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CATALYTIC EFFECTS ON
RADIATION-INDUCED POLYMERIZATION
OF METHYL METHACRYLATE

BY

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A

THESIS

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ABSTRACT

A study has been made of the effect of Kaolin clay particle size and acidity on the degree of radiation-induced polymerization of methyl methacrylate. The results indicate that the degree of polymerization varies with the clay particle size, and that the amount of polymer produced is influenced by the pH of the clay.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. D. R. Edwards for his assistance and guidance throughout the course of this investigation. A special note of thanks goes to the Georgia Kaolin Company for their cooperation in providing the clay samples for this investigation, and to the Metallurgy Department for allotting laboratory space for the necessary equipment.

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I. INTRODUCTION

Radiation-induced polymerization of vinyl monomers is basically similar to conventional free radical polymerization, with the energy required for the initiation step being supplied by the ionizing radiation.

Using ionizing radiation to produce free radicals was first reported in the late 1930's. With the end of World War II and the rapid growth of nuclear-energy plants, research workers were attracted to radiation polymerization as a low-temperature chain initiator and as a use for nuclear reactor wastes.

Polymerization kinetics and the mechanism of radiation initiation have been studied with a wide variety of radiation sources and monomers. A recent aspect of investigation has been the tendency of some radiation-induced polymerization to proceed by ionic mechanisms under particular experimental conditions. Detailed studies are being made of commercial polymer preparation by radiation initiation.

This investigation was intended to determine the effect of varying the surface area of a clay catalyst on the molecular weight of the polymer produced by irradiation of a mixed clay-methyl methacrylate sample. A secondary purpose was to investigate the influence of the clay pH on the polymer molecular weight.

II. LITERATURE SURVEY

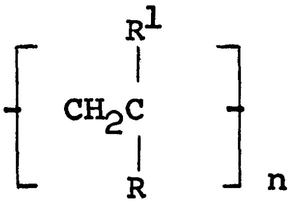
In passing through matter, forms of high energy radiation such as gamma radiation lose energy by reacting with the electrons and nuclei of the medium, causing displaced nuclei, free electrons, and ionized and/or excited atoms or molecules.(1) Radiation-induced polymerization is a chain reaction in which a large number of chemical changes may follow from each ionization or excitation. Polymerization of monomers involves three stages: chain initiation, propagation, and termination. Radiation primarily acts in the initiation stage, except at high intensities where primary(1) radicals can intervene in the termination mechanism.

Polymers can be classified into two groups according to their predominant behavior when exposed to radiation.

1. Crosslinking: Molecular weight increases and eventually forms an insoluble network.
2. Scission: Average molecular weight decreases.

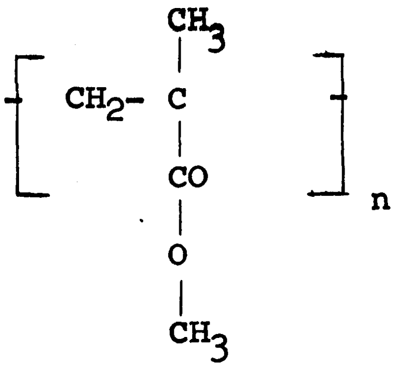
It is possible to predict which category a polymer will fall into by examining the heat of polymerization of the monomer. A low heat of polymerization indicates a tendency to return to monomer during pyrolysis and to undergo scission under irradiation. Polymethyl methacrylate, with a monomer heat of polymerization of 13K cal/mole, undergoes scission upon irradiation.(2)

K. Little(2) pointed out that all vinyl polymers in which chain scission predominates have the structure:



$$\left[-\mathrm{CH_2}\overset{\displaystyle R^1}{\underset{\displaystyle R}{\mathrm{C}}}-\right]_n$$

Polymethyl methacrylate shows this structure:



$$\left[-\mathrm{CH_2}-\overset{\displaystyle \mathrm{CH_3}}{\underset{\substack{\mathrm{CO}\\|\\\mathrm{O}\\|\\\mathrm{CH_3}}}{\mathrm{C}}}-\right]_n$$

The carbon atom with the side chain R does not have an attached hydrogen atom, but an α - substituted group R^1. The R^1 group, particularly if it is a methyl group, causes a steric strain which weakens the carbon-carbon bonds of the main chain.

Gases tend to form during the irradiation degradation of polymethyl methacrylate. A mass spectrographic analysis of the gases gave (by volume):(2) H_2, 44.1%; CH_4, 6%; CO, 22.8%; CO_2, 18.8%; O_2, 0.3%; other hydrocarbons 0.2%, and low alcohols and esters, 0.5%.

The composition of the products, especially the presence of CH_4, CO, and CO_2, indicates that the side chain ($-COOCH_3$) is undergoing decomposition to a greater extent than the main chain. J. Weiss has raised the question of how radiation-produced primary species enter into the mechanism of subsequent degradation and/or crosslinking.(3) Osamu Saito obtained differential equations describing the variation of molecular weight distributions in a polymer substance subjected to irradiation.(4) Solution of these equations gave the gel point and average molecular weights.

Although ions are formed upon irradiation of organic liquids, it is believed that they have a very short lifetime. Free radical mechanism is believed to be the method by which radiation polymerization of most vinyl monomers occurs.(5) Evidence for the free radical mechanism includes the action of free radical inhibitors, such as oxygen or benzoquinone, copolymerization studies, positive temperature coefficients, and the study of the overall reaction kinetics.

Polymerization kinetics in general have been described by Chapiro(5) in the following table:

TABLE I. DETAILED KINETIC SCHEME

A. Initiation

$$A + h\nu \rightarrow 2R^{\bullet}$$

B. Recombination of primary radicals

$$R^{\bullet} + R^{\bullet} \rightarrow R_2$$

C. Addition to monomer

$$R^{\bullet} + M \rightarrow RM^{\bullet}$$

D. Propagation

$$RM_n^{\bullet} + M \rightarrow RM_{n+1}^{\bullet}.$$

E. Mutual Termination

1. Combination

$$RM_n^{\bullet} + RM_n^{\bullet} \rightarrow P_{n+m}$$

2. Disproportionation

$$RM_m^{\bullet} + RM_n^{\bullet} \rightarrow P_m + P_n$$

F. Termination by primary radicals

$$RM_n^{\bullet} + R^{\bullet} \rightarrow P_n$$

In this outline A is any substance in the reaction system, and $R^{\bullet}$ is a primary radical. M is the monomer, $RM_n^{\bullet}$ is a growing polymer chain, and P_n is a "dead" polymer. P_{n+m} and P_m are also "dead" polymers.

The free radical polymerization of methyl methacrylate is a frequently-cited example of the gel effect. This effect has been observed as an acceleration in the rate of polymerization at low initial dose rates followed by a rise in viscosity at higher total dosage.

A free radical can only be destroyed by interaction with another free radical.(6) The gel effect seems to be controlled by the molecular weight of the polymer formed during the first part of the reaction and the temperature.(7) As the percent polymer conversion increases, the viscosity of the system increases, thereby reducing the probability of collision between two active chain ends, since the growing polymer chains are now less mobile. At relatively low temperatures and high percent polymerization, the rate of propagation approaches zero, and both radical chains and the remaining monomer are trapped in an almost solid system. The main results of the gel effect are an increased lifetime for the radical chains and a measureable post-effect.(8)

"Post-effect" polymerization studies have been made(9) in which monomer samples were exposed to an initiating dose of ionizing radiation and then quenched with a chemical inhibitor, for example, methyl ether of hydroquinone, at varying times. This method was advanced for kinetic studies with the idea of avoiding polymer degradation, but apparently it was difficult to obtain consistent data.

Most polymerization reaction rates are sensitive to temperature changes, and attempts have been made to determine the extent of this influence. An experiment (10) was designed to determine the effect of the temperature rise produced by the polymerization reaction itself inside the polymerization capsule. Results showed that the increase in the rate of polymerization was small, especially for reactions such as that of methyl methacrylate.

Many investigations have made use of the viscosity measurements of dilute polymer solutions in order to obtain data on the degree of polymerization. However, it seemed very difficult to duplicate results in different laboratories. T. G. Fox and his associates(11) experimented with dilute solutions of polymethyl methacrylate in a series of solvents. They developed sets of equations for fractionated and unfractionated samples relating intrinsic viscosities to the average molecular weights which "are generally accurate and reproducible within an uncertainty of three percent."(11)

T.J.R. Weakley and associates(12) used a chromatographic method to determine the molecular weight distribution of polymer in a solution. Their results showed that low molecular weight polymers with a narrow molecular weight distribution were obtained from thermal free-radical initiation. They further showed that high molecular weight polymers tend to form on the surface of a solid catalyst, while low molecular weight polymers form in the solution.

H. K. Liu(13) indicated that methyl methacrylate undergoes radiation-induced polymerization more rapidly in the presence of a kaolin clay than if it is alone.

III. EXPERIMENTAL

The purpose of this investigation was to note the effect of particle size of the clay catalyst on the degree of polymerization of methyl methacrylate. The effect of the hydrogen ion concentration in the clay was also investigated.

A. Plan of Experimentation

A series of samples of methyl methacrylate mixed with the same weight of clays with varying particle sizes, (or different surface-to-volume ratios), was subjected to a given dosage of gamma-radiation. The extent of polymerization of the product, polymethyl methacrylate, was measured in terms of the viscosity average molecular weight.

One selected clay was then used to prepare two samples. One was washed with 1M NH_4OH, and the other was washed with 1M HNO_3. They were then mixed with methyl methacrylate, and the resulting samples were treated as above.

B. Materials

Only a brief description of the clays will be given here. The complete description of all materials used is tabulated in Appendix 1.

Table 2. Clay Descriptions

Clay	Mean Particle Size (Microns)	Relation to 2μ (%< 2 μ)	Composition $\%SiO_2$	 $\%AlO_2$
Ajax	5.8	20%	53.08	44.40
Velvacast	4.2	30%	45.42	38.92
Pioneer	1.2	55%	45.68	38.51
Ajax 70	0.8	70%	45.56	38.43
Ajax P	0.4	95%	45.20	38.08

C. Apparatus

The apparatus used is listed in Appendix 2.

D. Irradiation Facilities

The University of Missouri at Rolla Nuclear Reactor Facility was used as the irradiation source. It is a swimming pool, (modified BSR - Type), heterogeneous reactor which is cooled and moderated by light water. The reactor is licensed to operate at 10KW.

Samples were irradiated in position C7 in the reactor core. (See Figure 1, page 12). A rotating sample holder was used to assure an equal dose rate for all samples in the holder. The nuclear reactor primarily produced neutrons and gamma radiation. Since it had been determined previously that the thermal neutrons had little effect on the degree

A1	A2	A3	A4	A5	A6	A7	A8	A9
B1	B2	B3	B4	S	B6	B7	B8	B9
C1	C2	C3	F	F	F	O	C8	C9
D1	D2	F	X	F	X	F	F	D9
E1	E2	F	X	F	X	F	F	E9
F1	F2	F3	F	F	F	F7	F8	F9

Figure 1. CORE CONFIGURATION 29-T

F = **Fuel**
S = Source
O = Sample Rotator
X = Control Rods

of polymerization achieved(14), it was assumed that the samples were subjected to a dosage of gamma particles and a few fast neutrons. The dose rate received by the samples, run at 10KW for one hour, was measured as 4×10^5 rads/hour by use of a Fricke dosimeter.(13)

E. Methods of Procedure

1. Preparation of the Samples

Twenty grams of clay were measured out and placed in an aluminum cylinder. Twenty grams of methyl methacrylate, (21.3 ml), were added slowly, with mixing. The cylinder was capped and sealed with a liquid sealant, and then allowed to sit until the sealant solidified. The tubes were further sealed by the liberal use of a very effective waterproof tape. For the samples containing NH_4OH and HNO_3 washed clays, only 10 g of methyl methacrylate were added, since only about half of the washed clay was retrieved from the wash solution by filtration.

2. Irradiation of the Samples

The samples were prepared and treated as indicated in the following table. All non-irradiated samples were allowed to sit for 24 hours before being examined.

TABLE III. SAMPLE COMPOSITION AND IRRADIATION

Sample No.	Composition (Methyl Methacrylate and)	Irradiation
1	No clay	No irradiation
2	Velvacast Clay	No irradiation
3	No clay	1 hr. at 10 KW
4	Ajax SC Clay	1 hr. at 10 KW
5	Velvacast Clay	1 hr. at 10 KW
6	Pioneer (H_2O washed) Clay	1 hr. at 10 KW
7	Pioneer (Air Float) Clay	1 hr. at 10 KW
8	Ajax 70 Clay	1 hr. at 10 KW
9	Ajax P Clay	1 hr. at 10 KW
10	Ajax 70 (NH_4OH washed) Clay	1 hr. at 10 KW
11	Ajax 70 (HNO_3 washed) Clay	1 hr. at 10 KW

3. Treatment of the Sample

The samples remained in the pool for one hour after irradiation, until the short-lived isotope of aluminum formed during irradiation decayed. The tubes were then removed from the sample holder and opened. The irradiated samples were then placed in flasks with about 200 ml. of acetone, and left in the acetone for about a day. The samples were frequently agitated or stirred during the first few hours. Next the suspension was allowed to settle overnight, and the acetone solution of methyl methacrylate was then decanted and centrifuged for one hour to remove the suspended clay. The acetone solution was transferred to a flask, and the acetone and methyl methacrylate monomer were drawn off by an aspirator, leaving a film of polymethyl methacrylate in the bottom of the flask. This polymer was dried under a hood to constant weight.

The weighed polymer sample was dissolved in a measured volume of benzene, with thorough mixing. Three successive dilutions were performed for each sample, giving four solutions of differing concentration. These solutions were than placed in a constant temperature water bath at 30°C for 20 minutes in stoppered containers, to allow the samples to come into equilibrium with the bath temperature.

A sample solution was then transferred into a Series 50 Ostwald Fenske viscosimeter, and the average efflux time of the solution was determined. After running each set of solutions, the viscosimeter was checked by determining the efflux time for benzene. Whenever the time differed by more than two seconds from the standard, (calibrated) time of 161 seconds, the viscometer was cleaned with acetone and rinsed with benzene until its accuracy was established again.

4. Calculation of Intrinsic Viscosity and Viscosity Average Molecular Weight.(15)

(a) Observed Viscosity = ηobs

ηobs = Efflux Time x Viscometer Constant

(b) Specific Viscosity = $\left(\frac{\eta obs}{\eta o} - 1 \right) = \eta sp$

where ηo = Solvent Viscosity (at 30°C)

and $\frac{\eta obs}{\eta o} = \frac{P_1 t_1}{P_o t_o}$ with P = density
t = efflux time

Since the density of a 1% solution of polymer and methyl methacrylate in benzene approached the density of benzene to within the bounds of experimental error, the density correction was omitted. Kinematic corrections were also omitted, so that $\frac{\eta obs}{\eta o} = \frac{t_1}{t_o}$

(c) Reduced Viscosity = $\eta_{red} = \frac{\eta_{sp}}{C}$

where C = polymer concentration in grams per 100 ml of solution.

(d) Intrinsic Viscosity = $[\eta] = \lim_{C \to 0} \left(\frac{\eta sp}{C}\right)$

$[\eta]$ was obtained by a linear least square fit of data representing a graph of η_{red} vs C. This gave the optimum equation of the line in the form A + BX, with A the intercept and B the slope. A is therefore = $[\eta]$.

(e) The viscosity average molecular weight $(\overline{Mv})$ was then computed by the use of the relationship $[\eta] = k\ (\overline{Mv})^{d}$, where k and d are determined by measuring $[\eta]$ for samples of a known molecular weight polymer in a given solvent at a constant temperature. $[\eta]$ for fractioned* polymethyl methacrylate in benzene at 30°C has been found to be(11) $[\eta] = 5.26 \times 10^{-5}\ (\overline{Mv})^{.76}$

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*A partial fractionation of the polymethyl methacrylate occurs during evaporation of the sample. The equation for an unfractionated sample differed only by a constant factor from the fractionated equation. Since this investigation was only concerned with relative $\overline{Mv}$'s, either equation could have been used.

5. pH Determinations

Solutions were prepared containing approximately one gram of clay per 100 ml of water. The pH of these solutions was measured by use of a Coleman Metrion pH meter to determine that the clays presented acidic surfaces.

IV. DATA AND RESULTS

A. Unirradiated samples and irradiated MMA Monomer.

Neither sample No. 1, unirradiated methyl methacrylate, nor sample No. 2, unirradiated methyl methacrylate mixed with Velvacast clay, produced any polymer residue in the flask after aspiration.

Sample No. 3, methyl methacrylate irradiated for one hour at 10 KW, turned from a clear to a yellowish liquid, indicating polymerization. After aspiration, however, only a few small pieces of residue, (polymer) remained. An alternative method of concentration determination was therefore attempted. The accuracy of the concentration determination proved insufficient to give a determination of $\overline{Mv}$, but the following data indicates the presence of some polymethyl methacrylate.*

TABLE IV. SAMPLE NO. 3

Presumed Concentration (g/dl)	.950	.475	.317	.238	.000
Efflux Time	168.9	164.7	163.4	163.1	163.2

*Since methyl methacrylate monomer has a smaller viscosity, and hence efflux time, than benzene.

B. Irradiated MMA Monomer-Clay Samples.

The computer program printed out data for each sample as illustrated below for sample No. 4

TABLE IV. DATA FOR SAMPLE NO. 4, AJAX SC CLAY

Concentration (grams/100 ml)	Efflux Time (Seconds)	Viscosity (centipoise) at 30°C	Specific Viscosity	Reduced Viscosity
.6760	432.8	1.5087	1.6751	2.478
.4507	345.4	1.2041	1.1349	2.518
.3380	280.8	.9789	.7356	2.176
.2253	237.7	.8286	.4692	2.082

Limiting Viscosity = 1.916

Slope = .9416

Sum of Differences Squared = .0426

VISCOSITY MOLECULAR WEIGHT = 1.010×10^6

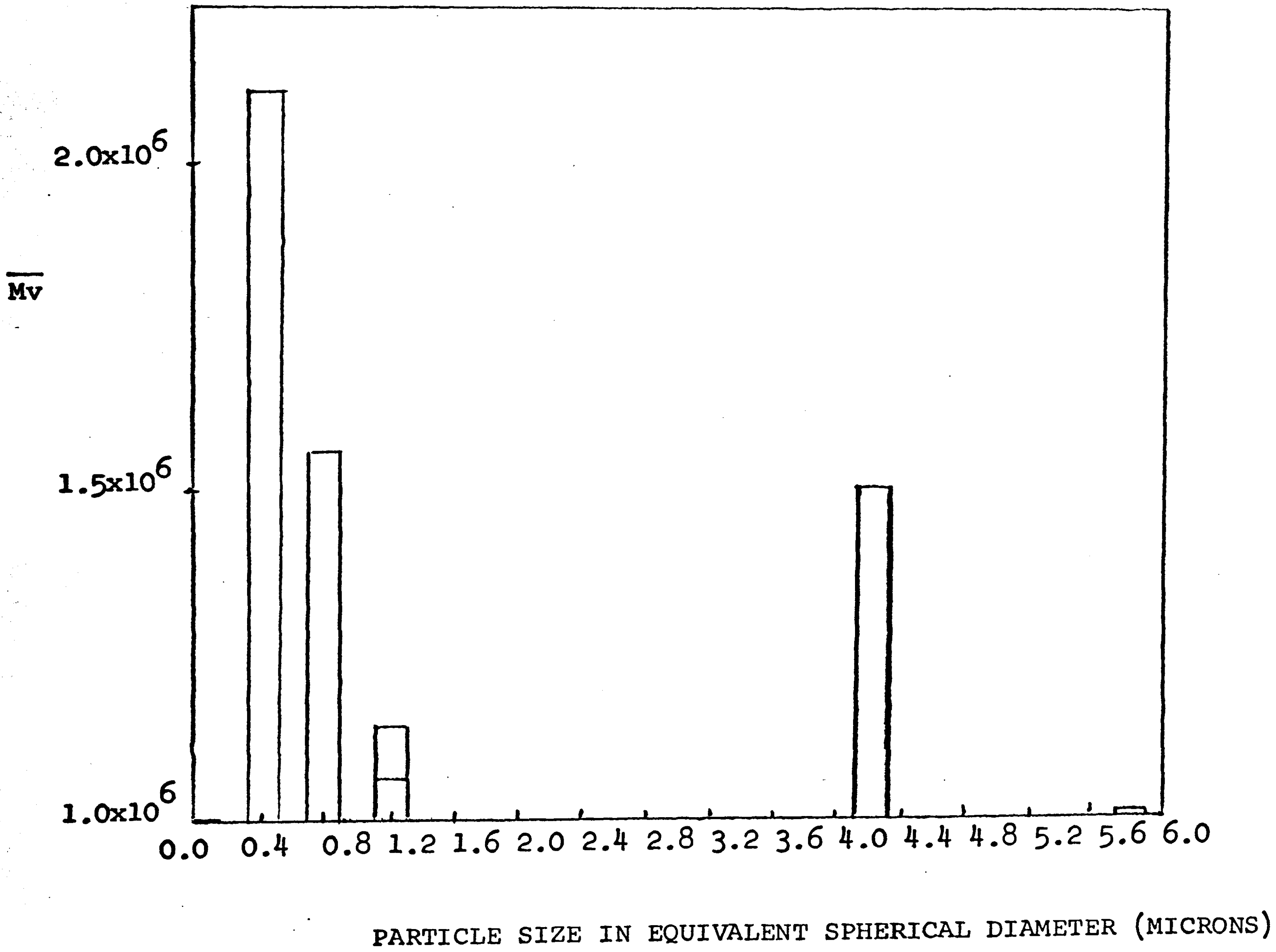
The full set of data for each sample is included in Appendix 4. Only the $\overline{Mv}$ results are presented here.

TABLE VI. $\overline{Mv}$ DETERMINATIONS

Sample Number	Clay	Average Particle Size (Microns)	$\overline{Mv}$ x 10^{-6}	σ x 10^{-6}	$[\eta]$ dl/g	$\frac{\sigma}{[\eta]}$
4	Ajax SC	5.8	1.01	.18	1.92	.44
5	Velvacast	4.2	1.50	.06	2.59	.09
6	Pioneer H_2O wash	1.2	1.16	.08	2.14	.18
7	Pioneer Air Float	1.2	1.09	.07	2.04	.14
8	Ajax 70	0.8	1.55	.19	2.66	.41
9	Ajax P	0.4	2.11	.12	3.35	.21

The above data are also presented in graphical form, Figure 2, page 2 to illustrate the relationship between size and $\overline{Mv}$.

FIGURE 2. $\overline{Mv}$ VS CLAY PARTICLE SIZE



C. Specially-treated MMA Monomer clay samples

The following table shows the results obtained for samples 10 and 11. The results from sample 8 are included for purposes of comparison, since all three samples were run using Ajax 70 clay.

TABLE VII. SPECIALLY TREATED SAMPLES

Sample Number	Clay Treatment	Amount of Polymer Produced from 10 g of Methyl Methacrylate(grams)	$\overline{Mv} \times 10^{-6}$	$\sigma \times 10^{-6}$	$[\eta]$ dl/g	$\frac{\sigma}{[\eta]}$
8	None	0.166	1.55	.19	2.66	.41
10	NH_4OH wash	0.544	1.93	.22	3.14	.46
11	HNO_3 wash	1.957	1.84	.26	3.02	.56

Samples 4, 5, 6, 7 and 9 were irradiated at one time, and samples 8, 10, and 11 were irradiated at a later time.

V. DISCUSSION OF RESULTS

The $\overline{Mv}$ values obtained were numerically evaluated in order to show a significant trend. The examination showed that the increase in $\overline{Mv}$ in going from sample 4 to Samples 5 and 8 indicated a probable trend, while the $\overline{Mv}$ increase from samples 4 and 5 to sample 9 indicated a definite trend. There was no significant difference in the $\overline{Mv}$'s obtained for samples 6 and 7, nor between the $\overline{Mv}$'s of samples 8 and 10. Overall, then, the $\overline{Mv}$ showed an apparent tendency to increase with increasing clay surface area or decreasing clay particle size.

An attempt was made to evaluate a mathematical relationship between surface area based on the assumption of spherical particles and $\overline{Mv}$. The failure of such an attempt was predestined, since the particles themselves were actually in the form of small plates which tend to stack up to varying degrees. The particle sizes quoted in this thesis were determined by the Georgia Kaolin Company and reported as equivalent spherical diameters. If the surface areas for the various clays had been determined by a method which did not involve particle size, as by measurement of the surface ability to adsorb gaseous nitrogen, a relationship might have been determined.(16)

Alteration of the pH of the clays had an effect upon both the amount and degree of polymerization. There was a serious question regarding the significance of the $\overline{Mv}$ determination for sample No. 11, since the η_{red} vs Concentration plot gave a negative slope, while the plots of all other samples gave a positive slope. Therefore, only the yield is discussed for HNO_3 washed Ajax 70. There was also a bad point in the data of sample No. 4, which led to a large standard deviation for $[\eta]$ and $\overline{Mv}$. All the clays used were mildly acidic (pH of approximately 6) as received from the factory. It was interesting to note that washing Ajax 70 with HNO_3 produced a much higher percent yield of polymer and washing the same clay with NH_4OH also produced a significant increase.

These correlations between pH and yield suggested a change in the effectiveness of the clay surfaces in promoting polymerization. This change might be attributed to an increase in the effectiveness and/or the number of active sites on the clay surfaces. It seems possible that the surfaces acted as a gathering point for free radicals, since the amount of polymerization increased, and the polymerization presumably occurs by a free radical mechanism.

In obtaining the results discussed above, several sources of uncertainty arose. These problems affected the data obtained here, and should affect any following investigations.

Attempts to filter out the clay particles were unsatisfactory. Only standardized centrifugation produced useable results, and it was not determined absolutely that all clay was removed from the samples even then.

Several attempts to produce polymer samples by aspiration failed when the polymer, instead of forming a uniform removable film, formed as widely dispersed bubbles. The polymer resembled glue in texture, then hardened into globules which were removable only by redissolving. Coating the flask with teflon would have removed this difficulty. Teflon plugs for the centrifuge tubes might have improved accuracy, since the rubber stoppers used tended to "flake" near the end of the investigation.

During the filtration for recovery of the clay from the acid and ammonia washes, it is probably that the finer clay particles were lost, thus increasing the effective particle size. The effects of the pH changes, then might have been greater on the $\overline{Mv}$ than the data indicate.

The inhibitor was not removed from the methyl methacrylate before irradiation. Although only present at the concentration of 50 ppm, this inhibitor was used up. The overall effect of the inhibitor's presence was to reduce the polymer yield, and possibly to reduce the degree of polymerization.

VI. CONCLUSIONS

Analysis of the data obtained in this investigation leads to the following conclusions:

1. Gamma radiation increases the rate of polymerization of methyl methacrylate. The addition of fine particle-size clay to the methyl methacrylate increases the amount and molecular weight of the polymer produced under irradiation.
2. The viscosity average molecular weight of the polymer produced is apparently related to the surface area of the clay present.
3. The percent conversion of the polymer formed is related to the pH of the clay.

VII. LIMITATIONS AND RECOMMENDATIONS

1. The variation of polymer yield and possibly molecular weight with the pH of the clay surface should be investigated to determine the optimum pH for this reaction.
2. The effect of surface area on molecular weight should be determined by accurately measuring the surface area according to its ability to adsorb nitrogen. This may lead to a mathematical relationship between the surface area of the clay and the molecular weight of the polymer produced.
3. An investigation should be made in which the dose rate and the total dosage are varied.
4. The effect of clay composition on the radiation-induced polymerization of methyl methacrylate should be studied.
5. A study might be run to determine the molecular weight distribution of the polymer in order to study the kinetics of the reaction.
6. It is suggested that samples intended for direct comparison be irradiated at the same time to insure uniform dosage as was done in this investigation.

Since the sample rotator will hold eight samples, this does not place a severe limitation on an investigation.

7. The accuracy and efficiency of the investigative procedure would be facilitated by the use of an ultracentrifuge, or a high-capacity traditional centrifuge.
8. The amount of acetone used and the time during which it is in contact with the clay should be standardized.
9. The aspirator flasks should be coated with teflon to facilitate removal of the polymer sample. Teflon stoppers should be used in the centrifuge tubes.
10. The polymer sample should be thoroughly dissolved in benzene, with mixing, and the resulting solution should then be transferred to a 100-ml volumetric flask and benzene added to fill the flask. This would increase the accuracy of the concentration measurements, thus increasing the reproducibility of the data.
11. A brief study should be made of the effect of adding acid or base to the monomer before irradiation, without the presence of a clay surface.

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VITA

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In June 1965, he entered the University of Missouri at Rolla as a graduate student in Nuclear Engineering to pursue the Master of Science degree.

The author is married and has three children.

APPENDICES

APPENDIX 1. MATERIALS

Methyl Methacrylate Monomer: Liquid, analyzed reagent grade; 50 ppm monomethyl ether of hydroquinone added as inhibitor; Matheson, Coleman and Bell Company, Norwood, Ohio. Used as subject of investigation.

Sample Cells: Aluminum tubes of 3/4" internal diameter and 5-3/8" length, with caps; Corral, Wodiska and Company, Tampa, Florida. Used as the sample container.

Liquid Sealant: Weldwood All Purpose Contact Cement; U.S. Plywood Corporation, Kalamazoo, Michigan. Used to seal the sample containers.

Tape Sealant: Arno Tape; Michigan City, Indiana; Used to seal the sample containers.

Kaolin Clays: Georgia Kaolin Company, Elizabeth, New Jersey. Used as catalysts in investigations.

Benzene: Analyzed reagent grade; Fisher Scientific Company, St. Louis, Missouri. Used as polymer solvent for viscosity determination.

Acetone: Analyzed reagent grade; Fisher Scientific Company, St. Louis, Missouri. Used as solvent for extracting polymer from the clay.

Ammonium Hydroxide: Analyzed reagent grade, assay 28-30% NH_3; Fisher Scientific Company, St. Louis, Missouri. Used to treat the clay before sample irradiation.

Nitric Acid: Analyzed reagent grade, assay 69-71% HNO_3; Fisher Scientific Company, St. Louis, Missouri. Used to treat the clay before sample irradiation.

TABLE VIII. CHEMICAL ANALYSIS OF CLAYS*

	Ajax SC	Velvacast	Pioneer	Ajax 70	Ajax P
Silicon Dioxide	53.08	45.42	45.56	45.56	45.20
Aluminum Dioxide	44.40	38.92	38.51	38.43	38.08
Iron Oxide	0.40	0.34	0.44	0.41	0.49
Titanium Dioxide	0.95	1.10	1.43	1.45	1.52
Calcium Oxide		0.25	0.24	0.24	0.26
Magnesium Oxide		0.18	0.14	0.16	0.30
Sodium Oxide	0.31	0.11	0.04	0.03	0.02
Potassium Oxide	0.39		0.14	0.05	0.04
Loss on Ignition		13.81	13.51	13.61	13.51
Mean Particle Size (In terms of Equivalent Spherical Diameter in Microns)	5.8	4.2	1.2	0.8	0.4

*Analysis supplied by the Georgia Kaolin Company

APPENDIX 2. APPARATUS

Viscometers: Ostwald-Fenske type, size 50, 0.42 ± 0.02 mm. capillary bore; No. P6700C, Schaar Scientific Company, Chicago, Illinois. Used to determine viscosities.

Magnetic Stirrer: Aluminum housing with teflon-coated stirring bar, for 115 volt a-c, 50-60 cycle; No. S5640, Schaar Scientific Company, Chicago, Illinois. Used to aid acetone in removing polymer from clay, to aid in redissolving polymer in benzene.

Kinematic Viscosity Bath: Constant temperature, unitized, meets required specifications in ASTM D445. Includes:

> Pyrex brand glass jar: 12" high x 12" diameter
>
> Electronic control box: Outlets for the stirrer, continuous heater, intermittent heater
>
> Rheostat thermoregulator: Controls temperature within ± .025°F, operates in range 50-220°F, equipped for use on 115 volt, a-c, 50-60 cycle
>
> Stirrer: Electrically driven, uses brushless induction motor, provided with clamp
>
> Intermittent heater: with clamp, pilot light

Continuous heater: with clamp

Thermometer clamp: used with -10°C + 110°C thermometer. No. P6200, Schaar Scientific Company, Chicago, Illinois. Used to maintain viscosimeter at 30°C.

Electronic Timer: Precision Time-It, records to .1 second; 115 volts, 60 cycles, 5 watts; Precision Scientific Company, Chicago, Illinois. Used to measure efflux times in viscosity determinations.

Analytical Balance: Electronic, measures to 0.0001 gram, capacity 160 grams; 115 volts, 60 cycles; Type H15, No. 138599, Mettler Instrument Corporation, Heightstown, New Jersey. Used to weigh clay and polymer samples.

Glassware: An assortment of standard laboratory glassware, obtained from the Chemistry Department Stockrooms, was used.

pH Meter: Coleman Metrion type, Coleman Instruments, Inc., Maywood, Illinois. Used to determine the pH of the clays.

APPENDIX 3. VISCOSITY DETERMINATIONS

COMPUTER PROGRAM FOR THE DETERMINATION OF THE VISCOSITY AVERAGE MOLECULAR WEIGHT

The following FORMO computer program was used to perform the calculations outlined in the experimental section. The following designations were used:

C (I) = Concentration in grams/100 ml
T (I) = Average Efflux Time in Seconds
S = Solvent Viscosity, Centipoise
Z = Viscometer Constant
V (I) = Observed Viscosity
VS (I) = Specific Viscosity
VR (I) = Reduced Viscosity
X1 = Slope of Graph of VR(I) vs C(I)
X2 = Limiting Viscosity or Intercept of VR(I) vs C(I)
VMW = Average Viscosity Molecular Weight
TS = Sum of Differences Squared

MOLECULAR WEIGHT OF POLYMETHYLMETHACRYLATE BY VISCOSIMETRY
THESE RESULTS ARE FOR SAMPLE NUMBER 7

```
      DIMENSION C(5),T(5),V(5),VR(5),F(5,2),FT(2,5),A(2,2),B(2)
      DIMENSION VRP (5)
      READ 100, (C(I),I=1,5)
      READ 100, (T(I),I=1,5)
      S=0.564
      Z=0.003486
      PRINT 200
      PRINT 201
      DO 1 I=1,4
      V(I)=T(I)*Z
      VS(I)=(V(I)-S)/S
      VR(I)=VS(I)/C(I)
 10   PRINT 202, I,C(I),T(I),V(I),VS(I),VR(I)
      DO 1 I=1,4
      F(I,1)=C(I)
  1   F(I,2)=1.
      DO 2 J=1,2
      DO 2 I=1,4
  2   FT(J,I)=F(I,J)
      DO 3 I=1,2
      DO 3 J=1,2
      A(I,J)=0.
      DD 3 K=1,4
  3   A(I,J)=A(I,J)+FT(I,K)*F(K,J)
      DO 4 I=1,2
      B(I)=0.
      DO 4 K=1,4
  4   B(I)=B(I)+FT(I,K*VR(K)
      BOT=A(1,1)*A(2,2)=A(1,2)*A(2,1)
      TOP1 = B(1)*A(2,2)-B(2)*A(1,2)
      TOP2 = B(2)A*(1,1)-B(1)*A(2,1)
      X1=TOP1/BOT
      X2=TOP2/BOT
      PRINT 300
      PRINT 301,X2,X1
      TS=0.
      DO 5 I=1,4
      VRP(I)=C(I)*X1+X2
  5   TS+(VRP(I)-VR(I))*(VRP(I)-VR(I))
      PRINT 500, TS
      Y=(1,/0.76)*(LOGF(X2)+4.28*2.303)
      VMW=EXPF(Y)
      PRINT 400
      PRINT 401,VMW
```

```
      DX2=(SQRTF(ABSF(A(2,2)/BOT)))*SQRTF(0.5*TS)
      DVMW=VMW*SQRTF((1.32*(DX2/X2))**2+(0.03)**2)
      DX95=1.96*DX2
      DV95=1.96*DVMW
      PRINT 501
      PRINT 502, DX2
      PRINT 503, DX95
      PRINT 504, DVMW
    6 PRINT 505, DV95
      STOP
  100 FORMAT (5F14.7)
  200 FORMAT (5X,1HI,3X,10HGRAMS/D.L.,2X,11HEFFLUX TIME,4X,9HVISCOSITY)
  201 FORMAT (48X,10HSPEC.VISC.,3X,9HRED.VISC.)
  202 FORMAT (4X,I2,5X,F8.5,5X,F8.2,3(5X,F8.5))
  300 FORMAT (15X,18HLIMITING VISCOSITY,20X,5HSLOPE)
  301 FORMAT (19X,F14.7,15X,F14.7)
  400 FORMAT (15X,27HVISCOSITY MOLECULAR WEIGHT)
  401 FORMAT (22X,F18.7)
  500 FORMAT (28H SUM OF DIFFERENCES SQUARED=,F14.7)
  501 FORMAT (13H0ERROR BOUNDS)
  502 FORMAT (31H0LIMITING VISCOSITY STD. DEV. = ,F8.5)
  503 FORMAT (30H 95 PERCENT CONFIDENCE LEVEL =,F8.5)
  504 FORMAT (29H0MOLECULAR WEIGHT STD. DEV. = ,E12.5)
  505 FORMAT (30H 95 PERCENT CONFIDENCE LEVEL = ,E12.5)
      END
```

APPENDIX 4.

COMPLETE DATA ON VISCOSITY AND MOLECULAR WEIGHT DETERMINATIONS

TABLE IX. DATA FOR SAMPLE NO. 4, AJAX SC CLAY

Concentration (grams/100 ml)	Efflux Time (Seconds)	Viscosity (centipoise) at 30°C	Specific Viscosity	Reduced Viscosity
.6760	432.8	1.5087	1.6751	2.478
.4507	345.4	1.2041	1.1349	2.518
.3380	280.8	.9789	.7356	2.176
.2253	237.7	.8286	.4692	2.082

Limiting Viscosity = 1.916

Slope = .9416

Sum of Differences Squared = .0426

VISCOSITY MOLECULAR WEIGHT = 1.010×10^6

TABLE X. DATA FOR SAMPLE NO. 5, VELVACAST CLAY

Concentration (grams/100 ml)	Efflux Time (Seconds)	Viscosity (centipoise)at 30°C	Specific Viscosity	Reduced Viscosity
.6574	537.2	1.872	2.3204	3.530
.4383	388.0	1.3526	1.3982	3.190
.3287	323.0	1.1260	.9964	3.031
.2191	265.5	.9255	.6410	2.926

Limiting Viscosity = 2.593

Slope = 1.403

Sum of Differences Squared = .0017

VISCOSITY MOLECULAR WEIGHT = 1.503×10^6

TABLE XI. DATA FOR SAMPLE NO. 6, PIONEER CLAY WATER WASHED

Concentration (grams/100 ml)	Efflux Time (Seconds)	Viscosity (centipoise)at 30°C	Specific Viscosity	Reduced Viscosity
.9335	679.4	2.368	3.199	3.427
.6223	474.9	1.656	1.935	3.110
.4668	368.6	1.285	1.278	2.738
.3112	291.4	1.016	2.8011	2.574

Limiting Viscosity = 2.135

Slope = 1.418

Sum of Differences Squared = .0130

VISCOSITY MOLECULAR WEIGHT = 1.164×10^6

TABLE XII. DATA FOR SAMPLE NO. 7, PIONEER CLAY, AIR FLOAT

Concentration (grams/100 ml)	Efflux Time (Seconds)	Viscosity (centipoise)at 30°C	Specific Viscosity	Reduced Viscosity
1.2506	873.0	3.043	4.396	3.515
.8337	566.0	1.938	2.437	2.923
.6253	450.1	1.569	1.782	2.850
.4169	330.4	1.152	1.042	2.500

Limiting Viscosity = 2.035

Slope = 1.167

Sum of Differences Squared = .0154

VISCOSITY MOLECULAR WEIGHT = 1.093 x 10^6

TABLE XIII. DATA FOR SAMPLE NO. 8, AJAX 70 CLAY

Concentration (grams/100 ml)	Efflux Time (Seconds)	Viscosity (centipoise) at 30°C	Specific Viscosity	Reduced Viscosity
.6426	645.3	2.250	2.988	4.651
.4284	445.8	1.554	1.755	4.098
.3213	358.8	1.251	1.218	3.790
.2142	273.6	.9538	.6911	3.226

Limiting Viscosity = 2.655

Slope = 3.201

Sum of Differences Squared = .0332

VISCOSITY MOLECULAR WEIGHT = 1.551×10^6

TABLE XIV. DATA FOR SAMPLE NO. 9, AJAX P CLAY

Concentration (grams/100 ml)	Efflux Time (Seconds)	Viscosity (centipoise) at 30°C	Specific Viscosity	Reduced Viscosity
.4700	498.8	1.739	2.083	4.432
.3133	372.0	1.297	1.299	4.147
.2350	310.2	1.081	.9173	3.903
.1567	255.4	.8903	.5786	3.692

Limiting Viscosity = 3.350

Slope = 2.363

Sum of Differences Squared = .0048

VISCOSITY MOLECULAR WEIGHT = 2.106×10^6

TABLE XV. DATA FOR SAMPLE NO. 10, AJAX 70 CLAY, NH_4OH WASHED

Concentration (grams/100 ml)	Efflux Time (Seconds)	Viscosity (centipoise) at 30°C	Specific Viscosity	Reduced Viscosity
.5444	565.8	1.9724	2.4971	4.587
.3629	413.2	1.4404	1.5539	4.282
.2722	334.9	1.1675	1.0700	3.931
.1815	266.3	.9283	.6460	3.559

Limiting Viscosity = 3.140

Slope = 2.790

Sum of Differences Squared = .030

VISCOSITY MOLECULAR WEIGHT = 1.934×10^6

TABLE XVI. DATA FOR SAMPLE NO. 11, AJAX 70 CLAY, HNO_3 RINSED

Concentration (grams/100 ml)	Efflux Time (Seconds)	Viscosity (centipoise) at 30°C	Specific Viscosity	Reduced Viscosity
.6524	354.2	1.2347	1.1893	1.823
.4349	298.7	1.0413	.8462	1.946
.3262	287.0	1.0005	.7739	2.372
.2175	256.5	.8942	.5854	2.691

Limiting Viscosity = 3.023

Slope = 1.999

Sum of Differences Squared = .0647

VISCOSITY MOLECULAR WEIGHT = 1.840×10^6

APPENDIX 5.

CALCULATION OF THE MOLECULAR WEIGHT STANDARD DEVIATION

Let $Y = X^{\alpha}$ represent the relationship between $[\eta]$ or Y, and $\overline{Mv}$, or X.

Then $dy = \alpha\, dx\, X^{\alpha-1}$

and $\frac{dy}{Y} = \frac{\alpha\, dx\, X^{\alpha-1}}{X^{\alpha}}$

to give $\frac{dy}{Y} = \alpha \frac{dx}{X}$, where $dy = \sigma\,[\eta]$

and $dx = \sigma_{\overline{Mv}}$

Now $\frac{1}{\alpha}\frac{dy}{Y}$ represents the error in X due to error in $[\eta]$

However, X already has a built-in 3% error.(11) The $\sigma_{\overline{Mv}}$ was then determined as the square root of the sum of the errors squared times X, or

$$dx = X\left[\left(\frac{1}{\alpha}\frac{dy}{Y}\right)^2 + .03^2\right]^{1/2}$$

APPENDIX 6.

CALCULATION OF TREND SIGNIFICANCE

The significance of the $\overline{Mv}$ values obtained was examined in an attempt to establish a trend in the $\overline{Mv}$ increases. η_3 and σ_3 were calculated as follows:(17)

$$|\eta_1 - \eta_2| = \eta_3$$

$$\sigma_3 = [\sigma_1^2 + \sigma_2^2]^{1/2}$$

where η_1, referred to the $\overline{Mv}$ for a particular sample, and σ_1 referred to the standard deviation for that Mv. The ratio η_3/σ_3 was then calculated and evaluated.

If $\eta_3/\sigma_3 > 2$, there is a definite trend.

If $1 < \eta_3/\sigma_3 < 2$, there is a possible trend.

If $\eta_3/\sigma_3 < 1$, there is no trend.

The following results were obtained from these calculations:

Sample 4 vs 5, $\eta_3/\sigma_3 = 1.53$, possible trend

Sample 4 vs 8, $\eta_3/\sigma_3 = 1.21$, weak trend

Sample 4 vs 9, $\eta_3/\sigma_3 = 3.02$, trend

Sample 5 vs 9, $\eta_3/\sigma_3 = 2.96$, trend

Sample 8 vs 9, $\eta_3/\sigma_3 = 1.50$, possible trend.

No other sets of samples indicated a trend.