MASTER

RADIATION-INDUCED EFFECTS IN POLYMERS

AND RELATED COMPOUNDS

FINAL REPORT

Contract DE-AS05-76ERO-2845

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The report is divided into two sections. The first section covers progress during the final contract period April 1, 1978 - October 31, 1979; it covers work performed in conjunction with the objectives of the contract some of which was recently completed. The second section is a general summary of the contract activities and accomplishments over the 19 year period covered by AEC-ERDA-DOE support.

Summary of Accomplishments Since April 1, 1979

1. Publications. Three were published and four more have been submitted for publication.
2. ESR measurements on alkyl single crystals. Successful modifications of our spectrometer were made to permit high precision ESR measurements. The results yielded one experimental paper and one theoretical paper based on the measurements. Both have been submitted for publication to Radiation Physics and Chemistry.
3. Polymer composites. Work on this subject was completed and a paper was published in Polymer Letters.
4. Styrene-polyethylene grafts. Work on the acid catalysis of the grafting of PE from styrene-MeOH solutions was completed. A paper was published in Radiation Physics and Chemistry.
5. Rheometry. Experiments were performed on the use of torque rheometry as a means of measuring the effects of ionizing radiation on polymers. A paper was published in Modern Plastics.
6. Melting and crystallization behavior of irradiated polymers. Extended studies, still in progress, are being performed on the effect of irradiation on the thermal and morphological properties of polymers.

One paper on polyethylene, polypropylene, poly(ethylene oxide) and polychlorotrifluoroethylene is complete and has been submitted to the Journal of Polymer Science. Another on crosslinking kinetics of polyethylene is in preparation. Another on a unique pulse radiolysis technique for measurements of a crystalline transformation in poly-(1-butene) has been completed; it has been submitted to Journal of Polymer Science.

7. Pulse Radiolysis. The electron linear accelerator is now in routine operation. Equipment for pulse radiolysis and data processing has been assembled. In addition to the work on poly(1-butene) cited above, preliminary results have been obtained on radical decay in irradiated polyethylene.

I. PROGRESS SINCE APRIL 1, 1979

A. ESR Measurements on Irradiated Eicosane

The principal objective of this work was to find the mechanisms whereby alkyl radicals produced in alkane crystals migrate and disappear. This is strongly related to a basic goal of our research, namely, the mechanism whereby crosslinking occurs and the investigation of methods which could enhance the radiation yield of crosslinks. A principal problem was the development or acquisition of ESR equipment capable of measurements at low power absorption levels because power saturation occurs below 100 μ W. The application of a technique suggested by Dr. Y. Ito proved to be an effective means of modifying our Varian V4502 spectrometer. It was implemented by Walter J. Chappas in radical decay studies on irradiated single crystals of n-eicosane ($n\text{-C}_{20}\text{H}_{42}$). The research yielded three major results: 1. A paper on radical fracture

patterns and migration mechanisms; 2. a theoretical paper on the radiation chemistry of crystalline alkanes; and 3. a substantial portion of the Chappas Ph.D. dissertation. The section of this report labeled Appendix A has been submitted for publication to Radiation Physics and Chemistry. It shows empirically that the so called "fracture pattern" of alkanes is not a random process. The interior secondary alkyl radical ($-\text{CH}_2\dot{\text{C}}\text{HCH}_2-$) appears to be the only one formed in the early stages; we are unable to detect the penultimate ($-\dot{\text{C}}\text{HCH}_3$) or terminal radical ($-\text{CH}_2\dot{\text{C}}\text{H}_2$). The conditions for radical formation and migration to other radical sites are presented; this information resolves conflict in data published by other laboratories. Another important contribution in this paper is the evidence that intramolecular migration of the radical site is more rapid than intramolecular hopping. The second paper (Appendix B) is more significant and more controversial. In our mechanism methane is distinct from all other alkanes. In the case of methane there is ionization, rapid neutralization, and hot hydrogen formation. For other crystalline alkanes, neutralization following the ionization step is slower than ionic mechanisms of H atom abstraction and H_2 expulsion as originally proposed by Joseph Weiss. The unique qualities of methane are based on the exceptionally high recombination time of cation radicals and geminate electrons in methane. As for the fracture patterns reported in Appendix A, we explain them in terms of rapid hole migration to the methylene groups in the interior of the crystalline alkane molecules; this is followed by the ionic reactions of the Weiss mechanism. For polyethylene single crystals hole migration to the chain folds appears to be the favored mechanism. Details can be found in Appendix B. The paper has been submitted to Radiation Physics and Chemistry.

B. Polymer Composites

A reprint of our paper, "The Effects of Trace Fillers on the Radiation-Induced Crosslinking of Polyethylene", (W. J. Chappas and J. Silverman, J. Poly. Sci., Polymer Letters Ed., 17, 5-14 (1979)) is attached as Appendix C describing much of the work performed in this study. Despite careful and intensive work we have been unable to confirm results obtained by Gordiyenko et al. ("Investigation of Radiation Crosslinking of Polyethylene in Heterogeneous Systems", Vysokomol. Soedin. 17, 8, 1737 (1975)) claiming that small amounts of silica added to polyethylene enhance the radiation yield of crosslinks. Additional studies were performed exploring the mechanochemistry of polyethylene. None of the techniques employed provided sufficient increase in the concentration of vinylene groups to justify the mechanical process. It appears that the irradiation step is less costly and more convenient for any known mechanical technique for sensitizing the radiation crosslinking. This work also formed a section of the Chappas dissertation. Supporting experimental work was performed by student assistants (Renu Garg and Jeffrey Porter).

C. Acid Effects on Radiation-Induced Grafting of Styrene to Polyethylene

As described in ORO-2845-17, we confirmed the unexpected enhancement by small amounts of acid of the grafting of styrene to polyethylene from methanol solutions. The problem is to explain why the presence of acid outside the styrene-swollen polyethylene affects the reaction rate inside the grafting system. This research formed a third portion of the Chappas dissertation which was awarded in October, 1979. As shown in our paper "The Effect of Acid on the Radiation-Induced Grafting of Styrene to

Polyethylene", (W. J. Chappas and J. Silverman, Radiat. Phys. Chem., 14, 847-852 (1979)) (Appendix D), the effect cannot be due to enhanced yield of hydrogen atoms as proposed by Garnett and Yen. A more likely cause is an acid catalyzed surface reaction which occurs even in the absence of ionizing radiation; it is the properties of this coating which then influences a reaction pattern of considerable complexity. The most important conclusion however is that there are no new phenomena of fundamental importance associated with the grafting system. Also the effect occurs only under conditions which have no practical value (extremely high grafts). The project has been terminated.

D. Rheometry

Rheometry is one of the most useful and practical means of determining the viscoelastic properties of polymers. Yet there are surprisingly few data in the literature providing a practical guide to the polymer processor concerning the properties of crosslinked polyolefins. Torque rheometry measurements were recently made on irradiated polyolefins at the Boris Kidric Institute for Nuclear Sciences (near Belgrade, Yugoslavia) by Dr. V. Markovic and his co-workers. The Principal Investigator has had a significant role in the development of the program and the interpretation of the results. An initial publication on the rheological behavior at various shear rates has been published in Modern Plastics. It shows how higher doses lead to the onset of lower shear rates with smaller relaxation times. This is related qualitatively to segmental motion in crosslinked polymers. It is listed here as Appendix E. Additional experiments providing time resolved torque rheometric data indicate they may provide quantitative crosslink density information comparable with

that obtained by pulsed NMR experiments of Charlesby and Folland. Further work on this subject is in progress.

E. Melt and Crystallization Behavior of Irradiated Polymers

Because of substantial problems with our electron linear accelerator (which were recently largely resolved) we shifted the focus of research from short-lived transient phenomena to a study of the morphological properties of polymers as determined by calorimetry. The acquisition of a differential scanning calorimeter by the University provided us with this opportunity. We undertook DSC and infrared absorption measurements of irradiated morphological forms of poly(1-butene). Pulse radiolysis techniques were used to study radiation effects on a relatively short lived crystalline form. The unstable crystalline form, commonly known as Modification II, is formed directly from the amorphous phase. Pulse irradiations permitted measurements in time intervals shorter^{than} the time for transformation to the stable form. This is the only study of this kind we have encountered. The work was done with Dr. Markovic during his residence at our laboratory; a paper based on the research has been submitted to the Journal of Polymer Science for publication and is given here as Appendix F.

A second paper based on our work with Dr. Markovic has been completed. It concerns the measurements of melting temperature, fusion endotherms, and crystallization exotherms as a function of dose. The studies were done on low density polyethylene, high density polyethylene, polychlorotrifluoroethylene and poly(ethylene oxide). The depression of the melting points and heats of fusion are related by a means of the Hoffman-Lauritzen theory of the chain folded crystallization of the

polymers. The previous publications in this field are in substantial conflict and many of the experiments are poorly or incompletely described. We believe that the results presented in our paper resolve many (but not all) of the conflicts. Also the experiments are described in sufficient detail to permit a more meaningful discussion in those areas where conflict remains. The paper has been submitted to the Journal of Polymer Science (Appendix G).

Additional measurements have been made on the crystallization kinetics of polyethylene and polypropylene. Our analysis is incomplete at this writing. One of our principal objectives of this study is to explain the appearance of two maxima in the fusion endotherms of high density polyethylene following irradiation.

F. Pulse Radiolysis

Perhaps the most difficult and demanding task we have faced in the recent past has been the assembly and operation of the 10 MeV electron linear accelerator obtained on loan from NASA. The machine was received in damaged condition and was assembled almost entirely by student labor. Because of its advanced age (17 years) most of the instrumentation is based on vacuum tube technology. It has taken us some time to master its vagaries and its many modes of breakdown and repair. We had hoped to focus much of our research on the pulse radiolysis of polyethylene, molten polyethylene, single crystals of eicosane, and styrene solutions. In addition we planned to make a close tie-in in the optical information obtained in pulse radiolysis and ESR data. These objectives still stand and will be the basis of much of our future program.

In the meantime we have built an excellent pulse radiolysis system. The design is based on the Danish model at Riso with several modifications relating to data handling and analysis. Dr. Markovic took a leading role in this development and was ably assisted by a student, Mark Gee. A draft of the manual for our pulse radiolysis system is given in Appendix H.

G. Personnel

Since our last writing the following students received graduate degrees: Walter J. Chappas, Ph.D. Nuclear Engineering, October, 1979; Bradley Cohn, M.S. Nuclear Engineering, May, 1978. Two graduate students are still actively engaged in the program: Mark Gee and Fred Zoepfl.

II. Accomplishments Over 19 Years of AEC-ERDA-DOE Support

Following are areas of significant developments at the University of Maryland over the past 19 years of sponsorship: research, education; facilities; and professional advancement of the Principal Investigator.

A. Research

Our principal objective was to develop a solid and continuing program in radiation research related to polymers, vinyl monomers and related compounds. The underlying motive was the practical application of ionizing radiation to polymer science and technology.

This led to a three pronged effort:

1. Radiation source technology. Studies of electron and gamma transport, source optimization studies, electron accelerator concepts.
2. Applied radiation chemistry of polymer science. Polymerization, graft polymerization, crosslinking and scission of polymers. Unique sensitizing of grafting and crosslinking reactions. Systems for obtaining high yield of short grafted side chains as opposed to a few long side chains.
3. Fundamental phenomena related to the practically oriented objectives. How transient species (especially alkyl radicals and charge carriers) are born, migrate, and disappear. How spatially correlated radical pairs are related to crosslink formation. Why no crosslinks or scissions occur in polyethylene single crystals. How does the radiation polymerization of styrene begin? Why does 1% of methanol effect the polymerization rate so profoundly?

A significant list of publications was compiled in the course of pursuing these research objectives. In Appendix I the publications marked with an asterisk are related to and based in some significant way on the subject contract. The accomplishments in graft polymerization research are particularly gratifying: the elucidation of the methanol and acid effects in the PE-styrene system, the role of viscosity of the grafting medium, the problem of occluded homopolymer, the unique (and perhaps important) properties of hexafluoroacetone. The surprising sensitization of the radiation crosslinking of PE by grafted acrylic acid and acrylonitrile was explored and explained. There were substantial advances in the free radical chemistry of irradiated alkanes, particularly for spatially correlated pairs and radical migration mechanisms. We made perhaps the first reasonable measurement of the drift mobility of electrons in n-hexane by a new technique; our dependence on a flash x-ray machine at a classified facility (HDL) rendered fruitless our effort to exploit this initial advantage. We have published data on the molecular weight distribution of polystyrene produced by irradiation of the monomer and some unpublished data for the styrene-methanol system. They provide some insights into an important unsolved problem: the initial steps leading to the formation of the carbonium ion and the benzyl radicals which propagate the polymerization. We plan further experiments along these lines. Our recent work on morphological effects opens new vistas for future studies. From our laboratory has come some of the best work on electron transport measurements in complex absorbers. In addition, our papers on industrial applications of radiation chemistry have had a broad and, we believe, beneficial impact.

B. Education

One of our most important products is our students. The graduate students who received advanced degrees for work supported by the contract are given in Appendix J. In addition there are long-term visitors, especially S. Machi, K. Hamanoue, Y. Ito, and H. Harayama of Japan; V. Markovic of Yugoslavia; A. Charlesby of England; and K. Singer of Denmark. Little of their support was provided by the contract, most of it coming from home sources.

C. Facilities

The contract funds provided our laboratory with a moderate quantity of equipment. Our gamma source, the ESR equipment, data handling and spectrophotometric equipment were obtained with partial support of the sponsoring agency. The large array of thermal analysis, chromatography, rheology, and mechanical testing equipment were provided by the University. Our 10 MeV linac is "on loan" from NASA.

Equipment has been a limiting feature of our research. Our V-4502 ESR and our linac are old units based on vacuum tube technology. The former has significant shortcomings; until recently, the latter was unreliable and prohibitively expensive to operate. We believe it is good enough for pulse radiolysis with 0.1-2 μ s pulses.

D. Professional Benefits

The University in general and the Principal Investigator in particular has derived substantial benefits from the support of the sponsor.

Our laboratory is regarded as one of the major centers of research in radiation-polymer science. Our students are prized by the growing radiation processing industry. There is every indication that our efforts will be the basis of a lasting research and education program in the College of Engineering. For the Principal Investigator, there have been awards, lecture invitations and chairmanships of major meetings. He has also had a significant role in bringing radiation chemistry to industry.

These sentiments and judgments are expressed with a sense of profound gratitude for the sponsor's generosity, kindness, and patience. We trust that the results justify in some measure their efforts in our behalf.

Because of continuing student interest and attractive research opportunities we expect to pursue and even to expand our program.

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