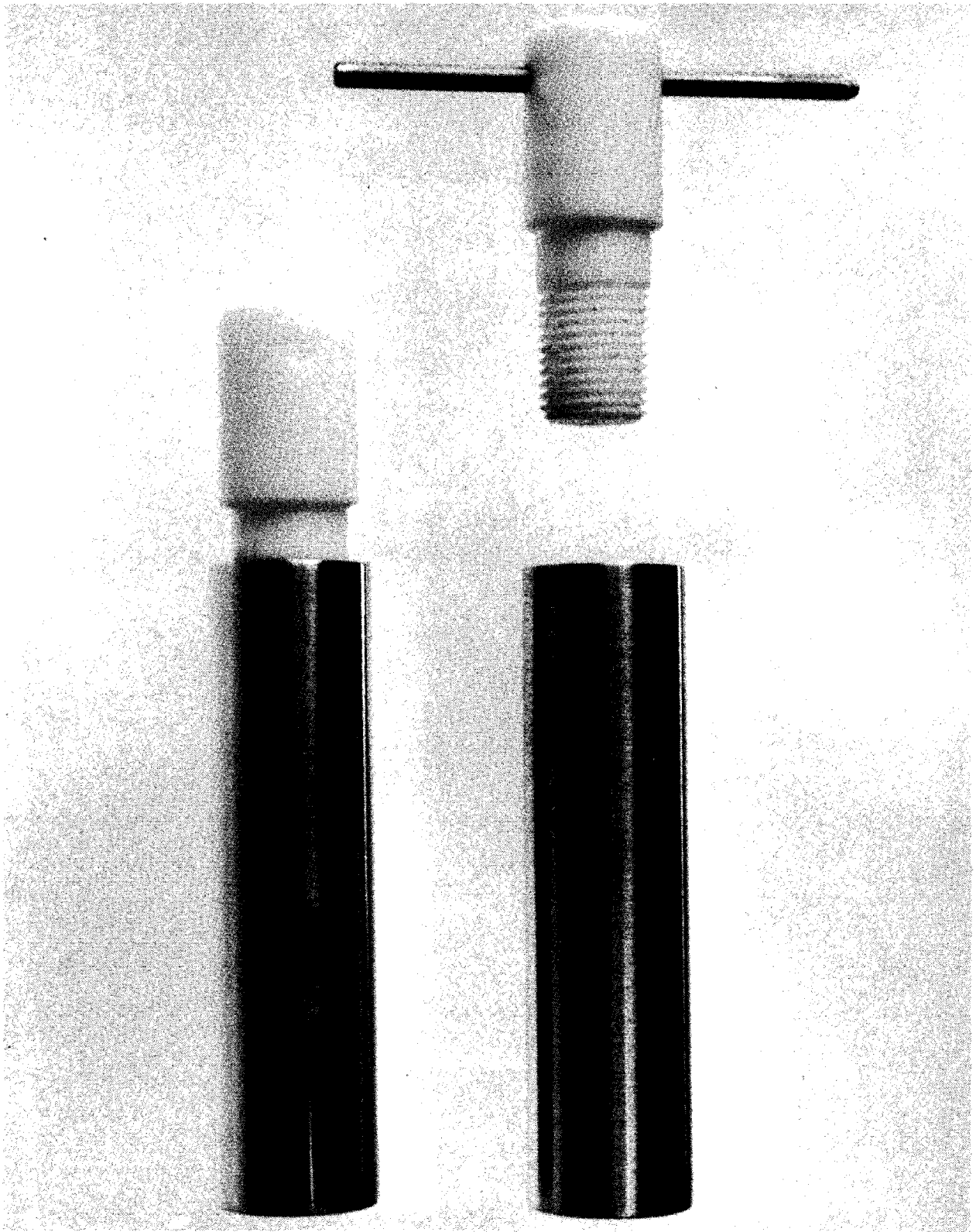


Figure 1. Sample Irradiation Bottles with Closures.

2. Separation of Polymer Fractions

Construction, calibration, and modification of the apparatus for chromatographic separation of polymer fractions has been completed. The inverted chromatographic column had been wrapped with aluminum foil to a thickness of approximately one inch to provide a temperature gradient between the heating element at the bottom and the cooling coils at the top. It was found, however, that the aluminum foil wrapping exhibited irregular heat transfer properties, and it was necessary to replace it with a conductive jacket machined from 3-inch aluminum bar stock. A source of refrigerated water is being installed; in the meantime refrigerated water is being supplied from two chests chilled with dry ice. The cooling coils have been redesigned to extend approximately two-thirds of the length of the column and provide a thermal gradient in the cooling water paralleling that required in the column. The completed polymer fractionator is shown in Figure 2.

The temperature gradient in the chromatographic column packed with glass beads and a typical solvent was measured at one-inch intervals using copper-constantan thermocouples and a sensitive potentiometer. The gradient was found to be nonlinear but unidirectional. The variance of temperature with distance from the base plate of the column is shown in Figure 3.

3. Preparation of Oil-Free Polymer

Turnings of commercial methyl methacrylate polymer are being extracted with hexane in a large Soxhlet extractor to provide oil-free polymer for solubility and viscosity experiments. This apparatus is shown in Figure 4.

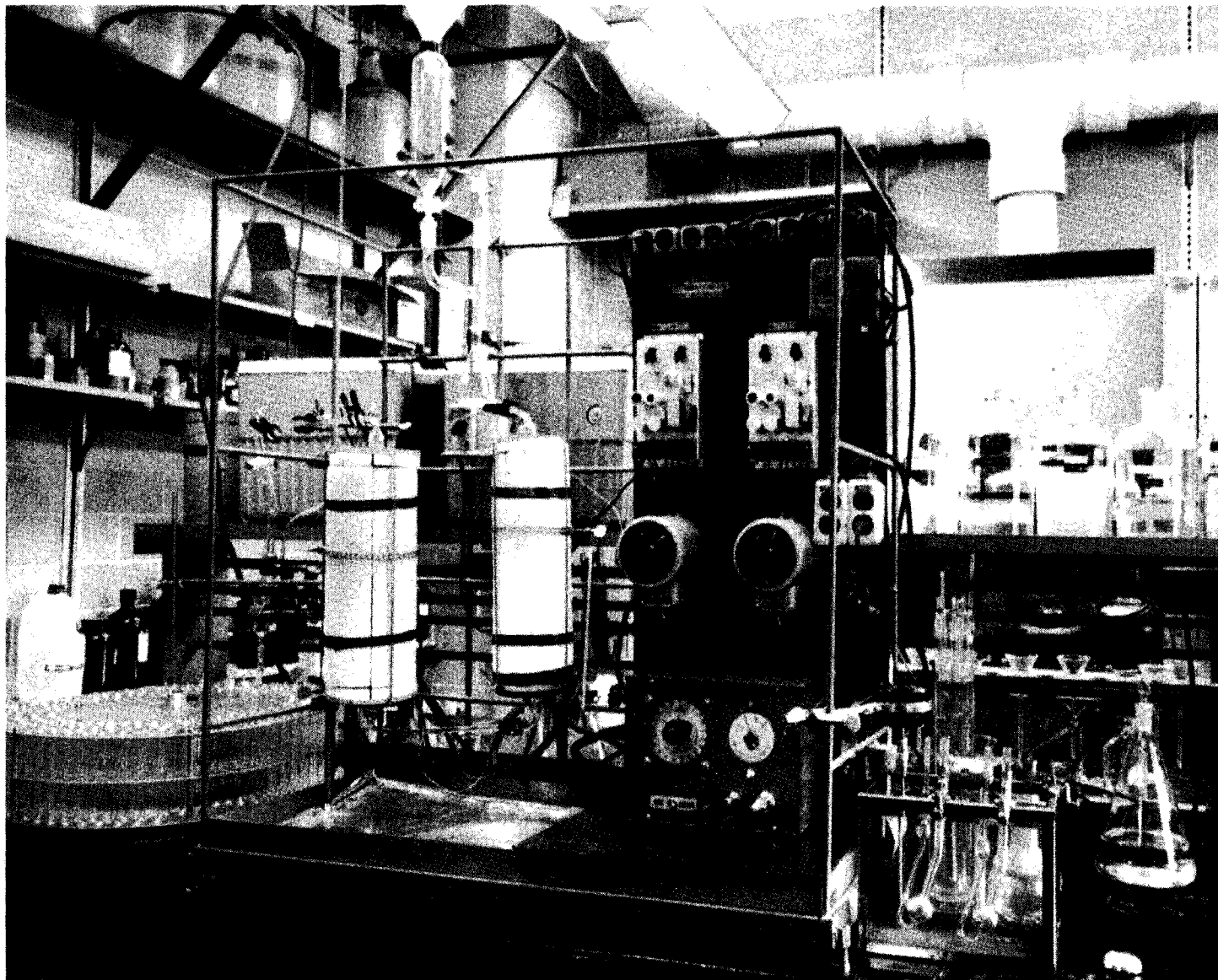
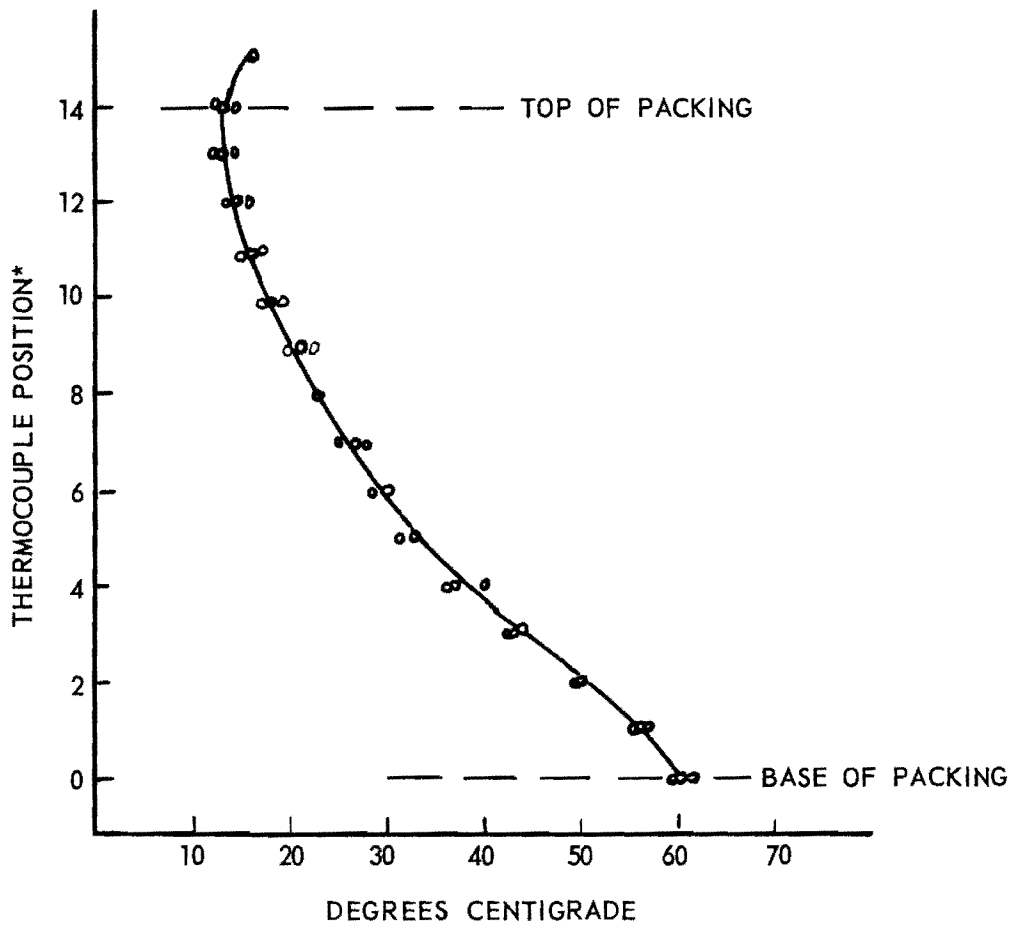


Figure 2. Solvent/Temperature Gradient Polymer Fractionator.



*Thermocouple position in inches from base of column packing.

Figure 3. Chromatographic Column Temperature Gradient.

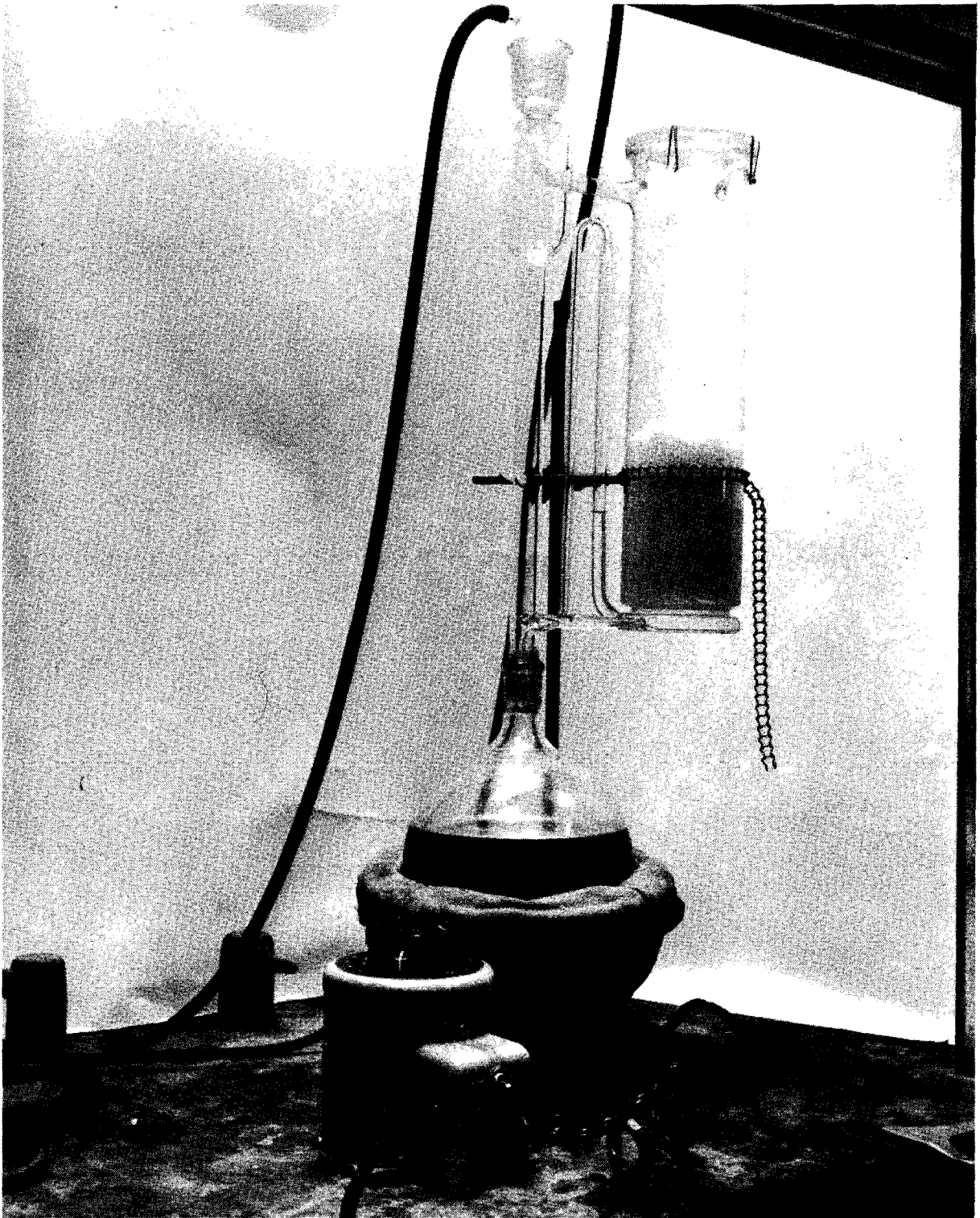


Figure 4. Oil Extraction of Commercial Polymer Turnings.

4. Purification of Solvents and Monomer

Stills for solvent and monomer purification are in operation. This system may readily be modified with components on hand to permit distillation of monomer under an inert (nitrogen) atmosphere.

5. Preparation of Gel-Free Polymer Solutions

Erratic results were obtained when viscosity measurements were made with solutions of commercial polymer at several concentrations in acetone and toluene. These results are believed to arise from the presence of gel in the polymer solution. Attempts were made to prepare gel-free polymer solutions by dissolving the ground material from a sintered glass crucible substituted for the paper thimble customarily used in a Soxhlet extractor; however, these attempts were unsuccessful. Preparation of an apparently gel-free solution has since been achieved by filtering a dilute polymer solution through a porous glass disc and subsequent dilution or concentration of the filtered solution by evaporation of solvent under reduced pressure.

6. Precipitation of Polymer on Column Packing

Samples of polymer for fractionation will be introduced into the chromatographic column as a precipitate on glass beads. Initial attempts to precipitate polymer on a slurry of glass beads in nonsolvent produced a gummy mass unsuitable for introducing chromatographic column samples. Satisfactory material was obtained by dropwise addition of polymer in a low boiling point solvent (methylene chloride) to a slurry of glass beads in an excess of hexane contained in a magnetically stirred open Teflon beaker. The slurry, though cohesive at first, became mobile upon continued stirring and periodic addition

of hexane to replace the solvent which evaporated. After approximately 6 hours of stirring and hexane addition, no odor of methylene chloride was detected above the slurry. Evaporation of a small portion of the supernatant liquid left no detectable residue of polymer. Failure to obtain mobile slurries by precipitation of polymer from acetone and toluene solutions on glass beads in hexane suggests that this technique of column sample preparation requires a solvent appreciably more volatile than the nonsolvent employed in the chromatographic system.

III. FUTURE PLANS

Experiments are currently in progress for determining the intrinsic viscosities of polymer fractions. Viscosimeters covering a wide range are being standardized against Bureau of Standards oils. The viscosities of polymer solutions will then be determined as functions of concentration and the intrinsic viscosities obtained by extrapolation to the viscosity axis.

Fractionation of commercial polymer, as reference material, is in progress. Samples of the fractions obtained are being separated from the solvent by evaporation for introduction into the chromatographic column. Because of the high boiling solvent required in the column, this evaporation is time consuming. A flash evaporator is being considered to speed this process.

Initial irradiation experiments are anticipated in the near future, possibly utilizing a small x-ray unit in the Industrial Products Laboratory before proceeding to the Cesium 137 Research Irradiator for more extensive studies.

Respectfully submitted:

W. H. Burrows
Project Director

Approved:

Frederick Bellinger, Chief
Chemical Sciences and Materials Division

FINAL REPORT
PROJECT NO. A-446-10

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

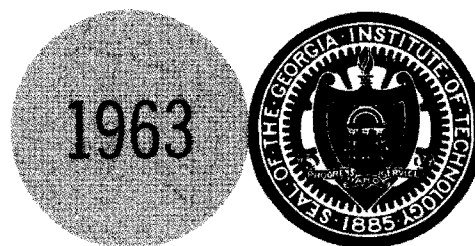
by L. W. Elston and W. H. Burrows

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

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United States Atomic Energy Commission
Savannah River Operations Office
Aiken, South Carolina

Performed for
United States Atomic Energy Commission
Division of Isotopes Development
Germantown, Maryland



Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

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

CONTRACT NO. AT (38-1)-202
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UNITED STATES ATOMIC ENERGY COMMISSION
SAVANNAH RIVER OPERATIONS OFFICE
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DIVISION OF ISOTOPES DEVELOPMENT
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 ($23^{\circ} \pm 2^{\circ} \text{C}$) 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.

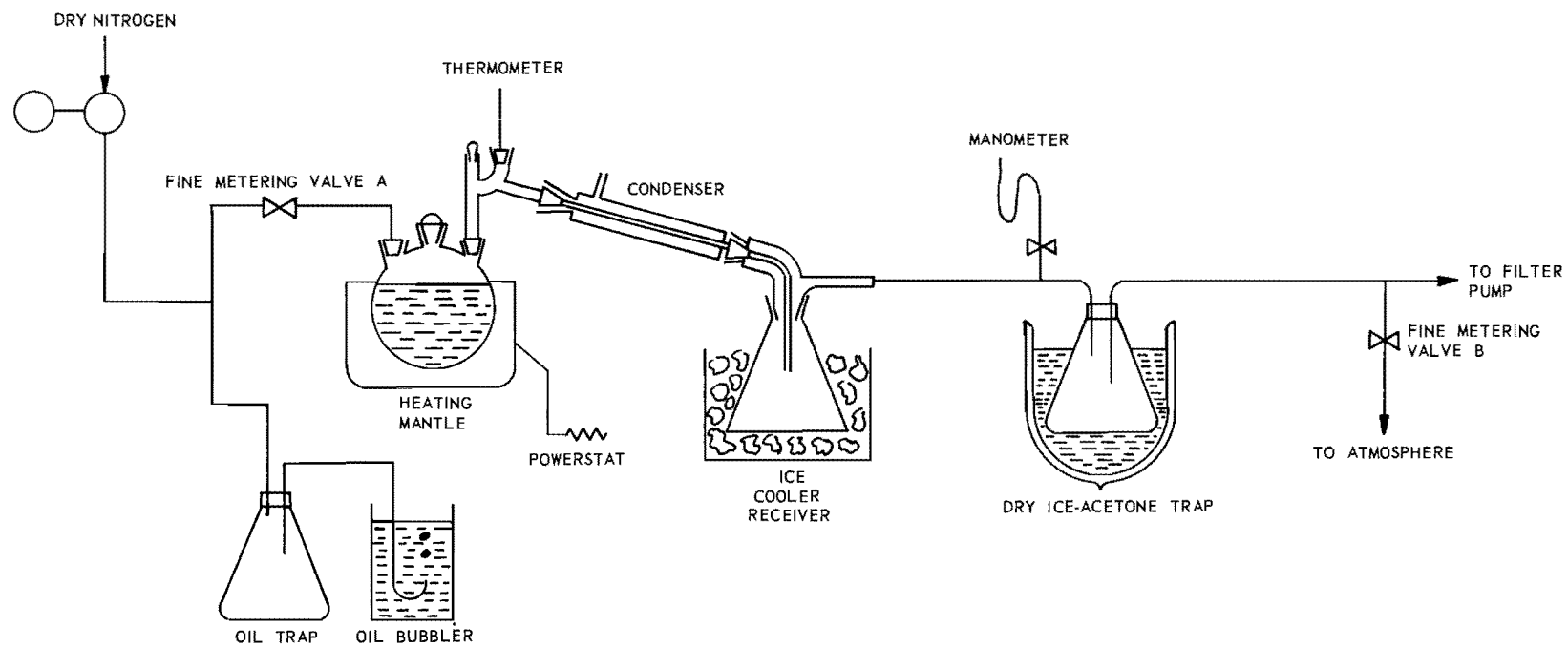


Figure 1. Inert Atmosphere Still.

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

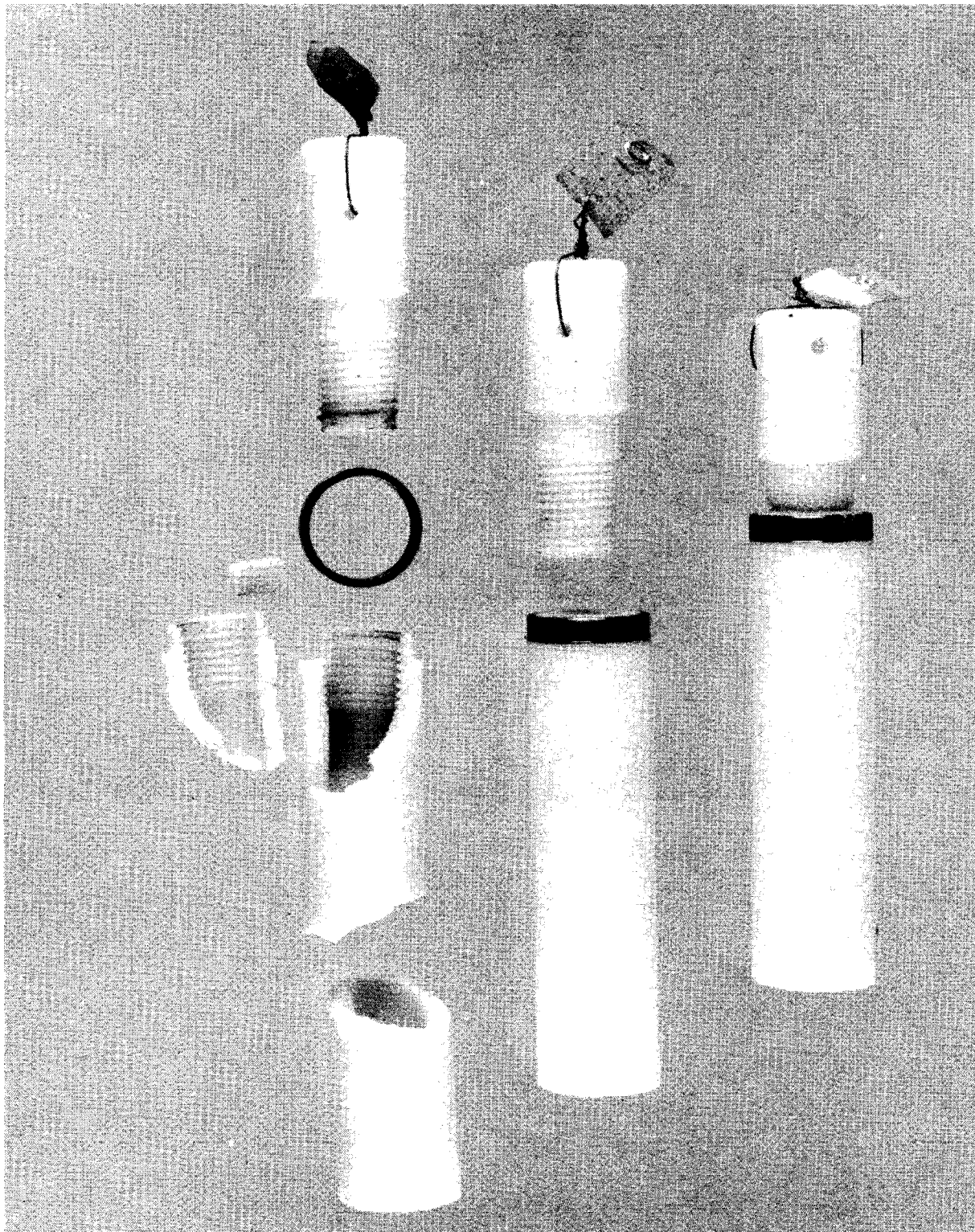


Figure 2. Teflon Vessels Used for Monomer Irradiation.

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.

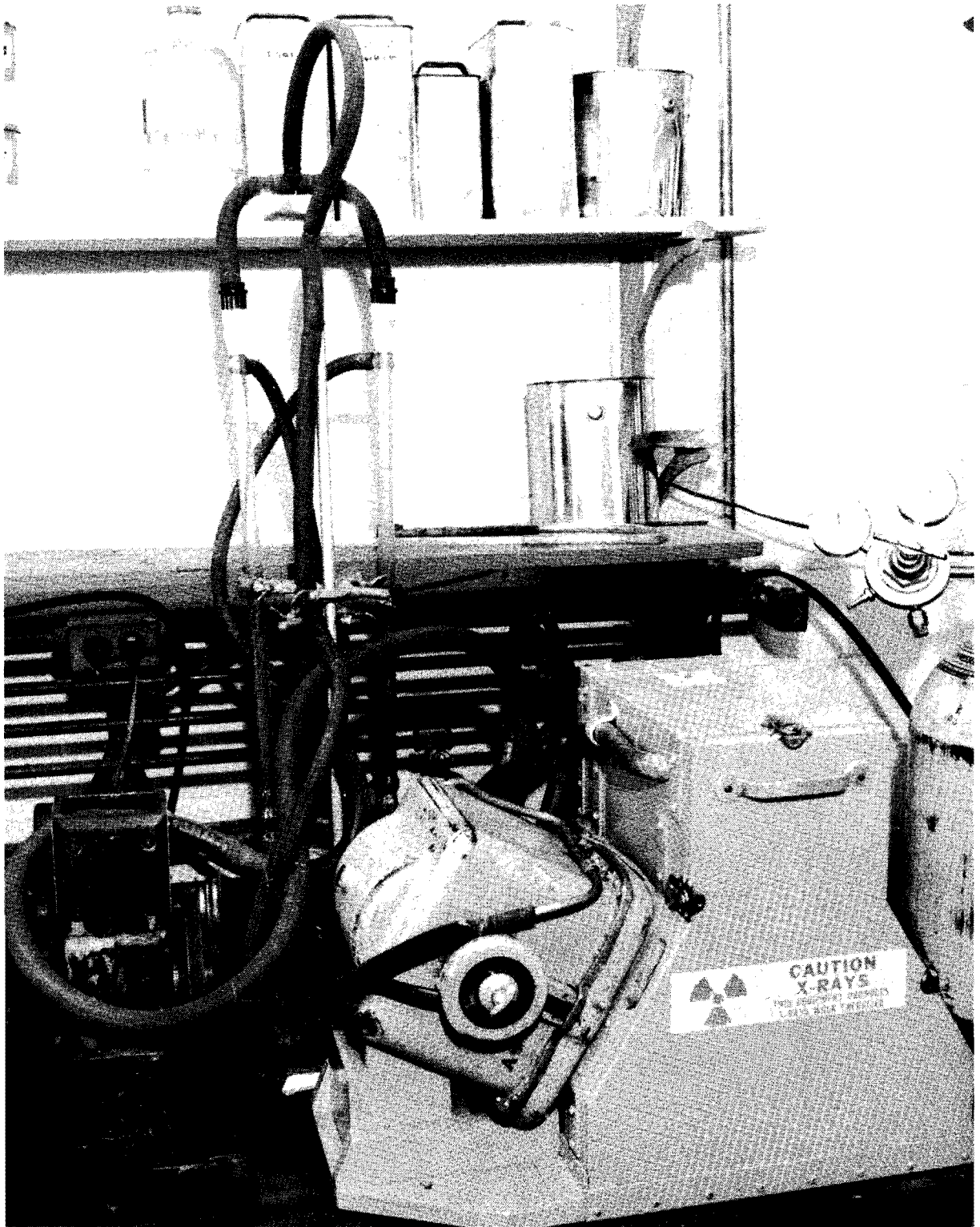
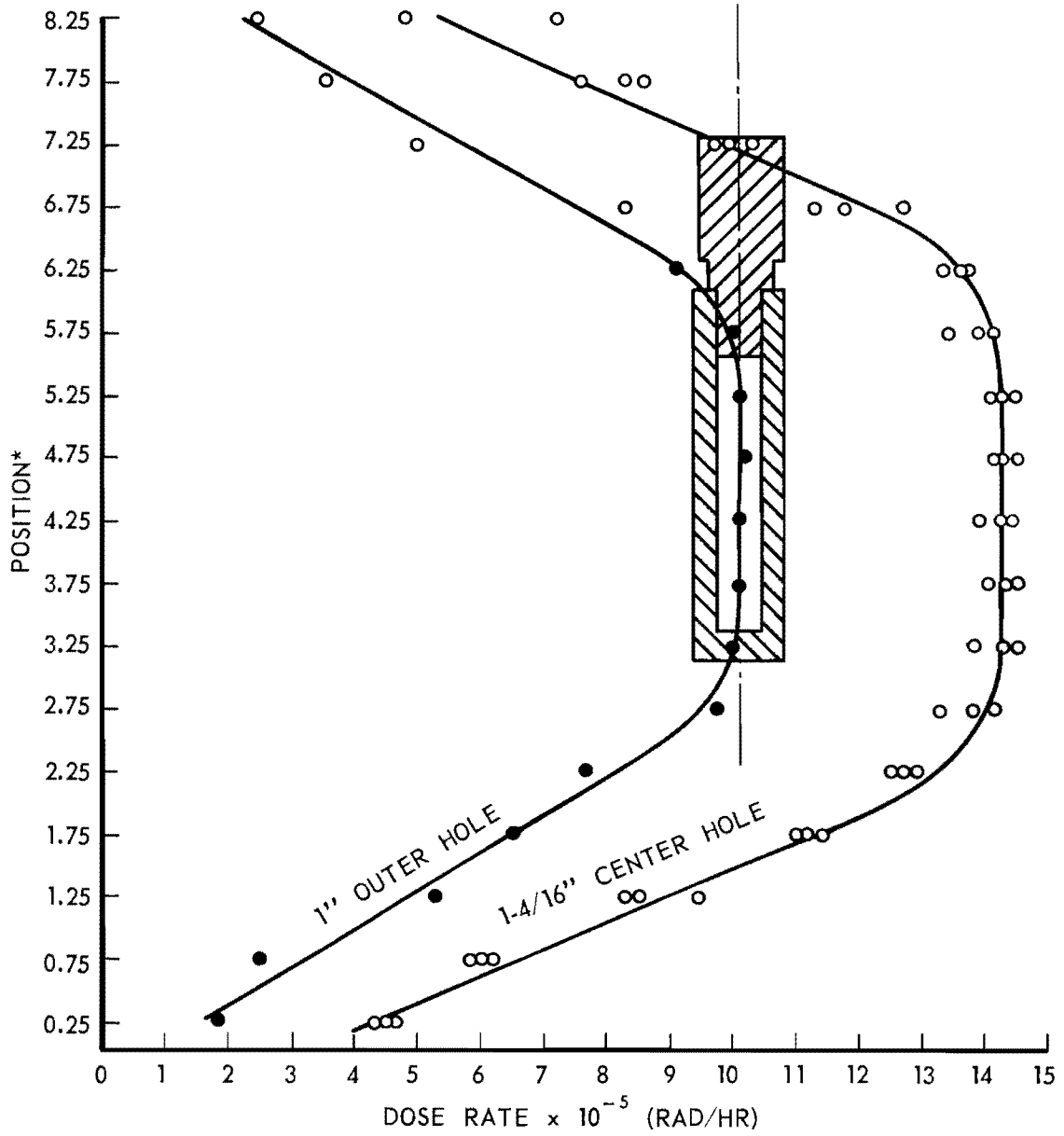


Figure 3. Laboratory X-Ray Equipment.



*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^o 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 (Trömsdorff) 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

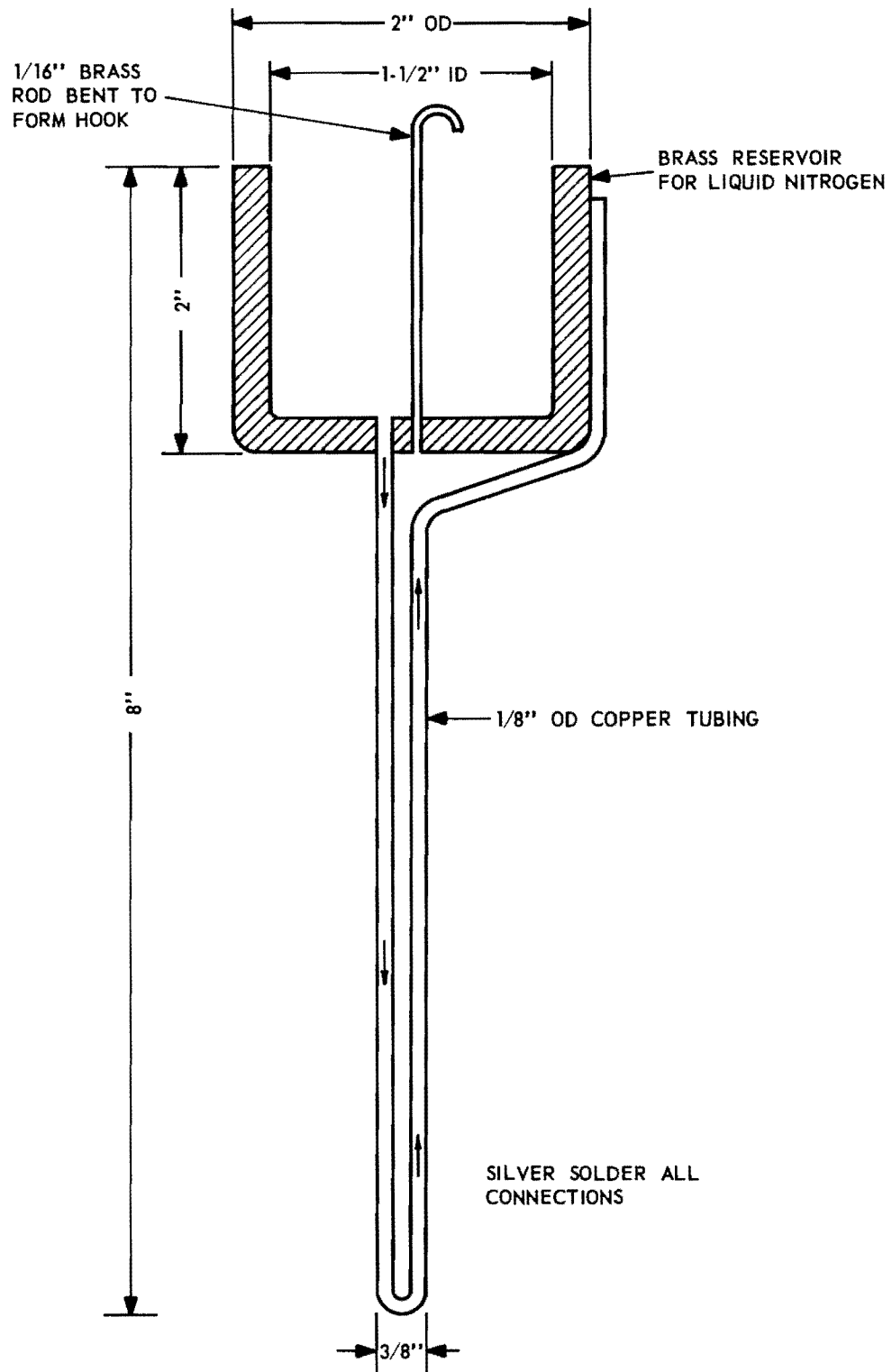


Figure 5. Cold Quenching Device.

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.

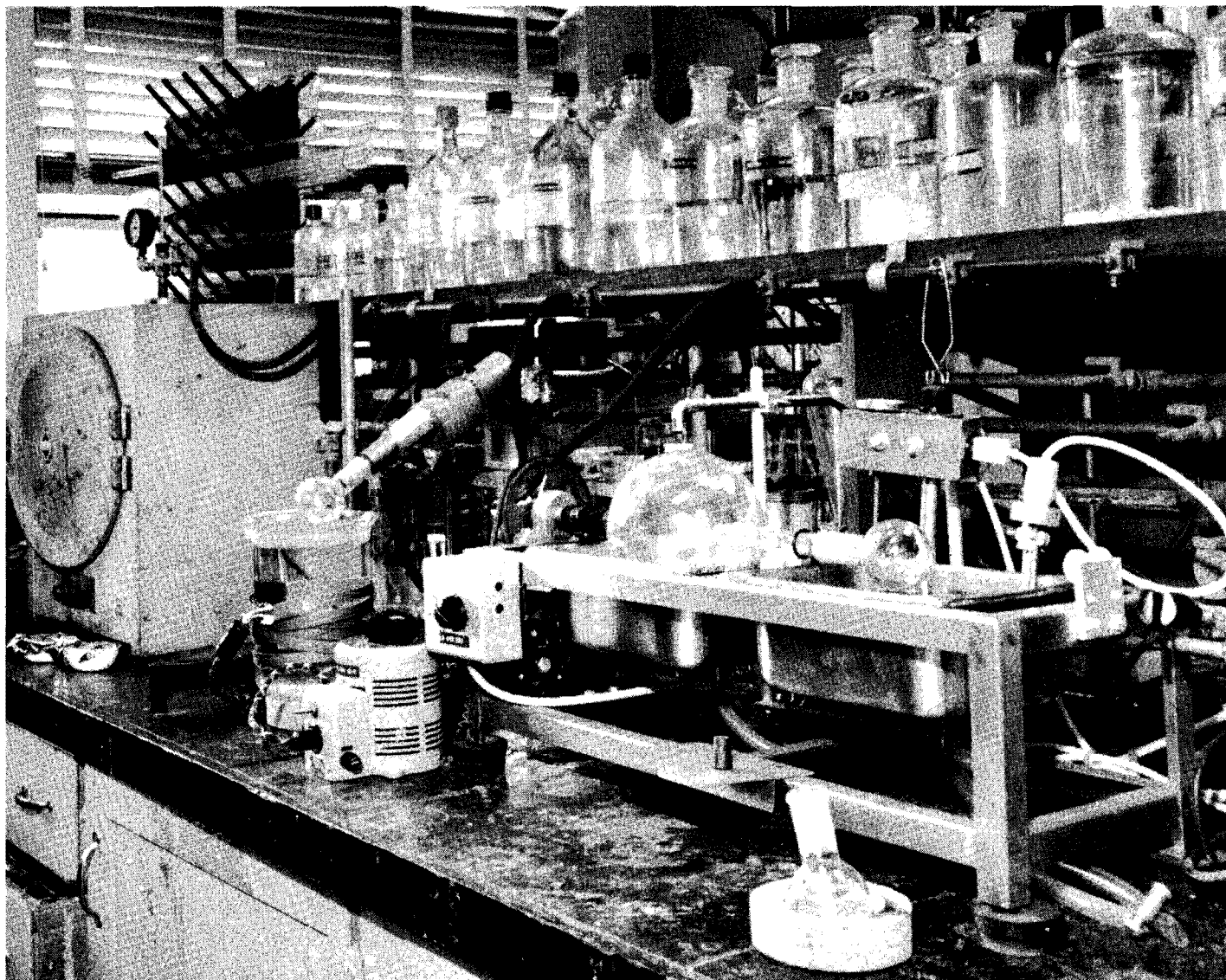


Figure 6. Rotating Vacuum Evaporators and Vacuum Oven.

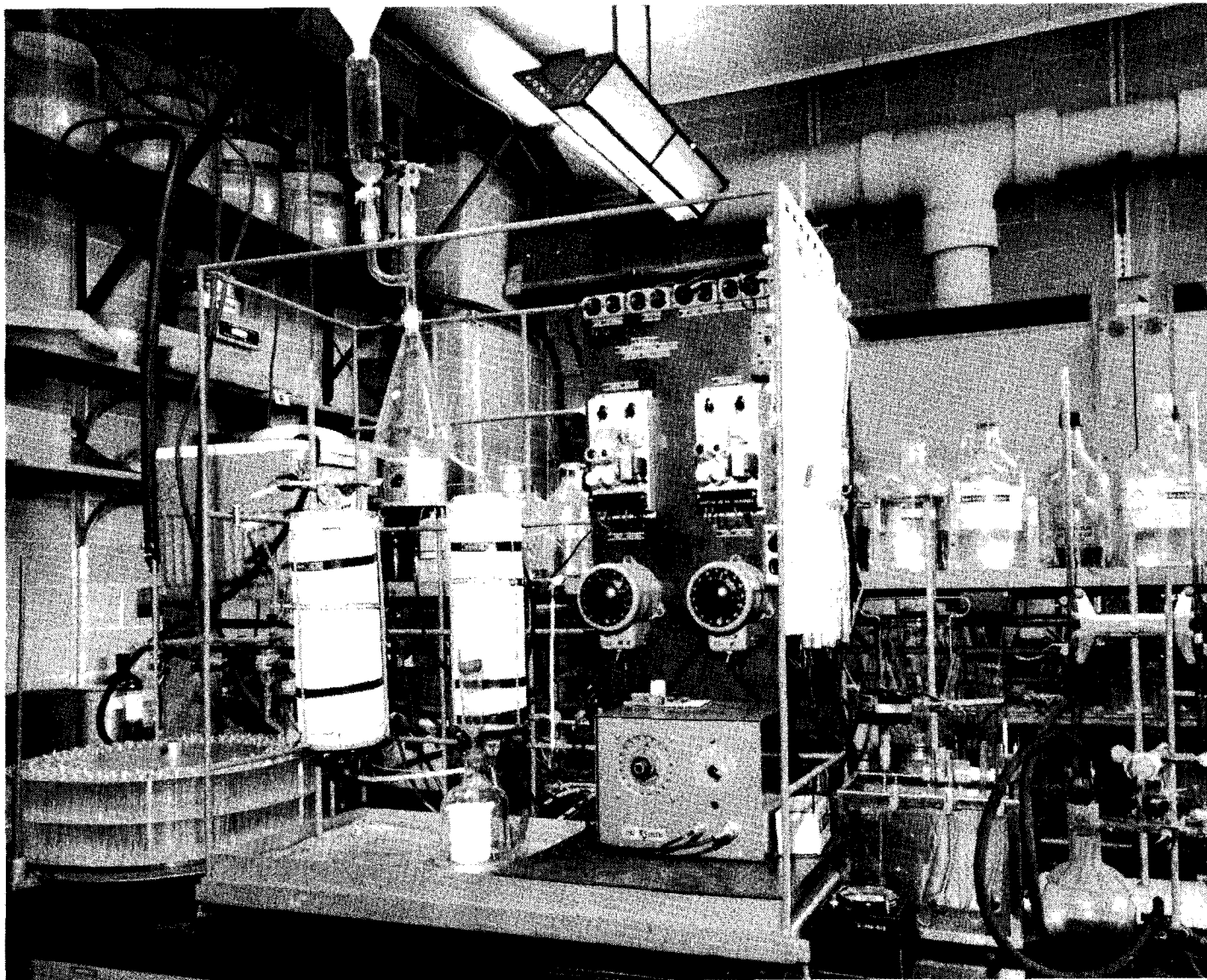


Figure 7. Solvent Temperature Gradient Polymer Fractionator.

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 glycerol 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

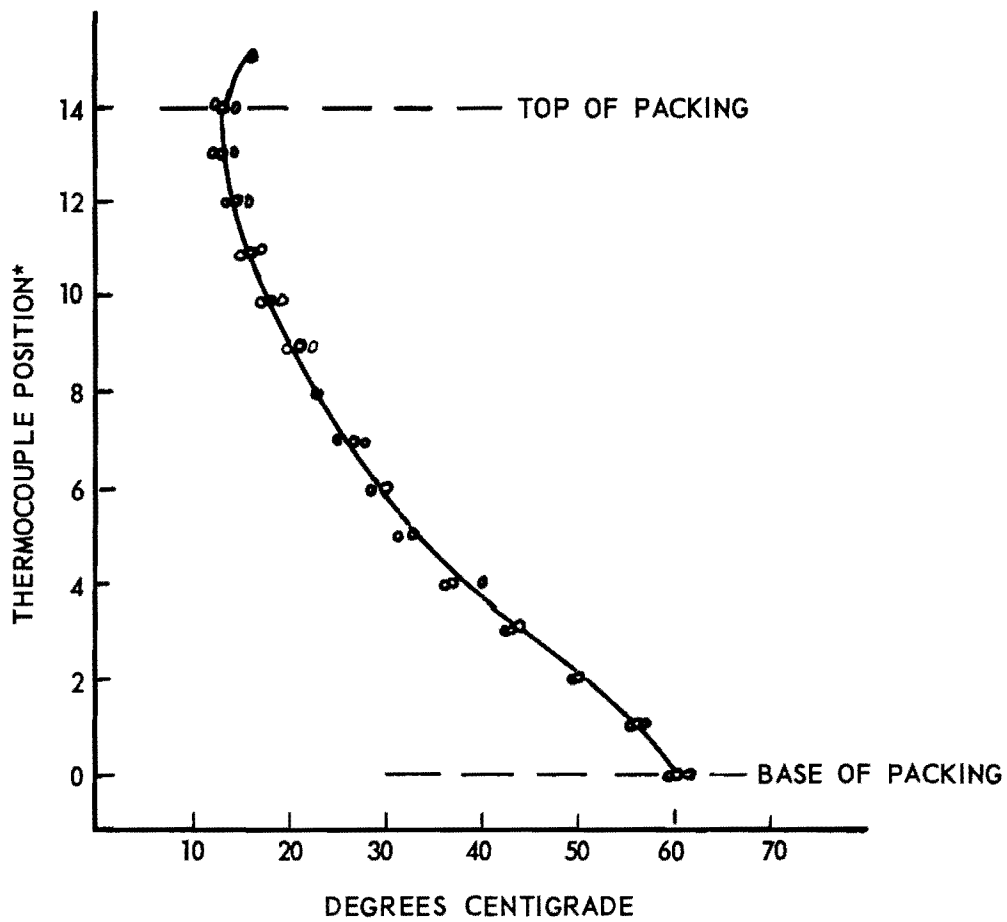
by a tightly wrapped nichrome coil at its base and cooled by chilled water flowing through copper coils extending approximately two-thirds of the way down the column, providing a thermal gradient in the cooling water paralleling that required in the column.

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 10⁰ 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 ($23^{\circ} \pm 3^{\circ} \text{ C}$). 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 Lomb 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 | d. Inhibitor extracted from polymer |
| b. Cold quench | e. Inhibition of reaction by atmospheric oxygen suspected |
| c. Portion of sample lost during transfer from irradiation vessel | 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 | = | $4.16 \times 10^{19} \text{ ev gm}^{-1} \text{ hr}^{-1*}$ |
| 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.

$$\frac{\text{Moles MMA monomer liter}^{-1}}{\frac{\text{Weight of liter of MMA}}{\text{Molecular Weight of MMA}}} = \frac{921.6}{100.11} = 9.208$$

$$\begin{aligned} \text{Moles of electrons liter}^{-1} \text{ of MMA} \\ = 54 \times 9.208 \end{aligned} = 497.23$$

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

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

$$\eta_{\text{CHCl}_3} = 6.6 \times 10^{-5} \text{ Mw}^{0.77} \quad (1)$$

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:

$$\eta_{\text{CHCl}_3} = \lim_{C \rightarrow 0} \eta_r = \lim_{C \rightarrow 0} \frac{\eta_{\text{obs}} - \eta_0}{\eta_0 C} \quad (2)$$

where η_r , η_{obs} , and η_0 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 $C_{\text{corrected}} = C_{\text{apparent}} \times \frac{\text{Wt. of polymer}}{\text{Wt. of polymer+inhibitor}}$ 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 (Trömsdorff 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 anomalously 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^o 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.

VI. APPENDIXES

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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 | |
| $RM_n^\cdot + M \rightarrow RM_{n+1}^\cdot$ | $K_p [RM_n^\cdot] [M]$ |
| (e) Mutual termination | |
| 1. Combination | |
| $RM_n^\cdot + RM_n^\cdot \rightarrow P_{n+m}$ | $K_t [RM_n^\cdot]^2$ |
| 2. Disproportionation | |
| $RM_n^\cdot + RM_n^\cdot \rightarrow P_m + P_n$ | $K_t [RM_n^\cdot]^2$ |
| (f) Termination by primary radicals | |
| $RM_n^\cdot + R^\cdot \rightarrow P_n$ | $K_{to} [RM_n^\cdot] [R^\cdot]$ |

In this outline A is any substance in the reaction system, and R^\cdot is a primary radical. M is the monomer, RM_n^\cdot 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

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

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

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

At low dose rates the expression

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

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

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

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

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

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

where the concentration of primary radicals $[R\cdot]$ 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



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 (\bar{P}_n) may be obtained. These expressions assume termination by disproportionation; for termination by combination, $\bar{P}_n(\text{combination})$ is equal to $2\bar{P}_n$.

Low dose rate, chain transfer neglected:

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

Low dose rate, chain transfer considered:

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

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

Higher dose rate, chain transfer neglected:

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

Very high dose rate, terminations involve only free radicals:

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

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 | .906 | .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 | .228 | 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 | 199.0 | 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 | .630 | .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.