

## Kinetic Analysis of the Radiation Polymerization of Methyl Methacrylate-Kaolin Clay Composites

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### Synopsis

In the first of a two-part series, a kinetic study has been made on the effects of gamma rays ( $^{60}\text{Co}$ ) in air and inert gas on the polymerization of a 50:50 weight-mixture methyl methacrylate (MMA)-kaolin clay system. The effect of dose rate (7.35-24.9 rads/sec), temperature (25° to 75°C), and total dose on the percentage conversion of monomer to polymer was studied. The rate of formation of polymer at 25°C in the composite system was found to be faster when compared to a bulk MMA system at the same dose rate. This acceleration showed that the clay had a catalytic effect on the formation of polymer. The effect decreased as temperature increased. Two types of poly(methyl methacrylate) (PMMA) were formed in the composite. One type was called homopolymer and could be removed from the composite by extraction with organic solvents. The other type was called inserted polymer and could only be removed by dissolving the clay matrix with hydrofluoric acid. The total polymer conversion was the summation of these two types of polymer formed. The kinetic analysis examined the orders of reaction and activation energies of the homopolymer, inserted polymer, and total polymer. The initial reaction orders of the homopolymer and total polymer based on dose were -0.46 and -0.49, respectively. These indicate a definite free-radical reaction. The reaction order of the inserted polymer was temperature dependent.

The activation energies for the homopolymer and total polymer in both atmospheres were approximately 1 kcal/mole less than the bulk activation energy at the same conditions. The inserted polymer had an activation energy which was dose rate dependent.

### INTRODUCTION

Since 1958, a new type of material which incorporates the use of polymer with inorganic additives to form composites has been studied. In some cases, there has been an accelerated rate of formation of polymer in the presence of these inorganic additives when compared to the bulk polymerization reaction. Various authors have studied the radiation polymerization (x-ray or gamma ray) of MMA (vapor and liquid) and styrene (liquid) in the presence of inorganic and metal oxides.<sup>1-7</sup>

The purpose of this work was to investigate the radiation polymerization using gamma rays on MMA in air and inert gas in the presence of a kaolin clay inorganic additive. This study was directed toward the determination of the kinetic parameters which govern the formation of polymer in the

presence of kaolin clay. The effects of dose rate, total dose, and reaction temperature on the rate of polymer formation were investigated.

## EXPERIMENTAL

### Air Atmosphere

The monomer used was red-label MMA obtained from Rohm and Haas. The monomer was distilled at atmospheric pressure to remove the inhibitor (10 ppm 4-methoxyphenol, MEHQ). It was then tested before each trial by adding an aliquot to a nonsolvent and noting any precipitation to insure that no polymer had been formed.

Ajax P Georgia kaolin clay was heated at 300°C for 4 hr to ensure removal of all surface water. It was then placed into a desiccator and cooled to room temperature. All solvents were CP grade and were used as received.

As shown in Figure 1, the irradiation system was essentially in three parts: (1) a source, (2) a controlled temperature bath, and (3) auxiliary equipment to control the bath, record temperature, and serve as a reference point for temperature. This system allowed for the control of the three main parameters of investigation, that is, temperature, dose rate, and total dose.

The different dose rates studied were obtained by placing the samples at various distances from the  $^{60}\text{Co}$  source. As shown in Figure 1, eight samples could be irradiated at the same dose rate simultaneously. These samples would then be removed at various times to check the effect of total dose on the polymerization studies. The temperature effect was studied in the bath at 25°, 50°, and 75°C.

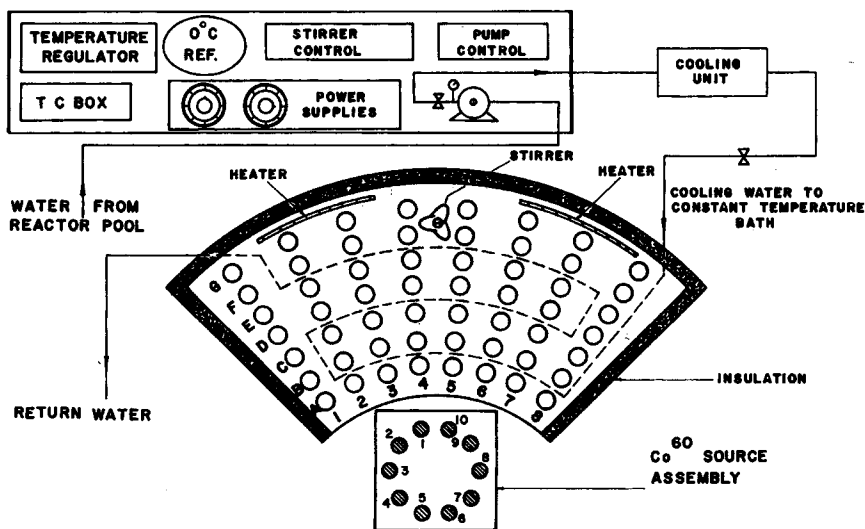


Fig. 1. Source assembly.

Dosimetry was accomplished using ferrous sulfate as a dosimeter.<sup>8</sup> Mass absorption coefficients were calculated, and the bulk polymer, composite system, and ferrous sulfate were found to vary within  $\pm 2\%$  of each other. Because of the nonuniformity of radiation from the source ( $\pm 4\%$ ), the dose rates of bulk, composite, and dosimeter systems were assumed the same.

The preparation of the bulk samples was accomplished by filling the aluminum sample containers ( $3/4$  in.  $\times$  5 in.) with the distilled monomer, capping, and sealing with epoxy.

Preliminary investigations indicated that mixtures of the composite above 50% monomer tended to separate into phases, while mixtures below 50% monomer did not allow uniformity of mixing. Therefore, the distilled monomer-dried clay composite was hand mixed as a 50:50 mixture by weight, placed in the sample containers, capped, and sealed as was the bulk monomer.

### Inert Atmosphere

The purified monomer from the atmospheric distillation was frozen in liquid nitrogen. A vacuum was then applied and the flask was allowed to slowly warm to room temperature in order to degas the monomer. This procedure was repeated at least three times. A Teflon stopcock was fitted to the flask to allow for sealing of the flask. This stopcock was necessary for transferring the degassed monomer from vacuum to an inert atmosphere.

The clay was heated as in the "in air" treatment just before use. It was then placed in the vacuum chamber of a dry box and oxygen removed by use of a fore pump followed by purging at least three times with argon. The same procedure was used as the "in air" mixing except that the degassed purified monomer and clay were mixed in a dry-box in an argon atmosphere.

### Initial Studies

A basis was required to determine the endpoint for all kinetic trials. In specific samples, thermocouples were inserted into the containers at the geometric center and the temperature of polymerization was followed. At the onset of gelation (Trommsdorf effect), a temperature rise was seen. The apex of this exotherm was designated as the endpoint of the trials. Samples were removed from the source at various intervals to obtain conversion data up to and including the endpoint.

In the early stages of polymerization, the composite mixtures were very fluid. However, as the polymerization progressed, the composites increased in viscosity and became rubbery materials. At the endpoint, the samples were tough, hard solids.

The conversion data for the study was obtained by determining the per cent conversion of monomer to polymer. There were two types of polymer formed in the composite. The first type, "homopolymer," could

be solvent extracted (dissolved) from the clay at ambient temperature. The second type of polymer was "inserted" and could not be dissolved from the composite by normal solvents.<sup>9</sup>

Immediately after a sample was "pulled" from the irradiation source, an aliquot of the composite was taken from the middle of the sample tube, placed into a stoppered 250-ml Erlenmeyer flask, and weighed, and 150 ml of dichloromethane was added into the flask. The composite and bulk samples were kept in dichloromethane for at least two weeks in order to allow maximum polymer dissolution. The solution with dissolved composite was then centrifuged at 0°C at 10,000 rpm for 20 min in order to separate the clay from the dissolved polymer. Fresh dichloromethane, 100 ml, was added to the centrifuged solids, and the solution was allowed to stand for one more week and then recentrifuged. The centrifugate was then allowed to evaporate to dryness to remove the dichloromethane. The "homopolymer" was then redissolved in benzene and freeze dried, and the resulting white, fluffy polymer was weighed and per cent conversion determined by a material balance.

Specific samples were tested to ensure that all homopolymer was extracted. This test was accomplished by adding fresh solvent for a third time and repeating the above procedure. The results indicated that two washings of the composite removed all homopolymer within a  $\pm 1\%$  error.

The quantitative analysis of inserted polymer remaining on the clay was determined by calculation of a portion of the composite from which the soluble homopolymer had been extracted.<sup>10</sup> The clay was dried at 100°C for 1 hr, weighed, and then ignited to 1000°C in a muffle furnace. The composite was then reweighed and the amount and per cent conversion of inserted polymer determined by a material balance. Care was taken to include loss of hydroxyl groups as water from the clay in the material balance.

## RESULTS

In both atmospheric conditions, the initial kinetic trials using the thermocouples to establish an endpoint showed that the exotherms generated in the composite were much smaller than the bulk system under the same experimental conditions (Table I). These exotherm temperatures also showed a dose rate dependency and decreased as dose rate decreased at a constant bath temperature.

Based upon the endpoint data (Table II) for both bulk and composite polymer, the total dose needed to reach the endpoint decreased as dose rate decreased.

The comparison of the bulk and composite systems at 25°C and constant dose rate showed a distinct acceleration of the endpoint in the composite polymerization regardless of the atmosphere. This acceleration, whether it be due to chemical or physical reactions, could only be caused by the clay. However, when the temperature of the system was increased, there

TABLE I  
Average Endpoint Temperatures ( $^{\circ}\text{C}$ ) of Bulk and Composite Systems

Dose rate rads/sec	Bulk polymer			Composite polymer		
	25 $^{\circ}\text{C}$	50 $^{\circ}\text{C}$	75 $^{\circ}\text{C}$	25 $^{\circ}\text{C}$	50 $^{\circ}\text{C}$	75 $^{\circ}\text{C}$
24.9	51.7			28.6	55.8	83.5
12.9	42.1	71.6	100.6	27.6	53.5	80.1
7.35	34.9			27.3	54.0	78.8

TABLE II  
Total Doses (rads  $\times 10^{-3}$ ) Necessary to Reach Endpoints for  
Bulk and Composite Systems

Dose rate, rads/sec	Composite polymer			Bulk polymer		
	25 $^{\circ}\text{C}$	50 $^{\circ}\text{C}$	75 $^{\circ}\text{C}$	25 $^{\circ}\text{C}$	50 $^{\circ}\text{C}$	75 $^{\circ}\text{C}$
	Air Atmosphere					
24.9	457	264		638		
12.9	300	182	120	457	210	130
7.35	220	140	90	278		
	Inert Atmosphere					
24.9	437			531		
12.9	309	180	124	384		124
7.35	203			256		

occurred a narrowing of the differences between the endpoints. The total endpoint dose also decreased as the reaction temperatures increased. The effect of air (oxygen) is shown in the total doses necessary for the bulk polymerization.

The kinetic analysis of the system will be considered in three parts: (1) homopolymer from the composite, (2) inserted polymer from the extracted composite, and (3) total polymer (homopolymer and inserted polymer) of the composite. In each case, the system will be compared with results obtained for the bulk polymer under the same conditions. The kinetic data reported represent the net result of polymer formation and degradation during the irradiation process.

### Homopolymer

The comparison of the rate of formation of homopolymer and bulk polymer in air is shown in Figures 2 and 3. At 25 $^{\circ}\text{C}$  (dose rate = 12.9 rads/sec), the polymerization reaction was accelerated by the presence of the inorganic substrate. However, when the reaction temperature was increased, the difference in the rate of conversion decreased until, at 75 $^{\circ}\text{C}$ , there were no differences between the homopolymer and bulk polymer conversion curves. These data coincide with the endpoints as designated by the temperature profiles.

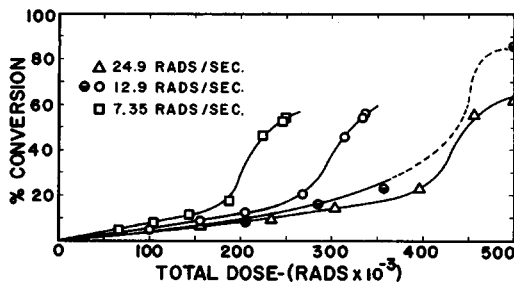


Fig. 2. Formation of homopolymer ( $\Delta$ ,  $\circ$ ,  $\square$ ) and bulk polymer ( $\ominus$ ) in air as a function of dose rate at 25°C.

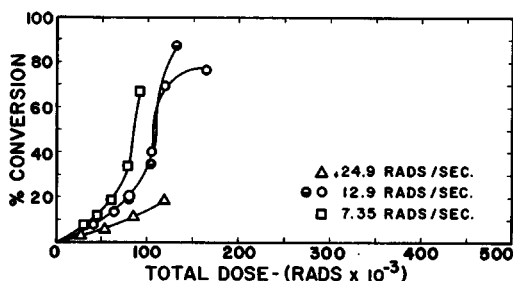


Fig. 3. Formation of homopolymer ( $\Delta$ ,  $\circ$ ,  $\square$ ) and bulk polymer ( $\ominus$ ) in air as a function of dose rate at 75°C.

The percentage conversion of homopolymer at a total dose of 12.9 rads/sec was greater in the inert gas atmosphere at 25°C and than in air by 1% to 6% at the same temperature. This percentage differential decreased as the temperature increased until, at 75°C, there was no difference between the inert gas and air system. Clay, which has a large surface area, was difficult to degas. Actually, such a procedure would be impractical. Even though precautions were taken in this work to condition the clay for a specific experiment, it was likely that the clay surfaces in all of the experiments had appreciable quantities of atmospheric gases still adsorbed on them. The various results and calculations obtained from the homopolymer conversion data will be discussed below.

At low doses, the conversion curves for the bulk and homopolymer were linear and can be described by an equation of the following type:

$$\frac{dP}{dD} = kI^n$$

where  $dP/dD$  = initial polymerization rate (per cent conversion per rad);  $I$  = absorbed dose rate in ferrous sulfate and system under study (rads/sec);  $k$  = apparent reaction rate constant; and  $n$  = apparent reaction order.

The initial average apparent reaction order shown in Table III was  $-0.46$ . This reaction order approximates the reaction order  $-0.5$  pre-

TABLE III  
Apparent Orders of Reactions ( $n$ ) of Composite Polymer Systems in Air

Temperature, °C	Composite polymer		
	Homopolymer	Inserted	Total
25	-.44	-.70	-.48
50	-.46	-.20	-.49
75	-.47	0.0	-.50

TABLE IV  
Apparent Activation Energy ( $\Delta E_a^*$ ) of Composite and Bulk Polymer Systems

	Dose rate, rads/sec	Air atmosphere	Inert atmosphere
		$\Delta E_a^*$ , kcal/mole	$\Delta E_a^*$ , kcal/mole
Homopolymer	24.9	5.0	
	12.9	5.4	4.4
	7.35	4.6	
Inserted polymer	24.9	6.4	
	12.9	4.8	1.6
	7.35	2.8	
Total polymer	24.9	5.4	
	12.9	5.6	4.0
	7.35	5.4	
Bulk polymer	12.9	6.6	4.9 <sup>a</sup>

<sup>a</sup> From refs. 12 and 13.

dicted by the simplified kinetic scheme for bulk free radical-initiated polymerization for linear polymers.<sup>11</sup> The minus signs were used in the plotting of  $dP/dD$ . If a plot of  $dP/dt$  were done where  $t$  is irradiation time, the reaction order would be positive and equal to  $n + 1$ .

A comparison of the apparent energy of activation for the homopolymer and bulk polymer ( $\Delta E_a^*$ ), as calculated from an Arrhenius-type equation, is shown in Table IV. The average  $\Delta E_a^*$  for the "in air" homopolymer is 1.6 kcal less than the "in air" bulk-polymer  $\Delta E_a^*$  value and compares with the  $\Delta E_a^*$  of the "inert gas" bulk polymer. The "inert gas" homopolymer  $\Delta E_a^*$  is 2.2 kcal less than the "in air" bulk and 0.5 kcal less than an inert bulk system.<sup>12,13</sup> These values indicate that the clay does exert a catalytic influence on the polymerization even in the presence of the retarding air atmosphere.

### Inserted Polymer

The formation of inserted polymer at 25° and 75°C in air is shown in Figures 4 and 5. One fact that must be considered is that polymer can be formed before irradiation begins (due to the ambient catalytic nature of the clay). If this is the case, the conversion curves would not pass through zero conversion at time zero. The other possibility is that, if the curves do

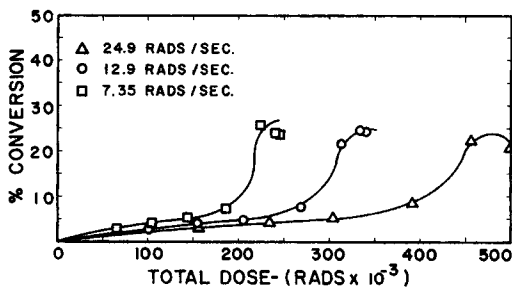


Fig. 4. Formation of inserted polymer in air as a function of dose rate at 25°C.

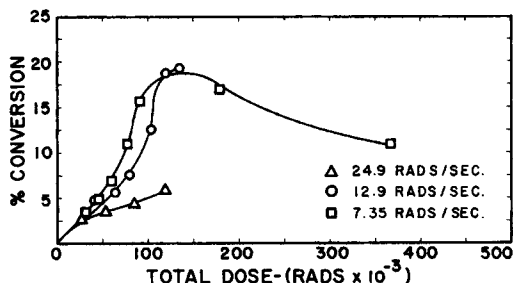


Fig. 5. Formation of inserted polymer in air as a function of dose rate at 75°C.

pass through zero, there is an initial acceleration caused by the catalytic effect of the clay which then decreases with time. From data obtained at room temperature without any type of initiator, it was found that polymerization could take place in the presence of the clay. From differential thermal gravimetry, ignition analysis, and using a material balance it was found that after 24 hr, 1.3% conversion to polymer had occurred. However, in weighing the mixture of monomer-clay, there is an error limit of  $\pm 1\%$  which could account for the percentage conversion found. Therefore, from the general shape of the curves and taking into account the limits of experimental error, there appears to be sufficient justification for drawing the kinetic curves for the insertion polymer through zero.

As shown in Tables III and IV, the order of reaction and the  $\Delta E_a^*$  values of the "in air" systems were temperature and dose-rate dependent. These data indicate at least two possible explanations: (1) that there is a change in mechanism of polymerization at the surface of the clay, and (2) that the data can be explained by physical monomer and polymer population changes at the surface of the clay which are also related to the dose rate. A change in polymerization mechanism does not appear reasonable in view of the fact that the activation energies for the homopolymer showed that the mechanism was the same at all dose rates and temperatures. It will be shown in part II that the characterizations of both homopolymers and inserted polymers are also consistent with each other. However, the amount of energy necessary to form a net amount of polymer per unit dose on the surface of the clay may change as dose rate changes. These changes in



energy requirements could be caused by a depolymerization reaction which would proceed at a faster rate at the higher dose rate. The amount of energy necessary to overcome this larger depolymerization reaction to form the same amount of polymer per unit dose at the clay surface would thus be increased. If the above were true, the rate of formation of inserted polymer would be lower at the higher dose rates for the same total dose. This can be seen in the conversion curves. Thus, it appears evident that the catalytic effects of the clay surface are affected by both dose rate and temperature. However, without some knowledge of clay site-gamma ray interactions as functions of dose rate and temperature, a quantitative explanation of these data cannot be presented.

In comparing the conversion studies of inserted polymer and homopolymer in air, it was demonstrated that the percentage conversion of homopolymer was equal to or larger than that of the inserted polymer at the same experimental conditions. At the same dose rate, the percentage conversion of homopolymer increased, but the percentage conversion of inserted polymer decreased as temperature increased (from 25°C to 75°C).

### Total Polymer Kinetic Analysis

The total polymer content is a summation of the soluble homopolymer and inserted polymer. Figures 6 and 7 show the total polymer conversion

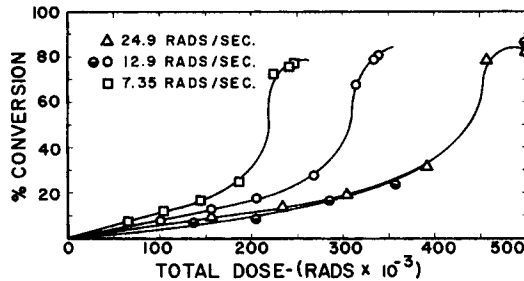


Fig. 6. Formation of total polymer ( $\Delta$ ,  $\circ$ ,  $\square$ ) and bulk polymer ( $\ominus$ ) in air as a function of dose rate at  $-25^{\circ}\text{C}$ .

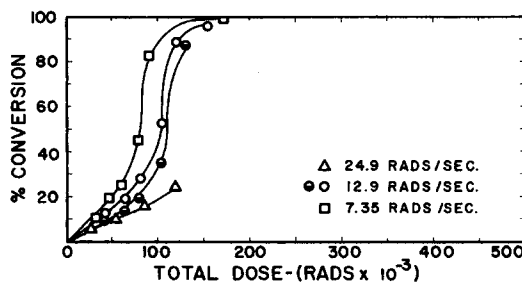


Fig. 7. Formation of total polymer ( $\Delta$ ,  $\circ$ ,  $\square$ ) and bulk polymer ( $\ominus$ ) in air as a function of dose rate at  $-75^{\circ}\text{C}$ .

curves in air at all dose rates as well as the bulk conversion curve at 12.9 rads/sec. The definite catalytic effect of the kaolin clay as well as its temperature dependency can be seen from these figures. The early influence of the inserted polymer gives the total conversion curves a slight concave downward trend. However, as polymerization proceeds and the homopolymer polymerization becomes more in evidence, the S-shaped curve characteristic of homopolymerization takes form.

In comparing the total composite polymerization with the bulk polymerization for the middle dose rate, it can be noted that the clay accelerates the polymerization and the polymer attains 80% conversion almost 125,000 rads, or 2.7 hr, before the bulk polymer does. However, as the reaction temperature increases, the acceleration of polymer formation by the clay decreases until, at 75°C, the bulk and total composite polymer attain 80% conversion at the same total dose. In all cases, the conversion of monomer to polymer in the composite is greater than that of the bulk polymer until at least 50% conversion is attained for the same total dose.

The apparent reaction orders (Table III) give an order which definitely defines the mechanism for this reaction as free radical.

The activation energy (Table IV) of the total polymer in air is approximately 1 kcal/mole less than for the "in air" bulk polymerization. The "inert gas" composite system is 0.9 kcal/mole less than the bulk "inert gas" polymerization.

## CONCLUSIONS

The presence of the inorganic substrate kaolin clay, either in air or inert gas, was found to have a catalytic influence on the polymerization reaction of MMA at 25°C. This effect was temperature dependent and decreased as temperature increased.

Two types of polymer were produced in the composite. One type (homopolymer) could be extracted by common organic solvents; the other type (inserted) could only be extracted by destroying the clay structure through hydrofluoric acid treatment.

The percentage conversion of homopolymer was always larger than the inserted polymer at the same experimental conditions.

The kinetic analysis showed that the total polymer order of reaction was indicative of a free-radical mechanism. The apparent activation energy for the composite polymerization was in both air and inert gas approximately 1 kcal/mole less than the bulk polymerization  $\Delta E_a^*$  in the same atmosphere.

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