Contract No. W-7405-eng-92

QUARTERLY PROGRESS REPORT
to
UNITED STATES ATOMIC ENERGY COMMISSION
OFFICE OF ISOTOPES DEVELOPMENT
on
RADIOISOTOPE AND RADIATION APPLICATIONS

January 18, 1961

Edited by Duane N. Sunderman

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

~~NOTICE~~

~~The information in this document is of a preliminary nature and is subject to revision and correction. It is not to be given dissemination without patent clearance by the Chicago Patent Group.~~

This document is
PUBLICLY RELEASABLE
H. Kinser
Authorizing Official
Date: 2/11/10

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

DISCLAIMER

TABLE OF CONTENTS

Page

I. USE OF INTRINSIC RADIOACTIVE TRACERS FOR PROCESS CONTROL

II. RADIATION-INDUCED GRAFT-POLYMERIZATION STUDIES

RADIOISOTOPE AND RADIATION APPLICATIONS

Duane N. Sunderman

This is the Seventh 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 October 1 to December 31, 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.

Two aspects of the use of intrinsic radioactive tracers for process control are reported here. The first is the experimental evaluation of intrinsic-tracer control of the removal by precipitation of manganese from process water. Manganese-54 is the intrinsic tracer, and removal is effected by coprecipitation with iron hydroxide. The second aspect under study is the potential radiation hazard to the consumer resulting from large-scale industrial applications of the intrinsic-tracer technique. The hazards of ingestion and external exposure are evaluated in terms of existing background radiation levels and recommended limits for nonoccupational exposure.

Fundamental knowledge of the process of radiation-induced graft polymerization is in its infancy. The possibility of modifying the physical and chemical properties of polymer materials in this manner has attracted wide interest in industrial circles but much must be learned about the kinetics and mechanisms of the process before its full impact can be realized. To this end the effect of molecular structure upon radiation-induced graft polymerization is receiving extensive theoretical and experimental study in this program. Results are presented for experimental determinations of the effect of dose and dose rate upon free-radical formation in compounds of the methylacrylate series. Ester side-chain attack is indicated by a complete analysis of volatile reaction products.

I. USE OF INTRINSIC RADIOACTIVE TRACERS FOR PROCESS CONTROL

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

SUMMARY

This report contains the initial results of two studies. One is an evaluation of the possible hazards to consumers from radioisotope residues in consumer products. The other is the laboratory demonstration of the use of manganese-54 to facilitate removal of manganese from process feed water.

It was found in the hazards evaluation that the "worst case" of radiation exposure from residual radioisotopes in steel gives a radiation exposure somewhat less than the maximum allowable dose levels for occupational exposure. Initial study indicates that for actual cases, the radiation exposures to be expected from radioisotope residues in steel products would ordinarily be small compared to natural background. An exception to this generalization might be found when a longer lived isotope like manganese-54 was present.

Preliminary results of the laboratory demonstration of using manganese-54 to monitor the removal of manganese from feed water indicate that the method may allow a considerable improvement in accuracy of process control.

INTRODUCTION

The broad objectives of this program are to delineate more clearly promising intrinsic-radiotracer control applications and to demonstrate the proof of principle of this process-control concept on a laboratory scale. Both of these over-all objectives are aimed at acquainting industrial process industries with the potential advantage of using intrinsic radiotracers as process-control tools.

The work discussed in this report deals with an evaluation of possible hazards to consumers from use of intrinsic radiotracers in processing as well as with the continuing laboratory proof-of-principle program.

EXPERIMENTAL WORK

Evaluation of Potential Hazards in Large-Scale Use of Intrinsic Tracers

One of the most serious factors retarding the application of intrinsic radiotracers to industrial process control is the fear of radiation hazards involved in such uses of radioisotopes. It is the purpose of this evaluation to delineate more precisely where radiation hazards may exist and to place these hazards in a realistic perspective.

The initial emphasis has been to define criteria to be used in the evaluation and to give some representative examples of the external biological hazard resulting from the incorporation of radioisotopes in consumer products. Steel has been chosen as the representative product for the study because of its widespread consumer use.

Hazards-Evaluation Criteria

The principal criteria used in this study for comparison of radiation doses are:

(1) AEC maximum permissible dose levels for occupational exposure

(2) The same for nonoccupational exposure

(3) Average exposure levels from natural radiation plus general man-made radiation.

The first of these criteria is the maximum dose level set for persons working in radiation areas. This maximum dose level is 5 rems per year of whole-body radiation.(1)

The second criterion applies to persons outside areas covered by the first case. The maximum permissible dose for these people is 0.5 rem per year of whole body radiation.

The third criterion applies to the population as a whole and represents the average minimum radiation exposure which everyone receives. This exposure is broken down in Table I-1 into its various components, and is assumed to be 0.2 rem per year. The maximum permissible dose levels given for the two previous criteria are meant to be in addition to the dose for normal background, the third criterion.

---

(1) References at end of section.

TABLE I-1. AVERAGE DOSE OF RADIATION TO GONADS FROM ENVIRONMENTAL SOURCES(2)(3)

Radiation Source	Gonad Dose, rad per year
Natural Background	
External radiation	
Cosmic rays	0.028
Local γ rays	0.047
Radon in air	0.001
Internal radiation	
Potassium-40	0.019
Carbon-14	0.001
Radon and disintegration products	0.002
Man-Made Contributions	
Medical radiology	0.100
Shoe-fitting fluoroscopes	0.001
Luminous watch and clock dials	0.001
Occupational exposure	0.002
Television sets	0.001
Fall-out from weapons tests	0.001
Total	0.204

Estimation of Biological Radiation Hazards Using Simple Models

General Considerations

As a basis for evaluation, a "worst-case" approach where the maximum conceivable radiation dose would be received by an individual using some product containing residual radiotracers was taken. The quantities of radioisotopes present initially in each case were assumed to be the maximum allowable limits for license-exempt use. (4)

Simple models were used for the estimation of dose levels since it is felt they give a fair approximation to many general cases of interest. The first model is a hollow shell of uniformly generating material. This model approximates the case of a steel truck cab or a steel automobile. According to Primak(5), the general expression for the flux in the center of such a spherical shell, assuming no self-absorption, is:

$$\theta = \frac{S}{2}\left[T + \frac{1 - X^2}{2\,X^2} R_2 \ln \frac{1 + X_2}{1 - X_2} - \frac{1 - X_1{}^2}{2\,X_1} R_1 \ln \frac{1 + X_1}{1 - X_1} \right],$$

where

S = generation, ev per cm^3

R = radius of circular section, cm

Inner wall = R_1

Outer wall = R_2

r = radial distance from center of circular shell, cm

X = ratio r/R

$T = R_2 - R_1$, thickness of the shell, cm.

For the case of the central flux, which is a minimum, the expression reduces to:

$$\phi_c = \frac{ST}{2} \ .$$

For the more general case of the average flux in the hollow sphere, one obtains:

$$\phi_a \cong \frac{3\ ST}{2\ y^2} \ ,$$

where

$$y = R_1/R_2 \ .$$

The last expression is used for this calculation.

The second model is that of a generating hollow cylindrical shell of infinite length. This model is used to approximate the case of a large truck trailer or steel railway car. From Primak(5), the central flux is in this case $\phi_c = 1/2\Pi\ ST$; and when the cylinder is closed with a disk of thickness 2 T, the flux at the end $\cong$ 1.8 ST. The latter expression is used in this calculation.

The limiting maximum dose can be imagined to be delivered in a hollow steel sphere with infinitely thick walls containing the maximum allowable concentration of radioisotopes. In this case, the average flux(5)(6) would be:

$$\phi \cong \frac{3}{2}\frac{S}{\mu} \ ,$$

where

S = flux generation, cm^{-3}

μ = linear absorption coefficient.

For steel, this equation reduces to:

$$\phi \cong 3\ S \ .$$

After one obtains an estimate of the gamma flux for a particular case, the dose may be calculated using the conversion factors of Goldstein.(7)

Experimental Study of Manganese Removal From Process Water

The results of the study using iron-59 to facilitate removal of iron from a nickel-refinery stream have appeared in previous quarterly reports and are summarized in a topical report in preparation. The emphasis in the experimental phase of the program has now been shifted to other precipitation-purification systems.

One of the most commonly used methods of removing trace impurities from solution is to carry them on a precipitate of another material. The carrier may be present in solution originally or added just prior to the precipitation step. This type of purification step has been chosen for demonstration purposes, the specific application being the removal of manganese from process water by coprecipitation with iron.

The reasons for this particular choice for the proof-of-principle demonstration are the following:

(1) The demonstration illustrates the use of radiotracers to facilitate removal of a critical impurity present in very low concentration

(2) The process demonstrated has wide application in industry and is technically similar to many other purifications

(3) The demonstration required only minor modification of the previously used process-model system

(4) Manganese-54 tracer was immediately available at Battelle.

The allowable concentrations of iron and manganese for several industrial processes are given in Table I-2. It is clear from the table that, although manganese is not ordinarily present initially in concentrations greater than 5 ppm, it must still in many cases be removed from feed water.

TABLE I-2. QUALITY TOLERANCES FOR INDUSTRIAL WATERS(8)

Industry or Use	Total Concentration of Constituents, ppm Iron	 Manganese
Brewing	0.1	0.1
Food, general	0.2	0.2
Ice	0.2	0.2
Plastics, clear	0.02	0.02
Kraft pulp	0.2	0.1
Sulfite pump	0.1	0.05
Rayon (viscose), pulp production	0.05	0.03
Tanning	0.2	0.2
Textile dyeing	0.25	0.25

The results of the preliminary experiments indicate that the concentration of manganese can be monitored even at very low levels through the use of manganese-54 as an intrinsic radiotracer. There is a real problem in providing accurate chemical analysis of the manganese content at these low levels to provide a basis of comparison. However, an accurate comparison can be made for concentrations down to 0.5 ppm, and these results can then be extrapolated to lower levels if necessary.

RESULTS AND DISCUSSION

Maximum Exposure Doses

The cumulative doses from several residual radioisotopes which might be used as intrinsic tracers are given in Table I-3. The doses are estimated using the following assumptions:

(1) The geometry in one case is that of a hollow sphere with radioactivity uniformly distributed in a 2-mm-thick steel shell to approximate a steel truck cab. In the other case the geometry is that of an infinitely long cylindrical shell 3 mm in thickness, closed at one end with a 6-mm steel cap to approximate a steel railway car.

(2) Continuous exposure is assumed.

(3) Self-absorption and shielding are disregarded. For comparison purposes, the three dose criteria discussed above are also shown in the table.

The limiting case of an enclosure surrounded by "infinitely thick" walls is not shown in the table. The cumulative doses in this case are about ten times those for the 2-mm-thick shell shown in the table. The thin shell would be expected to approximate a much larger number of cases than does the thick shell.

It is obvious that the dose rate will fall off with time due to decay of the particular isotope involved. This effect is shown more clearly in Figure I-1, where the cumulative doses from various isotopes for the spherical-shell geometry are compared with the dose from ordinary background and the maximum permissible dose allowed for nonoccupational exposure.

Factors Tending to Reduce Hazards to Consumers

It has been shown that the limiting radiation dose from residual radioisotopes in steel in the worst case is no higher than that allowed for occupational radiation exposure. Nevertheless, this is an undesirably high exposure for the average consumer. Many factors tend to reduce the likely radiation exposure to a level far below the maximum dose which is shown in Table I-3. Some of the more significant of these factors are discussed below.

TABLE I-3. ESTIMATED CUMULATIVE RADIATION DOSES FOR CONTINUOUS EXPOSURE TO RADIOISOTOPE RESIDUES IN STEEL

Geometry	Isotope	Maximum Allowable Concentration, μc per g	Initial Gamma Dose, 10^{-4} rem per hr	Cumulative Dose, rem				3-Year Cumulative Dose From Natural Background, rem	3-Year Maximum Permanent Nonoccupational Dose, rem	3-Year Maximum Permanent Occupational Dose, rem
				2 Month	6 Months	1 Year	3 Years			
Hollow sphere, 2-mm-thick steel (truck cab)	Mn^{54}	10^{-3}	1.35	0.184	0.478	0.796	1.273	0.60	1.5	15
	Co^{58}	9×10^{-4}	1.39	0.155	0.288	0.338	0.348			
	Fe^{59}	5×10^{-4}	0.92	0.087	0.138	0.146	0.147			
	Cr^{51}	2×10^{-2}	0.95	0.069	0.086	0.087	0.087			
Inside end of infinite cylindrical shell, 3-mm-thick steel with 6-mm-thick cap (railway car)	Mn^{54}	10^{-3}	2.43	0.328	0.863	1.430	2.190	0.60	1.5	15
	Co^{58}	9×10^{-4}	2.49	0.278	0.516	0.605	0.623			
	Fe^{59}	5×10^{-4}	1.63	0.157	0.243	0.260	0.261			
	Cr^{51}	2×10^{-2}	1.71	0.123	0.155	0.156	0.156			

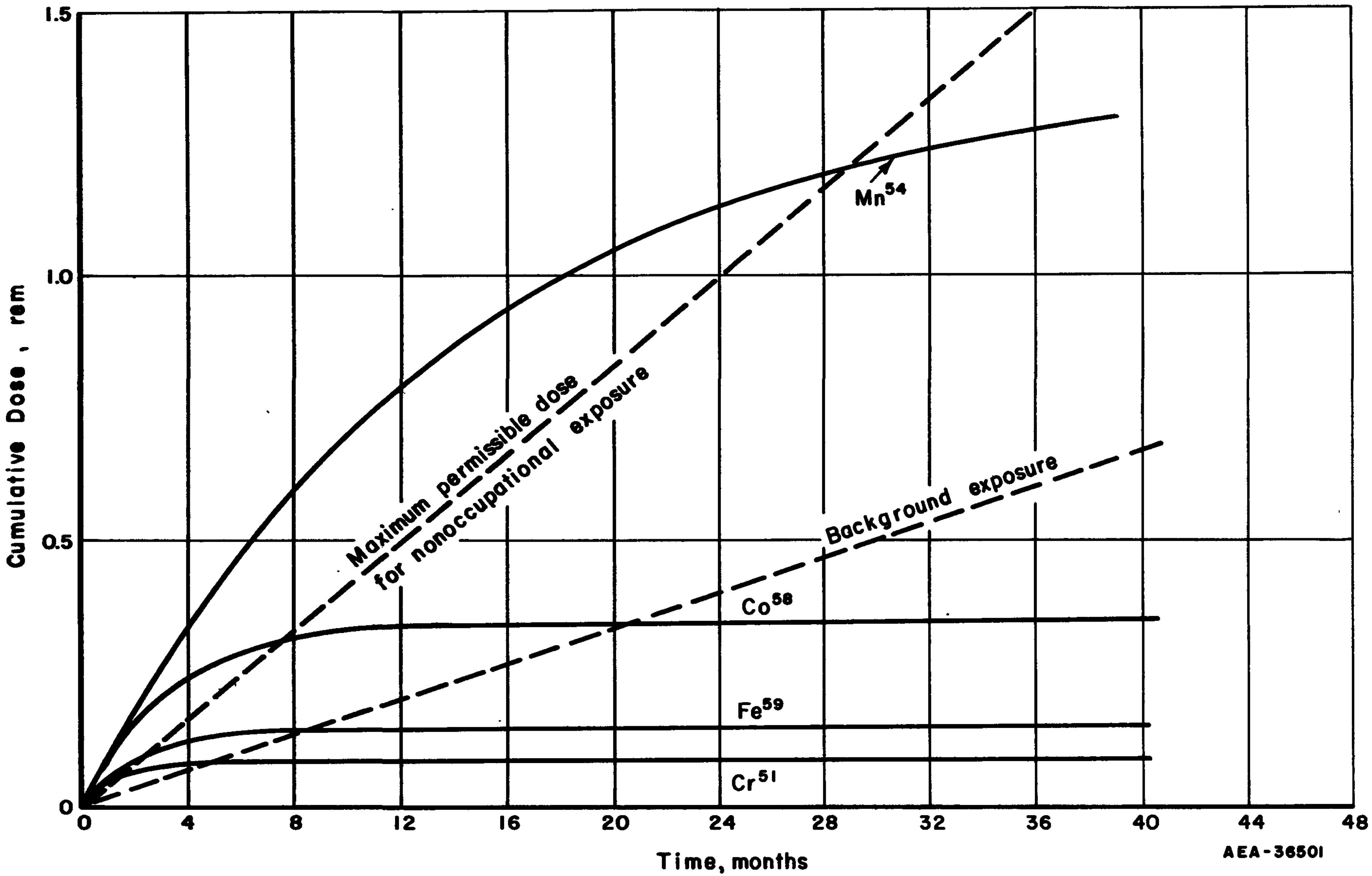


FIGURE I-1. CUMULATIVE DOSE AS A FUNCTION OF TIME FROM SEVERAL RADIOISOTOPE RESIDUES ORIGINALLY PRESENT IN MAXIMUM PERMISSIBLE CONCENTRATION, ASSUMING SPHERICAL-SHELL GEOMETRY

Effects of Shielding and Exposure Time

The dose estimates in Table I-3 are calculated on the basis of negligible shielding and continuous exposure. In many actual cases, significant shielding material might normally be present to reduce the dose received by an individual. Exposures would ordinarily not be continuous and this would also reduce the dose received. It is obvious, for example, that reducing the exposure time from continuous to 40 hr per week would reduce the estimated dose some 75 per cent.

Effect of Radioisotope Decay

The radiation-dose estimates in Table I-3 have assumed that the various radioisotopes were present in the maximum permissible levels at the beginning of the exposure period. This could not be true for most consumer products, since there would be some delay in manufacturing, transportation, sales, etc. If one assumes a nominal delay of 3 months between the time the raw steel is produced and the time the consumer starts using the product, it is obvious from Figure I-1 that the consumer would receive negligible radiation from chromium-51, and only small amounts from iron-59 and cobalt-58. Only the radiation from the longer-lived manganese-54 would give a significant dose.

Effect of Concentration of Isotope Residues

The radiation dose levels under discussion are based on maximum allowable concentrations of isotopes being present in the consumer products. These levels of residual radioactivity are undoubtedly higher than would ordinarily be expected. An accurate estimate of the actual level depends on a knowledge of the particular intrinsic-radiotracer applications used in producing the product, in this case steel.

The only such application studied in detail at Battelle is the use of iron-59 to facilitate removal of iron from a nickel-refinery stream. In this particular case, it was estimated that the residual concentrations of radiotracer in the cobalt product would be no higher than $\sim 10^{-5}$ μc per g, which is 1/50 of the maximum allowable concentration. Although this case is not general, it serves to illustrate the fact that a realistic appraisal of the hazards from residual radiotracers can only be made if sufficiently detailed information is available. In the case mentioned here, it is obvious that the radiation dose delivered by the radiotracer residue is negligible compared with that from ordinary background radiation.

FUTURE WORK

Work on both the hazards-evaluation and experimental-demonstration phases of the program will be continued next quarter. The initial goal of the hazards study will be to complete the evaluation of external biological radiation hazards for uses of steel other than those covered. Following this work, emphasis will be shifted toward the evaluation of any internal biological hazards resulting from ingesting steel corrosion products containing radiotracer residues. The effect of radiation from radiotracer residues in steel on sensitive industrial products also will be studied to determine the seriousness of these nonbiological radiation hazards.

Work on the proof-of-principle demonstration of manganese removal from process water is expected to be completed next quarter, and the study of another precipitation-purification process will be initiated.

REFERENCES

(1) *Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water For Occupational Exposure*, National Bureau of Standards Handbook 69, U. S. Department of Commerce (June 5, 1959).

(2) "Report to the General Assembly", Official Records, U. N. Scientific Committee on Effects of Atomic Radiation, 13th Session, Supplement 17 (A/3838), (1958).

(3) *The Hazards to Man of Nuclear and Allied Radiation*, Medical Research Council (British), (1956).

(4) *Federal Registry*, Title 10 – "Atomic Energy", part 30 – "Licensing of Byproduct Material".

(5) Primak, W., "Gamma-Ray Dosage in Inhomogeneous Nuclear Reactors", J. App. Phys., *27*, 54-62 (1956).

(6) Price, B. T., Horton, C. C., and Spinney, K. T., *Radiation Shielding*, Pergamon Press, New York (1957).

(7) Goldstein, H., "The Attenuation of Gamma Rays and Neutrons in Reactor Shields", Superintendent of Documents, Government Printing Office, Washington 25, D. C. (May, 1957).

(8) "Progress Report, Committee on Quality Tolerances of Water for Industrial Uses", J. New Engl. Water Works Assoc., *54*, 271 (1940).

II. RADIATION-INDUCED GRAFT-POLYMERIZATION STUDIES

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 polymeric materials was continued. Emphasis has been placed on an examination of the effect of structural factors on the efficiency of free-radical site formation in acrylate polymers. The investigation has been extended to include an examination of the influence on free-radical formation of the constituents on the carbon atom located alpha to the ester group. Polymethylacrylate, polymethylmethacrylate, and polymethyl-α-chloroacrylate were used in this study. Measurement of the volatile products from the irradiation of polymethyl-α-chloroacrylate by means of mass spectrometry and vapor-phase chromatography has been completed. The data substantiate earlier findings which indicated that the point of attack in free-radical formation occurs on the ester side chain. A paper describing this work was presented at the December Meeting of the American Nuclear Society.

INTRODUCTION

The objective of this research program is the determination of structural and configurational factors in polymers which influence (1) the formation and stability of free-radical sites, and (2) the mechanisms and products of graft-copolymerization reactions.

During the present quarter the investigation of the relationship of site formation and dose in a number of acrylate polymers has been continued. The study of the effect of structural factors has been extended to include an examination of the influence on free-radical formation of the constituents on the carbon atom located alpha to the ester group.

EXPERIMENTAL WORK

All polymers were prepared by radiation polymerization at the Battelle Cobalt-60 Gamma Facility. For the measurement of free-radical sites, samples of polymers were sealed in tubes under vacuum and irradiated to various dosages. Free-radical concentrations were determined with a Varian EPR spectrometer.

Effect of Molecular Weight on Free-Radical Formation

Earlier evidence(1) indicated that the efficiency of site formation in polymethylmethacrylate (PMMA) decreases with increasing molecular weight in the high (2 to 4×10^5) molecular-weight range. Further, these high-molecular-weight polymers gave EPR spectra having much better resolution than had been obtained with PMMA of low ($<2 \times 10^4$) molecular weight. Based on earlier work(2) these results suggested the possibility that monomer had not been removed completely from the polymers.

To determine if monomer doping actually occurred, several additional samples of these polymers were placed in tubes and sealed under vacuum following a 15 to 30-min preheat at 100 C. The sealed samples were then irradiated and subjected to EPR measurements. Data from these later experiments suggest that the observed molecular-weight effect may have been caused by monomer doping. The EPR spectral resolution, however, appears to be a true function of molecular weight. Additional work is planned in this area.

Free-Radical Determination for the Poly-n-Alkylmethacrylates

Earlier in the program(1, 2), curves of total free-radical sites versus dose were obtained for the methyl-, ethyl-, n-propyl-, isopropyl-, n-butyl-, sec-butyl-, isobutyl-, and n-amylmethacrylate polymers. It had been observed, without exception, that the free-radical site concentration began to decrease quite rapidly at the higher doses. During the quarter, these data were extended to include a total dose of approximately 1.4×10^8 rads.

At this dosage, the n-butyl and n-amyl polymers degraded to waxlike materials, and, consequently, EPR measurements could not be used to determine total site concentrations. Moreover, nearly all of the other polymers contained fewer total measurable sites than had been observed at very low doses (5×10^5 rads) using the same dose rate.

Free-Radical Determination for Polymethylacrylate

Samples of polymethylacrylate (PMA) were irradiated to doses in the range 3×10^5 to 1.4×10^8 rads. No evidence of site formation was obtained by EPR measurements below approximately 10^7 rads. At higher doses, the data indicate that considerable numbers of sites have been formed. However, the results further show that an unidentified reaction takes place within the irradiated polymer, resulting in a diminution of the total number of sites with time.

---

(1) References at end of section.

A comparison of the behaviors with increasing dose of PMMA and PMA with respect to (1) total site formation and (2) molecular-weight changes indicates that polymer mobility is of considerable importance in the production of long-lived free radicals. Irradiation of PMMA results in the formation of measurable numbers of sites even at very low doses (~10^5 rads). In addition, a decrease in molecular weight occurs as the dose is increased, and, consequently, polymer mobility increases. The decrease in total number of sites at doses in excess of some critical value can be explained in terms of this increased mobility. At this point, the production of free radicals can no longer compete with the destruction of sites by the combination scavenger effects of the low-molecular-weight by-products of the reaction and the more mobile polymer itself.

On the other hand, in the irradiation of PMA, doses of the order of 10^7 rads are required to produce measurable numbers of free radicals. The cross-linking nature of this material results in a continuous increase in molecular weight with dose. Thus, the polymer becomes more and more rigid. At some intermediate rigidity, the polymer still has sufficient mobility to destroy sites but much more slowly. This behavior probably accounts for the gradual decay noted above. Finally, a network is built up in which polymer mobility has been reduced to the point where relatively stable free radicals are produced by further irradiation.

To test this hypothesis, samples of PMA will be irradiated to doses of the order of 10^8 rads. Following the determination of the total number of sites, these materials will be heated to destroy the sites and reirradiated to lower total doses. An immediate buildup of sites would lend support to the hypothesis. An alternative approach would be the use of low total doses at reduced temperatures.

Determination of Products in Irradiated Polymethyl-α-Chloroacrylate by Vapor-Phase Chromatography

Five-gram samples of polymethyl-α-chloroacrylate (PMCA) were sealed under vacuum in reaction tubes of the type described earlier(2) and irradiated to 3.1×10^7 rads. The volatile products from the irradiation were quantitatively measured by means of mass spectrometry and vapor-phase chromatography. No hydrogen chloride or chlorine was found. All compounds detected were identified and are listed in Table II-1.

TABLE II-1. COMPOUNDS FORMED DURING IRRADIATION OF POLYMETHYL-α-CHLOROACRYLATE

Compound	Relative Concentration, microliters
Carbon monoxide	900
Carbon dioxide	3100
Hydrogen	350
Methane	200
Methanol	5
Methyl chloride	3000
Methyl formate	0.1
Methyl acetate	<0.1

Analysis of the data in Table II-1 indicates, in agreement with earlier findings, that free-radical formation takes place by ester-chain scission. Either CO_2 or CO is eliminated. If CO_2 is formed, the free methyl radical reacts with either a chlorine or hydrogen atom from the polymer chain to form methyl chloride or methane. Methyl chloride appears to be formed about 90 per cent of the time. If CO is formed, the results suggest that the methoxy radical recombines with the chain free radical with no apparent net gain in free-radical concentration. This recombination was also noted in the work with the polybutylmethacrylates.

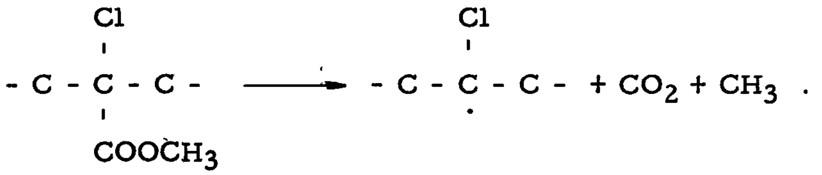
CONCLUSIONS

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

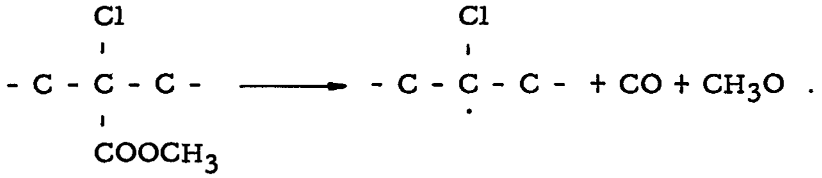
(1) Free-radical formation in acrylate polymers is influenced appreciably by the constituents on the carbon atom located alpha with respect to the ester group.

(2) A comparison of the behavior with increasing dosage of PMMA and PMA indicates that polymer mobility is of considerable importance in the production of long-lived free radicals.

(3) An analysis of the volatile products from the irradiation of PMCA indicates that ester scission takes place in one of two ways:



$$-C-\underset{COOCH_3}{\overset{Cl}{C}}-C- \longrightarrow -C-\underset{\cdot}{\overset{Cl}{C}}-C- + CO_2 + CH_3 \ .$$



$$-C-\underset{COOCH_3}{\overset{Cl}{C}}-C- \longrightarrow -C-\underset{\cdot}{\overset{Cl}{C}}-C- + CO + CH_3O \ .$$

In the case of the first reaction, the methyl radical combines with either a chlorine or hydrogen atom of the chain to form methyl chlorine or methane. The methoxy radical, formed when CO is eliminated, recombines with the chain free radical.

FUTURE WORK

During the coming quarter the investigation of the mechanism of formation and decay of radicals in irradiated polymers will be continued. The anticipated program will include work in the following areas:

(1) The study of free-radical formation in PMA will be continued. The effect of polymer mobility on site formation will be examined using the approaches suggested above.

(2) The effect of molecular weight on site formation will be established using PMMA.

(3) The sites-versus-dose curves for the series of alkyl methacrylate polymers will be extended to include measurement at a dose of the order of 3×10^8 rads.

(4) Mass spectrometry and gas chromatography will be employed to identify and measure quantitatively the fragments formed during the irradiation of PMA, PMMA, polycyclohexylmethacrylate and polyphenylmethacrylate.

(5) If possible, the tertiary-butylmethacrylate polymer will be prepared and subjected to the same treatment given the other isomeric butyl polymers. To date, considerable difficulty has been encountered in attempting to prepare this polymer. It apparently is quite easily hydrolyzed to the acid.

(6) The iodine tracer studies will be continued. It is anticipated that identification of the fragments associated with free-radical formation can be more readily determined in this way. Background studies in this area are being conducted at the present time.

(7) A preliminary examination of several other polymer types, including the polyvinyl esters, ethers, and ketones, will be initiated.

REFERENCES

(1) "[Sixth] Quarterly Progress Report on Radioisotopes and Radiation Applications" to the Office of Isotopes Development from Battelle Memorial Institute (October 31, 1960).

(2) "[Fourth] Quarterly Progress Report on Radioisotopes and Radiation Applications" to the Office of Isotopes Development from Battelle Memorial Institute.