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- SECTION I. USE OF INTRINSIC RADIOACTIVE TRACERS FOR PROCESS CONTROL
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- SECTION II. RADIATION-INDUCED GRAFT-POLYMERIZATION STUDIES
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RADIOISOTOPE AND RADIATION APPLICATIONS

Duane N. Sunderman

This is the Tenth Quarterly Progress Report on research programs in radioisotope technology and radiation chemistry under the sponsorship of the Division of Isotopes Development of the United States Atomic Energy Commission. The report period is July 1 to September 30, 1961. During this period research continued in the areas of intrinsic radioactive tracers for industrial process control and the influence of structural factors in radiation-induced graft polymerization.

During the current report period emphasis has been modified on both of these programs. In the study of the application of intrinsic radioactive tracers to process control a new technique for producing the intrinsic tracer is to be evaluated. This technique is the use of an isotope neutron source to perform in-stream activation of the element under study. Initial experiments will be conducted using a 10-curie polonium-beryllium source. Information gained on this program should be applicable to a wide variety of isotope neutron sources as well as the newer machine neutron sources.

The graft-polymerization program is continuing to study the effect of molecular structure on free-radical site formation under irradiation. However, in the current report period increasing effort has been placed upon the relationship of previous data on site production to the extent and nature of grafting.

I. USE OF INTRINSIC RADIOTRACERS FOR PROCESS CONTROL

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SUMMARY

This report describes initial work on a new phase of the general program on intrinsic radiotracers. This phase involves the use of in-process isotope neutron sources to produce short-lived radiotracers. The objectives of this study have been formulated, and an experimental program has been planned. A suitable isotope neutron source has been evolved.

A 10-curie polonium-beryllium neutron source has been obtained for exploratory experiments. The design and construction of a neutron-source storage shield and an activation-cell holder are under way.

INTRODUCTION

Battelle is currently conducting a research program for the Division of Isotopes Development on the use of intrinsic radioactive tracers for process control. Since its inception, the program has passed through several phases. Major areas of emphasis have been:

- (1) The evaluation of a large number of industrial processes as potential radiotracer-control applications
- (2) The study of the applicability of the radiotracer-control concept to chemical engineering unit operations
- (3) The pilot-scale demonstration of the use of intrinsic radiotracers to aid in removing low-percentage metallic impurities from process streams by precipitation-filtration
- (4) The evaluation of potential hazards to consumers from large-scale use of intrinsic radiotracers.

The results of the process evaluation indicate that many promising potential applications of radiotracer control exist in industry, a conclusion which is supported by several industrial research studies.

In laboratory demonstration work, iron-59 was used to follow iron removal from nickel-cobalt solutions, manganese-54 was used to facilitate manganese removal from process water, and cadmium-115m was used to study cadmium removal from zinc sulfate electrolyte. The results of these experiments have demonstrated the technical feasibility of the intrinsic radiotracer-control method.

Although the proof of principle of the intrinsic radiotracer-control concept has been demonstrated, serious impediments exist to its large-scale application. One of the greatest obstacles is management's reluctance to allow residual radioactivity to appear in manufactured products even in insignificant amounts. This reluctance is understandable in view of the present status of public knowledge of radioactivity in general and the large amount of emotionalism attached to the subject.

The intrinsic radiotracer process-control concept is applicable, however, to short-lived intrinsic tracers as well as to the longer lived isotopes used in previous study. Where short-lived tracers were used, product contamination would no longer be a problem, but it would be necessary to produce the isotopes close to their point of use. One means of producing such radiotracers is through use of in-process isotope neutron sources.

It is believed that the flux from currently available isotope neutron sources, even though relatively low, would be useful in radiotracer-control applications with a number of isotopes in a variety of processes. Work is now under way on this new phase of the intrinsic radiotracer-control program. The objective of the present study is to investigate the feasibility of using in-process isotope neutron sources to produce short-lived intrinsic radiotracers useful for stream analysis and process control.

SELECTION OF AN ISOTOPE NEUTRON SOURCE

Since the aim of the present program is to test the feasibility of industrial process applications, it was considered expedient to obtain a neutron source of relatively high intensity for the experimental study. Some of the desirable characteristics of a neutron source for industrial applications are the following:

- (1) Relatively low cost
- (2) Ready availability
- (3) High neutron flux
- (4) Reasonably long half-life
- (5) Low gamma-ray flux.

Table I-1 gives a comparison of properties of several isotope neutron sources. The only two sources considered for this work were polonium-beryllium and americium-beryllium. However, the americium source is not available at present, so the polonium-beryllium was selected.

Because of the relatively short half-life of polonium, two sources will be used for the experimental study. The first source, of about 10 curies, will be used for the initial exploratory experiments. This source has been received from Mound Laboratories. The second source, containing about 30 curies of polonium, will be obtained later for the simulated process studies.

TABLE I-1. A COMPARISON OF ISOTOPE NEUTRON SOURCES

	Po-Be(a)	Pu-Be(a)	Ra-Be(b)	Sb-Be(c)	Am-Be
Half-Life	138.4 days	24,600 yr	1620 yr	61 days	458 yr
Specific Activity, curies per g	4460	0.0625	1	High ^(d)	3.25
Neutron Production Reaction	α, n	α, n	α, n	γ, n	α, n
Neutron Energy ^(e) , Mev					
Maximum	10.8	10.6	(10)	--	(11)
Average	4.5	4	(4)	0.025	(4.5)
Neutron Flux Available ^(e) , n/(sec)(curie)	2.85×10^6	2.2×10^6	$1-1.5 \times 10^7$	$\sim 1 \times 10^7$	(2.6×10^6)
Radiation Dose ^(e) from Neutron Source at 1 M, mr/(hr)(curie)	0.11	(0.15)	825	≥ 1000	(0.11)
Source Size Available, curies	≤ 100	≤ 10	≤ 1	--	$\leq 100 - ?$

(a) Mound Laboratory Catalogue on Polonium and Plutonium Sources.

(b) AECL Catalogue D, Commercial Products Division.

(c) Nucleonics 19, No. 3, p 124.

(d) Depends on neutron-activation flux available.

(e) Values in parentheses are estimates.

CONSTRUCTION OF EXPERIMENTAL EQUIPMENT

Neutron-Source Storage Container

Details of the neutron-source storage tank are shown in Figure I-1. Photographs of the unit appear in Figures I-2 and I-3. Figure I-1 shows the source in its stored position. It is surrounded by 16-1/2 in. of borated paraffin. In this position the activation-cell holder may be safely removed from the storage shield, as shown in Figures I-1 and I-2.

When the activation cell is in position as shown in Figure I-3, the source may be lowered into the cell by moving out the shielding plug to align the source channels.

Neutron Activation Cell and Holder

The holder for the neutron activation cell and shield is shown in the lower part of Figures I-1, I-2, and I-3. Figure I-1 shows the equipment as it will be set up for the preliminary optimization experiments. In this case the neutron shielding around the cell consists of small polyethylene pellets. Polyethylene is used in this instance to facilitate changes in the shielding for different cell geometries. As is evident from Figures I-2 and I-3, the lower cell holder assembly moves in and out under the source storage shield on rails. The activation cell is raised into operating position by means of the jack shown in Figure I-1. The source is then lowered into position in the activation cell to initiate an activation experiment.

EXPERIMENTAL PROGRAM

The experimental program currently envisioned consists of two principal phases. The first or exploratory phase is discussed in detail below while the later simulated process test phase is only touched on briefly.

Exploratory Experiments

During this phase of the experimental program, effort will be concentrated on establishing optimum conditions for in-process tracer activation. Once determined, these conditions will be incorporated in the design of the later simulated process experiments.

In the optimization experiments, a standard solution of a manganese salt will be used to compare the amount of manganese-56 tracer produced using different cell geometries, volumes, etc.

FIGURE I-1. CROSS-SECTIONAL VIEW OF NEUTRON-SOURCE STORAGE SHIELD AND ACTIVATION-CELL HOLDER

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FIGURE I-2. VIEW OF NEUTRON-SOURCE STORAGE SHIELD (TOP) WITH THE ACTIVATION-CELL HOLDER REMOVED

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FIGURE I-3. VIEW OF NEUTRON-SOURCE STORAGE SHIELD (TOP) WITH THE ACTIVATION-CELL HOLDER IN POSITION

Along with the optimization experiments, the neutron flux in the activation cell will be measured as a function of distance, moderator, solution concentration, etc. Gold and/or indium foil activation will be used for these measurements.

The detection system to be used for the optimization experiments is the same gamma scintillation dip counter used in the previous intrinsic-radiotracer studies.

Simulated Process Studies

Several different examples of actual industrial processes are to be studied in this phase of the program. Candidate processes being considered include the following:

- (1) Stripping of silver from waste solutions
- (2) Removing vanadium from petroleum
- (3) Controlling copper precipitation and removal on refining operations.

Two general types of application of the concept of in-process neutron activation will be studied, as follows:

- (1) The use of short-lived radiotracers produced and injected into the process stream just prior to the operation to be controlled
- (2) The use of a neutron source-detector system for radioassay of a small side stream in a manner analogous to automatic vapor-phase chromatography or mass-spectrometry techniques.

Both of these concepts shall be investigated, with major emphasis to be put on the one which appears most promising after preliminary study.

FUTURE WORK

Emphasis next quarter will be on completion of the optimization and flux-measurement experiments. Completion of the cell optimization study will allow work to proceed on the design and construction of the in-process activation cell.

II. RADIATION-INDUCED GRAFT-POLYMERIZATION STUDIES

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SUMMARY

The study of the mechanism of formation of free radicals in polymeric materials and of the potential applications of this information to the development of graft copolymers has been continued. Emphasis has been placed on an examination of the effect of structural factors on the efficiency of free-radical site formation in acrylate and methacrylate polymers. Site measurements versus dose have been made for poly-n-hexylmethacrylate.

Two additional methods for measuring free-radical concentrations, a chemical method employing diphenylpicrylhydrazyl and hydroquinone and a method based on molecular-weight decreases, have been developed and compared with EPR techniques. The grafting studies have been continued, with additional emphasis being placed on this phase of the over-all program.

INTRODUCTION

The objective of this research program is the determination of the influence of structural and configurational factors on the behavior of polymers subjected to gamma irradiation and to correlate the radiation-induced changes which occur with the ability of the polymer to form graft copolymers. It is anticipated that a mechanism of radiation attack on the various polymer systems can be established.

In previous work a number of polyalkylmethacrylates were extensively examined. The data suggested that: (1) free-radical formation is generally accomplished by means of an ester scission, (2) ester scission is accompanied, in most cases, by a scission of the polymer backbone, (3) the size and configuration of the hydrocarbon tail of the ester group and of the group alpha with respect to the ester group influence the efficiency of site formation, and (4) polymer mobility affects the rate of formation and/or decay of free-radical sites.

EXPERIMENTAL WORK

Unless otherwise noted, all polymers are prepared by radiation polymerization at the Battelle Cobalt-60 Gamma Facility. For the measurement of free-radical site concentrations, samples of polymer are reirradiated in vacuo to various total doses. Site concentrations are determined as a function of dose and, occasionally, as a function of

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time, using electron-paramagnetic-resonance (EPR) measurements. Vapor-phase chromatography and mass spectrometry are used to determine quantitatively the volatile fragments of the irradiation. Grafting techniques have been employed to correlate free-radical concentrations and amount of grafted copolymer.

Determination of Volatile Products of Irradiation in Poly-ter-Butylmethacrylate

An investigation of procedures for determining product concentrations from irradiated polymethacrylates was undertaken. Evidence has been obtained that absorption and/or solubilization of the low-molecular-weight fragments make their removal from the polymer difficult. This is particularly true in the case of the ter-butylmethacrylate polymer.

Techniques have now been devised for the quantitative removal of CO, CH₄, CO₂, hydrogen, and the low-molecular-weight hydrocarbons. Some difficulties are still being experienced with the higher molecular weight constituents, particularly the alcohols and esters. Preliminary evaluation indicates that the data obtained earlier will not be greatly affected by the procedural changes because most of the analytical difficulty is with minor constituents.

Free-Radical Formation in Poly-n-hexylmethacrylate

Site concentration has been determined as a function of dose for poly-n-hexylmethacrylate using EPR measurements (Table II-1). The results are in agreement with those which would be predicted from an examination of the sites-versus-dose curves for the C₁ through C₅ unbranched methacrylate polymers. Comparison of the EPR data obtained for the n-hexylmethacrylate polymer with those obtained for the cyclohexyl- and phenylmethacrylate polymers indicates, interestingly, that fewer stable sites exist in the former polymer. This is probably due to increased molecular mobility, which is suggested by the rubberlike nature of the material.

TABLE II-1. SITES VERSUS DOSE FOR
POLY-N-HEXYLMETHACRYLATE

Dose, rads	Sites Per Monomer Unit x 10 ^{3(a)}
2 x 10 ⁵	(b)
5 x 10 ⁵	(b)
1 x 10 ⁶	0.006
3.2 x 10 ⁶	0.054
4.8 x 10 ⁶	0.016
9.6 x 10 ⁶	(b)

(a) These values were determined by EPR measurements.

(b) In these cases, the total number of sites was too small for determination.

Chemical Measurement of Free-Radical Concentration

Several preliminary experiments have been completed in which free-radical concentrations have been determined chemically using the diphenylpicrylhydrazyl-hydroquinone method. For PMMA irradiated to a dose of 6×10^6 rads, EPR measurements indicate a site concentration of approximately 4×10^{-3} per monomer unit. Site-concentration values of 1.5×10^{-3} and 0.5×10^{-3} per monomer unit have been obtained from duplicate chemical measurements on the same material. The comparative measurements will be repeated at several lower doses in order to: (1) establish the sensitivity and reproducibility of the chemical method, and (2) determine if concentrations measured by the two methods are, perhaps, related by some factor which might provide insight into polymer conformation.

Calculation of Free-Radical Concentration From Molecular-Weight Changes

Free-radical concentrations in polymethylmethacrylate, determined as a function of dose by EPR and by changes in number-average molecular weight are compared in Table II-2. It has been assumed in the calculation based on M_N changes that one free-radical site is formed with each chain scission.

TABLE II-2. SITE FORMATION IN PMMA(a)

Dose, rads	Sites Per Monomer Unit $\times 10^3$	
	By EPR	By M_N Decrease(b)
1.7×10^4	--	2.7
5×10^4	--	5.2
1×10^5	--	20.9
1.7×10^5	0.31	--
2×10^5	--	17.5
3.4×10^5	0.49	--
5×10^5	--	24.9
1×10^6	--	21.5
1.4×10^6	1.3	--
5×10^6	--	23.8
6.1×10^6	3.9	--
1×10^7	--	24.2
1.3×10^7	6.0	--
3×10^7	--	43.2

(a) The number-average molecular weight of this polymer was 4900.

(b) These values were calculated assuming the formation of one site per chain scission

Agreement between the two methods is poor at all doses (sites calculated from molecular-weight changes being greater). A graph of the data indicates that the two curves are diverging. This is to be expected since the site concentration calculated from molecular-weight changes should increase regularly with dose whereas that determined by EPR, although increasing with dose, should not increase at the same rate.

he retardation would be due to the increasing effect of molecular mobility on free-radical formation and/or destruction.

Grafting Studies

All grafting experiments completed to date have been carried out at 25 C using polymethylmethacrylate as base polymer and vinyl pyrrolidone as graft monomer. In this work, the water-insoluble fractions of the total copolymers have been collected by precipitation from a solution of the excess monomer and washed with methanol. Residual monomer has been removed from each copolymer by extraction with water for 24 hr in a Soxhlet. Following extraction, the material has been dried in vacuo at 70 C.

Using the revised grafting procedures described above, approximately 25 copolymers have been prepared for the purpose of establishing: (1) the correlation between concentration of grafted polymer and total free-radical sites, and (2) the effect on total grafting of contact time of the polymer and graft monomer. Nitrogen concentrations and number-average molecular weights are being used to characterize the copolymers.

Table II-3 lists the results obtained to date. Because the results are incomplete, no attempt will be made to completely analyze the data at this stage. However, it is apparent that copolymer being recovered by present techniques is quite low in vinyl pyrrolidone. Apparently, the presence of quite small amounts (~5 per cent) of copolymerized vinyl pyrrolidone results in a water-soluble polymer. Moreover, the relatively high nitrogen contents of the blanks indicate that some monomer is apparently being absorbed by the polymer or is being grafted. This would also account for the decreased molecular weights of the blanks. It appears that the water-soluble residue will have to be recovered and fractionated to remove the homopolymer of vinyl pyrrolidone before meaningful results can be obtained. Some work is now being initiated in this area.

Polymer Preparation

Several additional polymers have been prepared by irradiation methods during the present period. These include, in addition to the n-hexylmethacrylate polymer described above, polyethyldimethyl-aminomethacrylate, polymethyl- α -cyanoacrylate, and polyacrylonitrile. Work has also been initiated on the preparation of α -bromo-, α -iodo-, and α -phenylmethacrylate polymers. These materials will be used in continuation of the study designed to correlate radiation susceptibility and polymer structure.

CONCLUSIONS

Several conclusions can be justified on the basis of the work reported here:

- (1) The efficiency of site formation is lower for poly-n-hexylmethacrylate than for the cyclohexyl- and phenylmethacrylate polymers.

TABLE II-3. GRAFT-POLYMERIZATION STUDIES ON PMMA^(a) AND VINYL PYRROLIDONE^(b)

Run	Weight of Base Polymer, g	Total Dose, rads x 10 ⁻⁷	Sites Per Monomer Unit x 10 ^{3(c)}	Graft-Polymerization Time ^(d) , hr	M _N	Nitrogen ^(e) , w/o
G-33	1.09	--	--	3	2745	0.18
G-32	1.31	0.60	3.5	3	2716	0.42
G-35	1.08	--	--	6	2536	0.15
G-34	1.13	0.60	3.5	6	--(f)	0.22
G-22	2.40	--	--	24	--(f)	--(f)
G-23	1.35	0.03	0.5	24	1315	0.40
G-4	2.88	0.11	1.2	24	1692	--(f)
G-26	1.46	0.60	3.5	24	2560	0.46
G-37	1.19	--	--	32	--(f)	0.30
G-36	1.15	0.60	3.5	32	--(f)	0.33
G-39	1.15	--	--	96	2490	0.68
G-38	1.15	0.60	3.5	96	--(f)	0.42
G-30	1.80	3.60	8.0	96	1970	0.28
G-40	1.15	0.60	3.5	144	--(f)	0.38

(a) The number-average molecular weight of this polymer was 4125.

(b) In all cases, grafting was carried out at 25 C using 100 cm³ of vinyl pyrrolidone.

(c) These values were determined by EPR measurements.

(d) These values represent the contact time between monomer and "active" polymer.

(e) These values for nitrogen are for the water-insoluble copolymer. Multiplication of these data by 7.93 gives percentage vinyl pyrrolidone in copolymer.

(f) These measurements are incomplete.

- (2) At relatively high doses (10^6 to 10^7 rads) free-radical concentrations determined chemically using the DPPH-hydroquinone method agree reasonably well with those measured by EPR.
- (3) Free-radical concentrations calculated from molecular-weight decrease are considerably higher than those determined by EPR. The agreement is probably best at very low doses.
- (4) It is probable that grafting procedures will have to be revised in order to obtain meaningful results. Recovery and fractionation of the water-soluble residues appears necessary.

FUTURE WORK

The anticipated program for the October 1 through December 31, 1961, period includes:

- (1) Continuation of the examination of polymer structure and its relationship to radiation susceptibility, with work directed primarily toward a continued examination of the acrylate polymers and, in addition, determination of the role of steric and inductive effects produced by various groups attached at the α -carbon position
- (2) Modification of the grafting procedures and expansion of the studies to include the examination of variables such as grafting temperature, type and concentration of graft monomer, type of base polymer, etc.
- (3) Determination of the effect of the temperature of irradiation and the dose rate on the types and concentrations of free-radical sites formed
- (4) Further evaluation of the DPPH-hydroquinone method and the method based on M_N changes for the determination of free-radical concentrations
- (5) Completion of the paper entitled "Radiolysis of Polymethacrylic Acid and Its Alkyl Esters" and publication of this paper and one entitled "Radiolysis of the Isomeric Polybutylmethacrylates".