Polymers for High Technology

Electronicsand Photonics



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Preface

The electronics revolution, which began with the invention of the transistor at Bell Telephone Laboratories in 1948, has continued at a frenetic pace and shows no sign of abating. Polymers have played and continue to play an integral part in this revolution in a wide variety of applications. For example, the increasing complexity of microelectronic circuits has been due in no small measure to improvements in the lithographic art. Advances in the design and development of polymeric resists have been pivotal to lithography. Polymers play an enormously important role in the packaging and interconnection of electronic components and find wide use in other applications such as dielectrics. Optical technology, with its tremendous potential for applications in communications, memory, and information retrieval, has given impetus to research on such topics as organic materials (including polymers) for nonlinear optics and optical fiber coatings.

Definitive advances in polymeric materials pertaining to these many technological thrusts continue to be made, even in technologies we might consider to be relatively "mature", for example, resist materials for microlithography. Here, new materials and processes will be required in the not-too-distant future to meet the demands of new and evolving lithographic processes. In some of the relatively recent areas of research, such as polymers for nonlinear optics, molecular electronics, and conducting polymers, many fundamental scientific principles are still not fully understood. Real breakthroughs will be needed to convince skeptics in the solid-state community of the potential advantages offered by organic materials in applications currently limited by the properties of conventional semiconductor materials.

These two powerful forces—the ongoing electronic and photonic revolution, and the significant potential of polymers to contribute to the materials needs of that revolution—continue to stimulate chemists to explore the fundamental, chemically related principles underlying these technologies. Heightened awareness of research opportunities in these areas can in turn lead to further advances.

This book has been organized into eight sections, each representing a specific field. Each section contains an introduction written by the respective session chairperson of the symposium from which this book was developed. All session chairs are recognized experts in their fields. We are indebted to many people and organizations for making the symposium

possible, especially the session chairs who assembled the technical presentations and served as coordinators of the reviewing process. We are particularly grateful to the Petroleum Research Foundation for providing a substantial grant that allowed several overseas speakers to attend the symposium. We also acknowledge the generous financial support of the IBM Corporation, Eastman Kodak Company, AZ Photoproducts Division of American Hoechst Corporation, Dynachem Division of Morton Thiokol Corporation, and the Division of Polymeric Materials: Science and Engineering. We are especially indebted to Lois Damick of Bell Communications Research who handled most of the administrative aspects in preparing this volume. Finally, we thank Robin Giroux and the production staff of the ACS Books Department for their efforts in getting this book published successfully.

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FUNDAMENTALS IN RADIATION CHEMISTRY OF POLYMERS

FUNDAMENTALS IN RADIATION CHEMISTRY OF POLYMERS

The history of radiation chemistry effectively started in 1896 with the discovery of X-rays by Roentgen, and of natural radiation by Becquerel. However, it was not until the advent of nuclear fission on a large scale for power generation (and military purposes) in the 1950s that progress in radiation chemistry really began to be made. The nuclear industry has needed increasing knowledge of the radiation chemistry of materials. Also, there has been a strong incentive to discover new industrial processes which could use the radiation available from reactors. The manufacture of electron accelerators has had an important influence on fundamental research in radiation chemistry and has led to a variety of commercial radiation processes. Chemists have utilized these radiation sources to learn more about the production of reactive species and the mechanisms of chemical reactions initiated by radiation.

The term "radiation" can be used to describe all regions of the electromagnetic spectrum, from radiowaves with wavelengths of meters to gamma rays with wavelengths of nm. Particulate radiations, such as electrons and alpha particles, also have equivalent wavelengths which vary with their energies.

The importance of the radiation chemistry of polymers stems from the large changes in physical and mechanical properties that can be produced by small amounts of radiation. Only a few scissions or crosslinks per molecule, for example, can dramatically affect the strength or solubility of a polymer molecule.

Traditionally, radiation chemistry and photochemistry have been considered as distinct phenomena, being differentiated according to the energy of the photon or particle and the chemistry which follows the initial absorption event. Radiation chemistry derived from photon energies capable of ionizing the parent molecule, whereas photochemistry corresponded to processes resulting from excitation of specific groups in the molecule. However, increasing interest in deep UV radiation for microlithography, the manufacture of excimer lasers producing high intensities of radiation in this special region, and the use of very low energy electron beams in order to maximize absorption in thin films have led to blurring of this boundary.

Radiation must be absorbed before it can produce chemical changes. The initial or primary chemical species resulting from the absorption of high-energy radiation consist of excited states, ions and radicals. Complex sequences of chemical reactions then follow, leading to permanent chemical changes in the molecular structure of the parent molecule. It is these chemical changes that cause the properties of polymers to be modified forming the basis of a variety of applications, e.g., resists for microlithography and graft copolymerization. Such processes can also lead to deterioration of polymers and failure in mechanical applications. This sequence of events is illustrated in Figure 1.

The way in which energy is deposited in a material depends upon the energy of the incident radiation. UV radiation is absorbed selectively by chromophores, whereas high-energy radiation is absorbed according to the electron density of the material. However, energy and charge can migrate after the initial absorption event and the chemical reactions frequently end up being determined by relative bond strengths in the molecule for both types of radiation.

Fundamental studies of the radiation chemistry of polymers can be divided into investigations of (1) permanent chemical changes, including chain scission and crosslinking, structural changes in the polymer, and the formation of small, molecular products, and (2) transient intermediates in the sequence of chemical reactions which follow the absorption event,

especially the formation and disappearance of the initial excited states, ions, and radicals. Pulse radiolysis using microsecond and nanosecond pulses of electrons with energies from 1-10 MeV has contributed greatly to knowledge of these intermediate species. Lasers have been used to provide pulses of UV radiation and for analysis. Studies of polymers in solution in various solvents have been compared with small molecules in the liquid phase and with polymers in the solid state. Studies such as these are providing us with an understanding of the relationships between the molecular structures of polymers and their radiation sensitivity/resistance.

It is important to recognize that fundamental research provides the foundation for technological developments. An understanding of the effects of radiation on polymers, for example, paved the way for the latter's utilization in the electronics industry today in the fabrication of integrated circuits, where polymers sensitive to UV light, electrons, X-rays, and ions are used as resists in lithographic processes. Such technological applications of the radiation chemistry of polymers are increasingly dependent on an inter-disciplinary approach to the development of new processes. Fundamental understanding of the radiation chemistry must be linked with a thorough knowledge of polymer chemistry. However, knowledge of chemistry alone is insufficient since polymers are used mainly in the solid state with all the implications of morphology on properties which is the province of materials science. Finally, any commercial process depends on the contribution of the engineer to convert a laboratory reaction up to an industrial scale. This cooperative approach is illustrated in Fig. 2 and is particularly important in utilizing radiation chemistry in the electronics field.

The following series of papers provides an overview of the fundamental chemistry of radiation-induced changes in polymers with special consideration of electronics applications. Such studies provide valuable insight into the chemical reactions that follow absorption of radiation, an understanding of which may provide the key to improving existing processes, perhaps even to developing new resist mechanisms.

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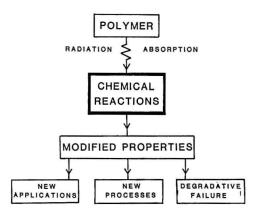


Fig. 1. The sequence of events from the absorption of radiation to its practical applications.

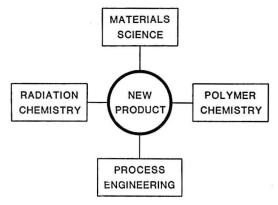


Fig. 2. Schematic representation of the cooperation necessary to utilize radiation chemistry in new technology.

Chapter 1

Development of Radiation Chemistry

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The scientific development of radiation chemistry is reviewed from the discovery in 1895 of x-rays and radioactivity by Roentgen and Becquerel through to the present.

The purpose of this article is to review the development of radiation chemistry which began with the discovery of x-rays by Roentgen(1) in 1895 and shortly afterwards of radioactivity by Becquerel(2), which in both cases involved the observation of chemical change in photographic plates and luminescence in certain phosphors. Clearly, in the space available, the review will be restricted and subjective, but will, it is hoped, give the general framework in which the subject has developed.

The Early Years

Very early studies of these radiations by the discoverers and by the Curies, Rutherford and others demonstrated that they were able to ionize the molecules of a gas upon which they acted. Indeed by 1900, the three kinds of rays, α , β and $\gamma\text{-rays},$ emitted by radioactive materials were characterised by their charges and their differing abilities to penetrate and ionize materials. Also, shortly after the discovery of radioactivity Pierre and Marie Curie(3) reported that radiation caused the coloration of glass and the formation of ozone from oxygen. Other chemical effects of radiation were quickly discovered. For example, Giesel(1900(4)) showed that radiation coloured alkali halides and decomposed water. Becquerel(1901(5)) showed that β - and γ -rays can induce many of the reactions that were known to be caused by absorption of light, such as the conversion of white to red phosphorus and the decomposition of hydriodic acid solutions. Jorissen and Woudstra(1912(6)) showed that the penetrating radiation from radium caused the coagulation of some colloidal solutions and Jorissen and Ringer(1906(7)) demonstrated that hydrogen and chlorine combine at room temperature under the action of these rays. during the first decade of this century the basic physical properties of ionizing radiations had been established as well as their ability to bring about chemical change.

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