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RADIOISOTOPE AND RADIATION APPLICATIONS

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SECTION I. USE OF INTRINSIC RADIOACTIVE TRACERS FOR PROCESS CONTROL
James L. McFarling, Peter Gluck, John F. Kircher, and Duane N. Sunderman

SECTION II. RADIATION-INDUCED GRAFT-POLYMERIZATION STUDIES
Israel S. Ungar, Francis A. Sliemers, William B. Gager, John F. Kircher, and Robert I. Leininger

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BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

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TABLE OF CONTENTS

RADIOISOTOPE AND RADIATION APPLICATIONS

Duane N. Sunderman

This is the Sixth Quarterly Progress Report on research programs in radioisotope technology and radiation chemistry under the sponsorship of the Office of Isotopes Development of the U. S. Atomic Energy Commission. The report period is July 1 to September 30, 1960. Studies are continuing to develop the technique of applying intrinsic radioactive tracers to industrial process control and to investigate the influence of structural factors in radiation-induced graft polymerization.

The use of a process-model system has demonstrated the applicability of intrinsic radioactive tracers to the measurement of precipitation and filtration efficiency in an iron-removal step under actual process conditions. Experiments under steady-state operating conditions have shown good correlation between continuous radioassay measurements and intermittent sampling followed by chemical analysis. Further experiments with this system will include an evaluation of response time and sensitivity of the intrinsic-tracer technique by deliberate changes in process parameters during operation. A report describing potential applications of intrinsic tracers to the control of other unit operations is in preparation.

The study of the effect of structure upon radiation-induced graft polymerization is directed toward a determination of reaction mechanisms in substituted methacrylate systems. An interrelationship between structure of the ester group, number of carbon atoms in the ester, and polymer molecular weight is postulated. Decay data indicate that at least two distinct free-radical species are involved.

I. USE OF INTRINSIC RADIOACTIVE TRACERS FOR PROCESS CONTROL

James L. McFarling, Peter Gluck, John F. Kircher, and Duane N. Sunderman

SUMMARY

A series of experiments has been completed using the process model for studying radiotracer control of iron removal from a nickel-refinery stream. The results of 13 experimental runs discussed in this report indicate that the radiotracer control concept is technically sound. The iron reduction ratios obtained by radioassay agree well with the iron reduction ratios given by chemical analysis. The radioactivity monitor on the filtrate stream provides a rapid and sensitive indication of changes in process operating conditions.

The survey of chemical engineering unit operations as potential intrinsic radiotracer applications has been completed and will be summarized in a separate report.

INTRODUCTION

The increasing use of radiotracers in industry has led to greater interest in using intrinsic radiotracers as process control tools. The objective of the present study is, first, to define areas where intrinsic radiotracer process-control applications exist and, second, to study the technology of such an application on a small pilot process scale.

The first phase has resulted in two major studies which evaluate: (1) the use of intrinsic radiotracers in hydrometallurgical purification operations, and (2) the application of intrinsic radiotracers in controlling the unit operations of chemical engineering.

The experimental phase of the program has consisted of the construction and operation of a small-scale operating process model of an iron-removal step in a nickel refinery. The results of this phase of the program comprise the principal subject discussed in this report.

EXPERIMENTAL WORK

Experiments Using Iron-Removal Process Model

A series of experiments with the model process iron-removal system was completed this quarter. The purpose of these experiments was to test the feasibility and reliability of the radiotracer control concept.

The concept proposes that the iron removal from a nickel-refinery stream could be controlled by introducing iron-59 tracer into the feed stream to the iron precipitator and measuring the solution radioactivity before and after precipitation. The measured radioactivity in the feed stream compared with that remaining after precipitation and filtration gives the iron reduction ratio at the time of measurement. The validity of using the activity reduction as a measure of the iron reduction was evaluated over a variety of process conditions in the model process system. The activity reduction ratio at any particular time was compared to the reduction in iron concentration determined by chemical analysis of feed and filtrate samples.

General Description of Experiments

The process-model system used in these experiments was described in detail in the quarterly report of July 25, 1960. Photographs and description of the system appeared in that report. Figure I-1 is a flow diagram of the system which shows the flow patterns used for the experiments described here.

The level of radiotracer activity which must be injected into the feed stream depends on the efficiency of iron removal by the system, as well as the desired accuracy in the residual filtrate radioactivity determination. It was found that the iron-removal efficiency of the system at the low flow rates used was much higher than originally anticipated. This led to the injection of higher activities in later runs in order to improve the accuracy of the readings. It was found that the level of radiotracer injection would be maintained satisfactorily constant by slight adjustments in the flow rate of feed solution.

The conditions under which the experimental runs were carried out were as follows:

(1) The pH of the feed solution was held between 2.1 and 2.3.

(2) The feed-solution flow rate in all experiments was between 200 and 250 cm^3 per min.

(3) Temperature of the iron precipitator was held close to 160 F.

(4) The running time for each experiment was from 4 to 5-1/2 hr.

The iron content of the feed and filtrate samples was analyzed in the following manner:

(1) The iron was extracted from the process solution as the iron III-cupferron complex.

(2) This complex was destroyed and the iron III reduced to iron II.

(3) The iron II-o-phenanthroline complex was formed and its concentration measured spectrophotometrically.

Based on analysis of standards, it is estimated that the sensitivity of this method is ±0.1 μg per ml.

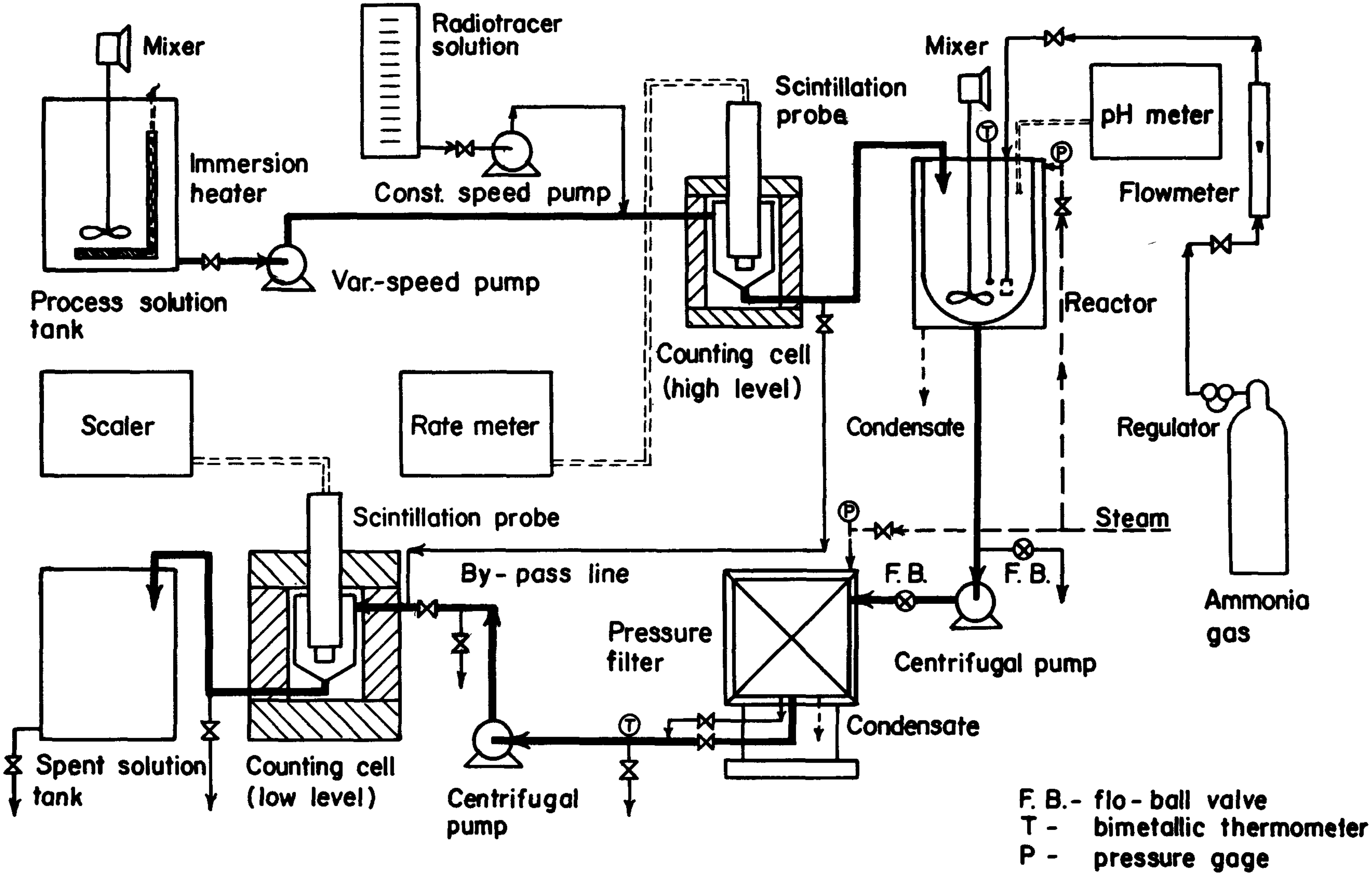

FIGURE I-1. PROCESS FLOWSHEET FOR THE STUDY OF RADIOTRACER CONTROL OF IRON REMOVAL FROM A SIMULATED NICKEL-REFINERY STREAM

Variation of Process Parameters

The experiments were performed within the following range of processing conditions:

(1) The pH of iron precipitation was either 4.5, 5.0, or 5.5.

(2) The iron concentration in the feed solution was varied between 0.16 and 0.89 g per liter.

(3) The concentration of dissolved metals was varied from 10 to 70 g per liter nickel plus cobalt, the metals being in equal concentrations.

(4) Various miscellaneous and/or unplanned variations in process conditions were noted such as sudden increases in filter flow rates, cake breakthroughs, etc.

All of these variations might occur in an actual production process. However, all except (4) were studied as steady-state or semiequilibrium conditions in order to obtain more accurate measurements. The results obtained will be compared with those of the dynamic experiments to be performed later in the program, at which time deliberate changes in operating conditions will be made to evaluate the response of the radioassay system.

Unit-Operations Survey

The survey of chemical engineering unit operations as potential applications of intrinsic radiotracers has been completed. The results will appear in a separate topical report. The survey report gives some general considerations regarding intrinsic radiotracer process-control applications and indicates several unit operations where radiotracers might be used advantageously. Specific examples of various process applications are also suggested in the report.

RESULTS

The results of 13 experimental runs are summarized in Table I-1. In this table, the experimental conditions for each run are given, as well as a comparison between radioactivity reduction ratio and the iron reduction determined by chemical analysis.

The filtrate iron analyses shown here were performed on filtrate samples collected during the time the corresponding filtrate count was being taken. Although the samples removed for analysis were generally not as large or homogeneous as those radioassayed, the samples should have essentially the same iron concentration except where the iron concentration is changing rapidly. The latter behavior is to be noted in certain instances, such as Runs 3 and 4.

In Runs 4 and 8 particularly, there occurred major discrepancies between the measured filtrate activity and that to be expected from the iron analysis. This

TABLE I-1. RESULTS OF EXPERIMENTAL RUNS WITH MODEL IRON-REMOVAL SYSTEM

Run	Iron Analysis of Feed Solution, μg per ml	Nickel Plus Cobalt Metal in Solution, g per liter	pH of Iron Precipitation	Net Count Rate From Feed Solution, cpm	Elapsed Time Since Start of Run, min	Net Count Rate From Filtrate, cpm ± σ	Iron Analysis of Filtrate, μg per ml	Iron Reduction Ratio: Radioassay, Feed Activity : Filtrate Activity	Iron Reduction Ratio: Chemical Analysis, Iron in Feed : Iron in Filtrate
1	160	10	5.5	2200 ± 100		13 ± 8 (average of all counts)	0.8 ± 0.1 (average of all counts)	170 ± 104	200 ± 25
2	220	10	5.0	7400 ± 200	105	38 ± 9	1.2 ± 0.1	195 ± 46	183 ± 15
					170	90 ± 9	2.3 ± 0.1	82 ± 8	96 ± 4
					200	105 ± 9	2.8 ± 0.1	70 ± 6	79 ± 3
					275	70 ± 9	2.7 ± 0.1	105 ± 14	82 ± 3
					320	67 ± 9	2.0 ± 0.1	110 ± 15	110 ± 6
3	200	10	4.5	3400 ± 200	120	89 ± 9	4.6 ± 0.1	38 ± 4	43 ± 1
					160	193 ± 10[a]	9.5 ± 0.1	17.6 ± 1	21
					180	87 ± 9	3.6 ± 0.1	39 ± 4	56 ± 2
					240	325 ± 10[a]	17.6 ± 0.1	10.5	11.4
					300	117 ± 9	4.5 ± 0.1	29 ± 2	44 ± 1
					320	130 ± 9	5.1 ± 0.1	26 ± 2	39 ± 1
4[b]	413	20	4.5	6300 ± 200	100	46 ± 9	1.5 ± 0.1	137 ± 25	275 ± 18
					160	53 ± 9	1.6 ± 0.1	119 ± 20	258 ± 16
					220	61 ± 9	2.9 ± 0.1	103 ± 15	142 ± 5
					320	88 ± 9[c]	6.2 ± 0.1	72 ± 7	68 ± 1
5	423	20	5.0	13,700 ± 300	115	81 ± 9	2.4 ± 0.1	169 ± 19	176 ± 7
					205	109 ± 10	3.9 ± 0.1	125 ± 12	108 ± 3
					235	55 ± 9	1.4 ± 0.1	245 ± 40	300 ± 22
					280	61 ± 9	2.0 ± 0.1	224 ± 33	212 ± 11
6	368	30	5.5	40,000 ± 1,000	135	90 ± 10	0.7 ± 0.1	435 ± 44	526 ± 75
					165	78 ± 10	0.6 ± 0.1	513 ± 51	613 ± 102
					225	98 ± 10	0.8 ± 0.1	408 ± 41	460 ± 57
					300	104 ± 10	0.6 ± 0.1	384 ± 38	613 ± 102
					345	307 ± 11[c]	6.1 ± 0.1	130 ± 5	60 ± 1
7	786	30	4.5	29,000 ± 1,000	110	938 ± 14	31	31 ± 1	25
					185	819 ± 13	26		30
					245	730 ± 2	23		34
					285	535 ± 12	16	54 ± 1	49
					315	462 ± 11	13.2	63 ± 1	60

TABLE I-1. (Continued)

Run	Iron Analysis of Feed Solution, μg per ml	Nickel Plus Cobalt Metal in Solution, g per liter	pH of Iron Precipitation	Net Count Rate From Feed Solution, cpm	Elapsed Time Since Start of Run, min	Net Count Rate From Filtrate, cpm ± σ	Iron Analysis of Filtrate, μg per ml	Iron Reduction Ratio	
								Radioassay, Feed Activity : Filtrate Activity	Chemical Analysis, Iron in Feed : Iron in Filtrate
8(b)	445	50	5.0	29,000 ± 1,000	125	202 ± 11	2.3 ± 0.1	143 ± 7	193 ± 8
					155	226 ± 11	2.2 ± 0.1	128 ± 6	202 ± 9
					25	192 ± 11	2.0 ± 0.1	151 ± 8	222 ± 11
					320	196 ± 11	1.8 ± 0.1	148 ± 8	247 ± 14
					350	181 ± 11	1.0 ± 0.1	160 ± 9	445 ± 45
9	830	20	4.5	14,300 ± 500	145	73 ± 9	4.0 ± 0.1	196 ± 24	208 ± 6
					160	89 ± 9	3.2 ± 0.1	160 ± 16	268 ± 9
					175	84 ± 9	4.1 ± 0.1	170 ± 18	202 ± 6
					220	111 ± 9	5.0 ± 0.1	128 ± 10	165 ± 3
10	840	30	5.0	29,000 ± 1,000	130	227 ± 11	5.2 ± 0.1	128 ± 6	161 ± 3
					155	32 ± 10	1.4 ± 0.1	906 ± 280	600 ± 43
					185	138 ± 10	2.5 ± 0.1	210 ± 15	335 ± 14
					215	83 ± 10	1.7 ± 0.1	350 ± 41	493 ± 29
					260	61 ± 10	2.2 ± 0.1	475 ± 78	382 ± 17
					315	36 ± 10	1.5 ± 0.1	806 ± 224	560 ± 37
11	890	30	5.0	43,000 ± 2,000	115	38 ± 10	0.8 ± 0.1	1130 ± 280	1110 ± 138
					160	35 ± 10	0.8 ± 0.1	1230 ± 350	1110 ± 138
					205	55 ± 10	1.3 ± 0.1	780 ± 142	685 ± 53
					235	40 ± 10	0.9 ± 0.1	1070 ± 270	990 ± 110
					260	35 ± 10	1.1 ± 0.1	1230 ± 350	810 ± 74
					320	20 ± 10	0.8 ± 0.1	2140 ± 1070	1110 ± 138
12	870	50	4.5	51,000 ± 2,000	110	410 ± 14	8.6 ± 0.1	124 ± 5	101 ± 1
					140	42 ± 12	1.4 ± 0.1	1210 ± 346	620 ± 40
					185	75 ± 12	1.6 ± 0.1	680 ± 110	545 ± 34
					280	216 ± 13	3.2 ± 0.1	236 ± 14	272 ± 9
					325	246 ± 13	3.3 ± 0.1	207 ± 12	264 ± 8
13	840	70	4.5	51,000 ± 3,000	120	87 ± 12	1.8 ± 0.1	585 ± 81	460 ± 25
					180	123 ± 13	2.0 ± 0.1	415 ± 43	420 ± 21
					240	394 ± 14	6.8 ± 0.1	129 ± 5	123 ± 2
					283	320 ± 14	5.2 ± 0.1	159 ± 7	161 ± 3

(a) In these cases the filtrate appeared cloudy.

(b) In these cases there was a considerable percentage of impurity radiotracer present.

(c) In these cases the flow rate through the filter was increased abruptly.

discrepancy was found to be due to small amounts of impurity radiosotopes originally present in the iron-59 tracer. Recycling of the process solutions from Runs 1 to 4 and 5 to 8 built up the impurity activity to a level where it was found in Run 8 to be from one-fourth to one-third the total activity present in the filtrate. This problem was alleviated in the later runs by a prepurification of the radiotracer solution. The observed effect does serve to emphasize the necessity of using pure radiotracers in process-control applications.

CONCLUSIONS

The experimental runs so far performed indicate that the radiotracer control of iron removal is technically feasible. Specific conclusions deduced from the experiments are as follows:

(1) In all cases the iron reduction ratios given by the radioactivity reduction agree well with those shown by the actual chemical analysis after corrections are made for impurity radiotracer

(2) It was shown in several experiments that the radioactivity monitor responds rapidly to sudden changes in the iron content of the filtrate. This monitor indicated changes in the operating conditions before the effects could be observed by other means

(3) The necessity of insuring pure radiotracer for control of a purification operation was emphasized along with the need for a sensitive and reliable low-level counting system.

FUTURE WORK

The major part of the laboratory work to be completed consists of performing several experimental runs where deliberate changes are made in operating conditions during the course of each experiment. The response of the radioactivity detection system to such changes will provide quantitative data useful in extrapolating to plant operating conditions.

Work on other intrinsic radiotracer control applications is contingent upon the extension of the present contract which ends the last of October. The proposal submitted for project renewal entails a study of radiotracer control of unit operations different from the iron precipitation-filtration now being studied. The first operation to be considered is that of ion exchange.

II. RADIATION-INDUCED GRAFT-POLYMERIZATION STUDIES

Israel S. Ungar, Francis A. Sliemers, William B. Gager,
John F. Kircher, and Robert I. Leininger

SUMMARY

The study of the mechanism of formation of free radicals in polymethacrylates has been continued. Particular emphasis has been placed on an examination of the effect of structural factors on the efficiency of free-radical site formation. The investigation of the influence on free-radical formation of the hydrocarbon constituent of the ester side chain has been continued. In addition, polymer molecular weight has been shown to influence site concentration.

INTRODUCTION

This is the Sixth Quarterly Report on the study of radiation-induced changes in polymers leading to graft copolymerization as influenced by structural factors. The objective of this research is to determine the structural and compositional factors influencing (1) radiation effects in polymeric systems, (2) mechanisms of graft copolymerization reactions, and (3) the products of graft copolymerization reactions.

During the last quarter the investigation of the relationship of site formation and dose for a number of polymethacrylates was continued. Gas chromatography was employed to identify and measure quantitatively the volatile products formed during irradiation. A mechanism was proposed and an attempt was made to correlate the number of active sites formed and the chemical changes found in the irradiated polymers with the suggested mechanism. During the present quarter the investigation of free-radical site formation has been continued. The study of the effect of structural factors on the efficiency of site formation has been emphasized.

EXPERIMENTAL WORK

All polymers were prepared by radiation polymerization at the Battelle Gamma Facility. For the measurement of free-radical sites, samples of polymer were sealed in tubes under vacuum and irradiated to various dosages. Free-radical concentrations were determined with a Varian EPR spectrometer.

Decay of Sites in Polybutylmethacrylates

Samples of normal-, iso-, and sec-butylmethacrylate polymers were prepared by irradiation of 10-per cent solutions of the monomers in dry n-hexane. The total radiation dose was ~5 x 10^6 rads in each case. Attempts to prepare poly-tertiary-butylmethacrylate in a similar manner yielded predominantly polymethacrylic acid.

For decay studies, samples of the three isomeric polymers were irradiated in vacuo to a total dose of 5.5 x 10^7 rads. This dose was, in each case, considerably in excess of that at which the maximum site concentration was obtained. The polymers were allowed to decay at room temperature. The number of free-radical sites in each sample was determined periodically after irradiation. These data are given in Figure II-1. As was observed with the other methacrylates, decay was quite rapid at first but gradually decreased until a nearly constant number of sites remained. The level portion of the curve for poly-n-butylmethacrylate was not obtained. This was due to the fact that the total number of sites fell below the level of sensitivity of the EPR spectrometer after about 30 hr.

An analysis of the decay data confirms earlier findings that (1) at least two distinct types of free-radical sites are formed during irradiation, and (2) the total number of sites formed increases with increased branching of the hydrocarbon tail of the ester side chain. This work will be extended to include the tertiary-butylmethacrylate polymer.

The relationship of number of sites to radiation dose for the three polymers[(1)] has been extended to the higher total dose of 5.5 x 10^7 rads (Figure II-2). These results are quite interesting in that the total number of available sites has decreased to a point considerably below the number present after short-term irradiations at the same dose rate. Apparently the production of scavenger (low-molecular-weight fragments) has increased to the point where the effective scavenger concentration, i.e., that portion of the total fragment concentration which actually reacts to destroy free radicals, is increasing at a more rapid rate than is the production of additional free radicals.

Free-Radical Determination for the Poly-n-Alkylmethacrylates

Dose-versus-site measurements have been made on the methyl-, ethyl-, n-propyl-, n-butyl-, and n-amylmethacrylate polymers. All but the amyl polymer were prepared by irradiation of a 10 per cent solution of monomer in n-hexane. In the case of the n-amyl polymer it was necessary to polymerize in bulk in order to obtain a usable polymer. The material prepared in solution was quite "sticky" when dried. This undoubtedly was a molecular-weight effect.

The data of Figure II-3 indicate that the total number of sites formed per monomer unit decreases with increasing length of the hydrocarbon tail of the ester side chain. Again, the sensitivity of the spectrometer limited definition of the curve of poly-n-amylmethacrylate, except at the peak.

In examining the effect of structural factors on the efficiency of free-radical site formation, the investigation of polymer molecular weight has been continued. Earlier work with PMMA[(1)] had shown no appreciable effect in the 4,000 to 15,000 number-average molecular-weight range.

In the present work considerably higher molecular weights have been studied. A sample of bulk methylmethacrylate was polymerized in the Battelle Gamma Facility.

(1) References at end.

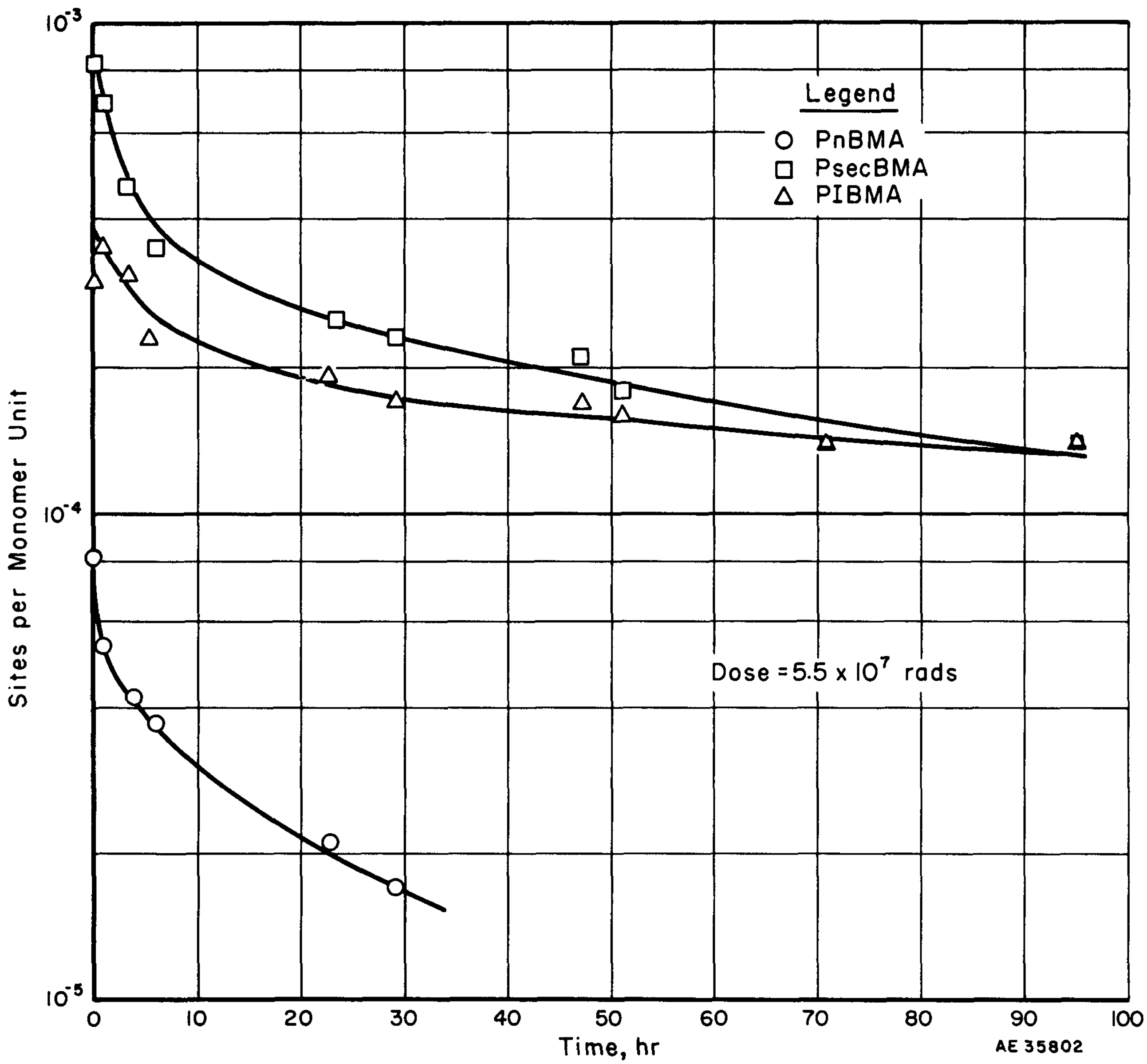

FIGURE II-1. FREE-RADICAL DECAY CURVES FOR POLYBUTYLMETHACRYLATES

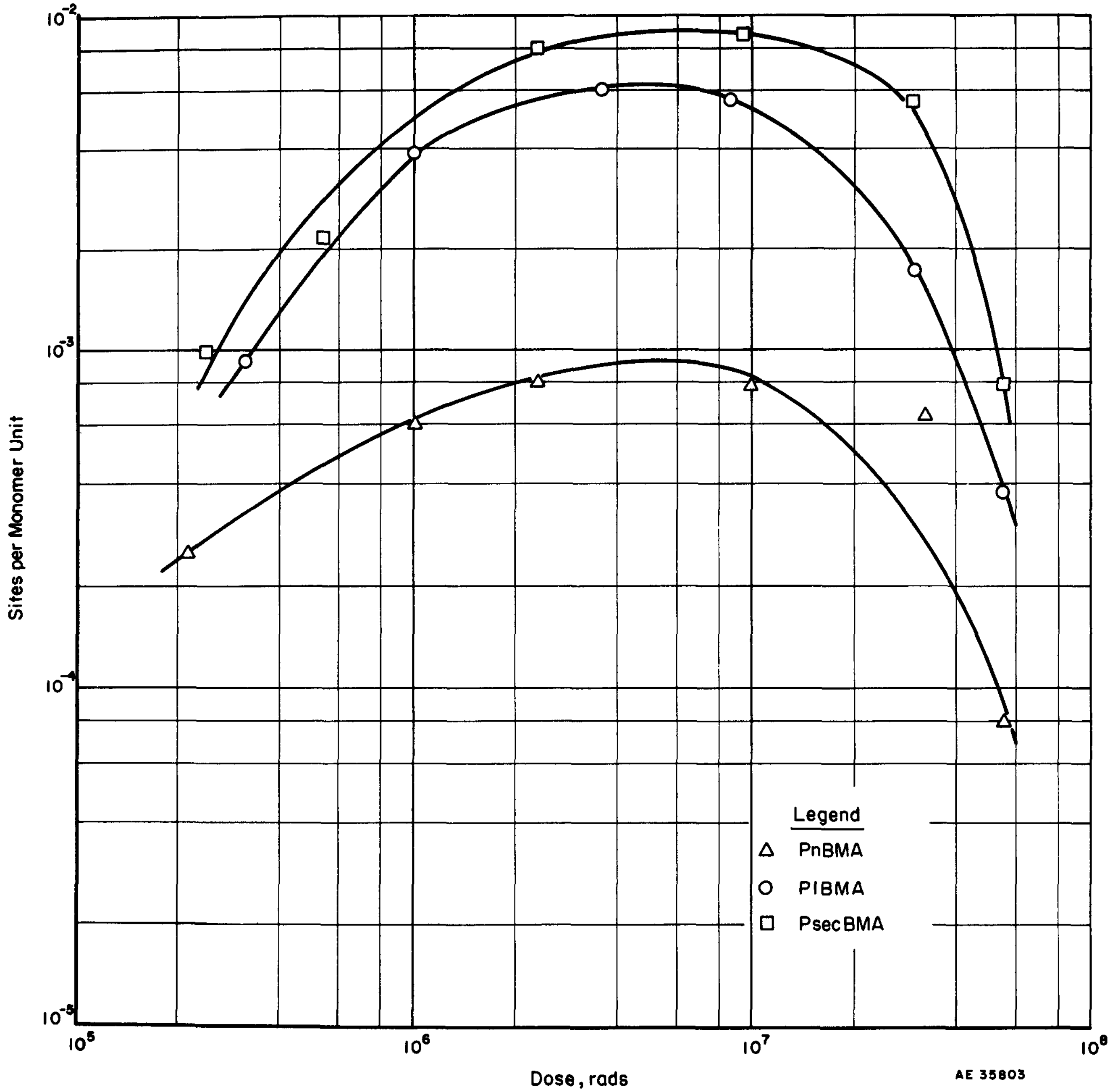

FIGURE II-2. SITES PER MONOMER UNIT VERSUS DOSE FOR POLYBUTYLMETHACRYLATES

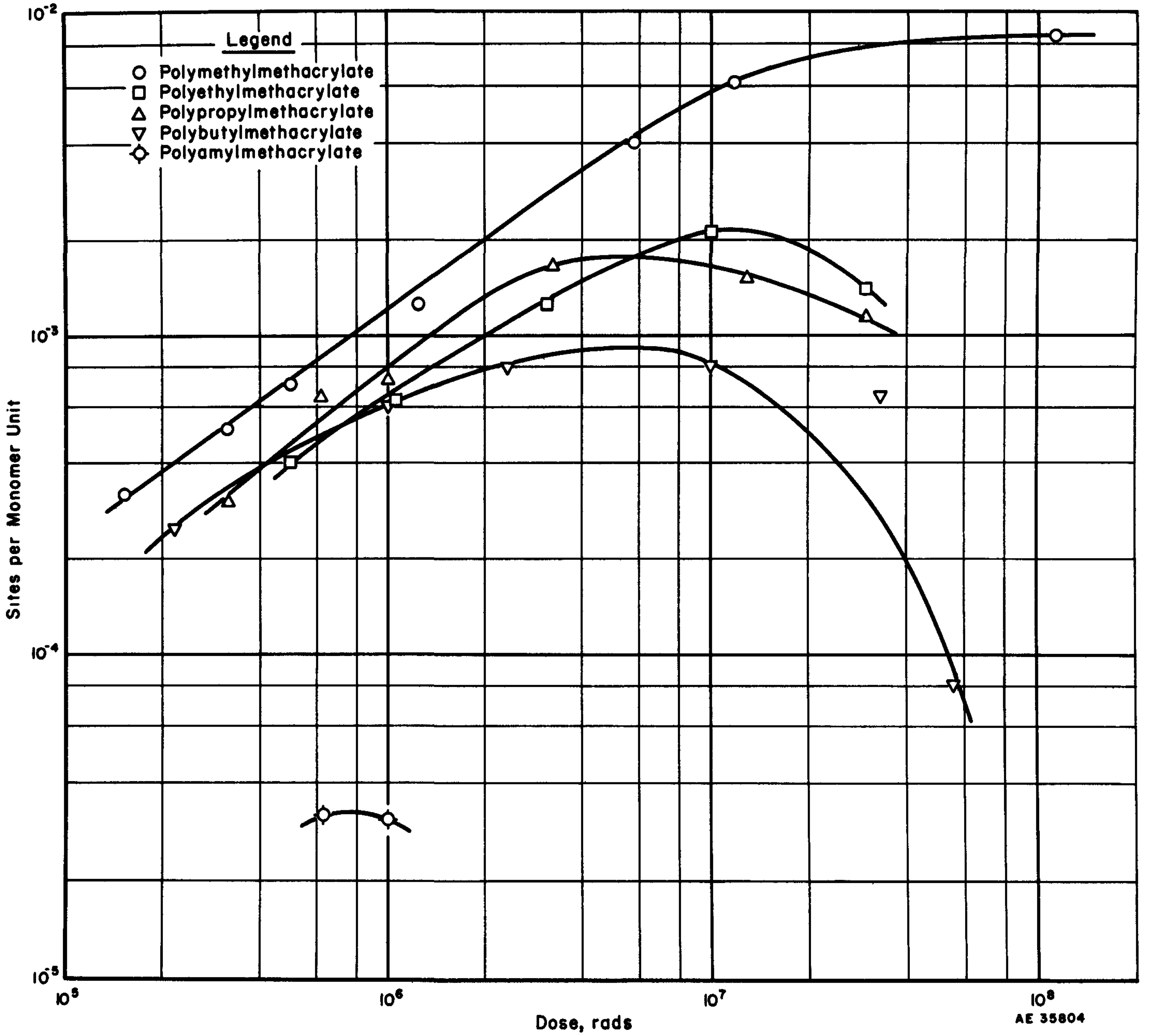

FIGURE II-3. SITES PER MONOMER UNIT VERSUS DOSE FOR THE POLY-N-ALKYLMETHACRYLATES

The weight-average molecular weight of the polymer, as determined from viscosity measurements in acetone[2], was 2.95×10^5. This polymer was fractionated by precipitation from acetone solution with methanol. The fractions had molecular weights of 2.25 and 4.35×10^5.

Site-versus-dose curves were obtained for the bulk polymer and the two fractions (Figure II-4). The data indicate that the greater the molecular weight, the lower the site concentration for a given dose in this comparatively high molecular-weight range. It is planned to check this point further. This effect of molecular weight could also account in part for the extremely low site concentrations observed above for the n-amyl polymer. This polymer, it will be recalled, was bulk polymerized which would be expected to cause higher molecular weights.

CONCLUSIONS

Several tentative conclusions can be drawn from the work reported here.

(1) Decay data for several butylmethacrylates confirm earlier findings that (a) at least two types of free radicals are formed and (b) the total number of sites formed is dependent on the structure of the ester group.

(2) The number of carbon atoms as well as their arrangement in the hydrocarbon tail of the ester group affect site formation.

(3) Polymer molecular weight influences site formation.

FUTURE WORK

During the coming quarter the investigation of the mechanism of formation and decay of radicals in irradiated polymethacrylates will be continued. The tertiary-butylmethacrylate polymer will be prepared and subjected to the same treatment given the other isomeric butyl polymers. This will include an analysis of the fragments formed during irradiation by the use of mass spectrometry and gas chromatography. These analytical procedures will also be employed to identify and quantitatively measure the fragments formed by polymethyl-α-chloroacrylate, polyphenylmethacrylate, and polycyclohexylmethacrylate.

Moreover, an attempt will be made to clarify further the mechanism of free-radical formation by employing radioactive iodine. It is anticipated that identification of the fragments associated with free-radical formation can be more readily determined in this way. It is hoped that the points of attack on the ester side chain and/or polymer backbone can also be established.

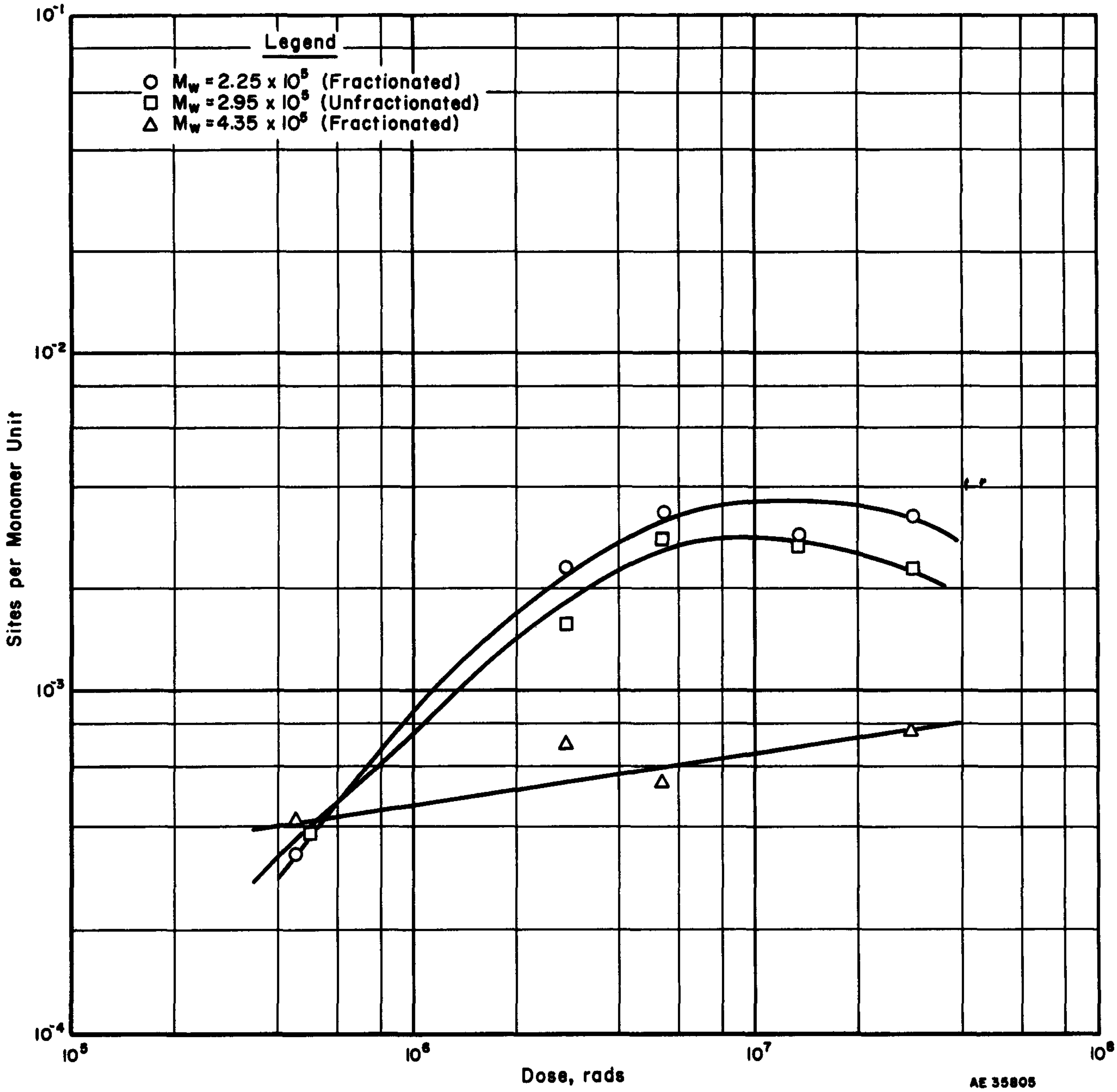

FIGURE II-4. EFFECT OF MOLECULAR WEIGHT ON SITE FORMATION FOR POLYMETHYLMETHACRYLATES

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Emphasis will also be placed on a continuation of the examination of structural effects such as the molecular weight, size and configuration of pendant groups, etc.

In line with this objective the program will be extended to include a preliminary examination of several representative polyalkylacrylates and polyvinyl esters.

REFERENCES

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(2) Bischoff, I. J., and Desreux, V., Bull. soc. chim. Belges, 61, 10-32 (1952).