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NUCLEAR RADIATION EFFECTS ON STRUCTURAL PLASTICS AND ADHESIVES

PART I LITERATURE SURVEY

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FOREWORD

This report was prepared by Stanford Research Institute under USAF Contract No. AF 33(616)-3632. This contract was initiated under Project No. 1252, "ANPP Support", Task No. 73023, "Radiation Effects". It was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. Arlook as project officer.

This report covers work conducted from April 15, 1956 to September 30, 1956.

ABSTRACT

The literature of radiation chemistry was surveyed. Information pertinent to the effect of radiation on the synthesis and the properties of polymers, elastomers, and adhesives was tabulated. A brief summary of the more general observations on the effects of radiation on these materials was prepared.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

R. T. Schwartz

R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory
Directorate of Research

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NUCLEAR RADIATION EFFECTS ON STRUCTURAL PLASTICS AND ADHESIVES

Part I Literature Survey

I Introduction

A study of the effect of nuclear radiation on commercially available adhesives and plastics, designed to disclose the type and degree of degradation suffered, could lead eventually to the development of new adhesives and plastics which would be more resistant to radiation than the present materials.

Although there is considerable published literature on the effect of nuclear radiation on high polymers, little research has been carried out on compounded, structural adhesives. However, the literature on the general subject of radiation effects should be helpful in guiding the scope of a research program directed toward development of radiation resistant plastics and adhesives.

Investigation of the effects of "atomic" particles and rays on the stability, structure, and reactions of matter began soon after the discovery of radioactivity. Many important observations were made by the early workers, but their efforts in radiation chemistry and physics were not industrially oriented or supported. The advent of the nuclear reactor, with its attendant massive radiation sources and its problems concerning constructional materials, has focused commercial and public interest on radiation effects. The result has been an increasing flow of published data describing the reactions and effects attributable to atomic radiation.

The rapid flow of current reports has made earlier literature relatively obsolete. In this project, emphasis has, therefore, been placed on a careful search of the literature appearing in later years. Some of the information relating to radiation effects is published in sources with restricted circulation, and consequent long delay between publication and general public availability. Every effort has been made to insure completeness of coverage of the literature published before August 1, 1956.

II Method of Approach

In any field in which there is great interest there are many news articles containing brief semi- and nontechnical summaries of current progress, and notes of recent promising advances from papers presented orally before publication. Such references, not usually found in scientific bibliographies, are

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presented here in some number for much the same reason as that which prompted the original publication: they offer a way of recording the latest advances in this rapidly changing field.

An attempt was made to arrange all pertinent articles into the categories indicated by the following outline. The papers were abstracted and the abstracts included in the bibliography.

INTERACTION OF "ATOMIC" RADIATION WITH PLASTICS

ELASTOMERS, AND ADHESIVES

1. Polymerization by Irradiation
   - A. General Studies
   - B. Thermosetting Materials
   - C. Thermoplastic Materials
   - D. Elastomers
   - E. Adhesives
   - F. Miscellaneous Materials
2. Irradiation of Polymers
   - A. General
   - B. Thermoplastic Materials
   - C. Elastomers
   - D. Miscellaneous Materials

The work surveyed and listed in the bibliography places a definite emphasis on the formation, improvement, and degradation of polyethylene by radiation. This is not surprising, since ethylene polymerization can proceed by a radiation-initiated chain reaction of high quantum yield, and polyethylene, once formed, is quite resistant to radiation damage. For these reasons, polyethylene has been carefully investigated and the results reported in many papers.

III Discussion

In this section, a brief review of the literature is presented. The references cited are those selected as representative of the best and most informative work in the field.

1. Polymerization by Irradiation

Studies of polymerization utilizing radiation are of commercial interest only if radiation costs are low (or product value high). Chain reactions of high quantum yield, for which the radiation requirements are small, are representative of favorable situations. Studies of chain-reacting systems are, then, more prevalent than others. Polymerization of compounds such as styrene, methyl methacrylate, acrylonitrile, ethylene, and acrylamide has been investigated. At the present state of development of the nuclear and chemical arts, it seems unlikely that radiation-induced polymerization will be utilized unless some special polymeric properties are desired. With normal polymerization techniques, both the chain-initiating and chain-stopping mechanisms are temperature-dependent. With radiation-induced polymerization, the chain-initiating step is independent of temperature but dependent upon radiation intensity (absorbed dosage). This permits a control of polymer molecular weight previously unavailable. Such control, properly applied, could lead to plastic and elastomeric materials with better properties. For example, polyethylene, slightly more dense and higher-melting than conventional material, has been prepared by radiation polymerization (2, 37).

Other potential advantages of radiation-induced polymerization which are described in the bibliography include elimination of catalytic agents and, therefore, reduction of the impurities in the polymer (N-vinyl pyrollidone polymer) (24, 76, 78), polymerization of otherwise unpolymerizable substances (polyperfluoropropylene) (24), polymerization in situ (adhesive formulation) (75), polymerization at low temperatures (polyethylene) (2, 56, 57), and polymerization in solid state (acrylamide) (26-32).

Radiation-induced polymerization which results in elastomer formation has been studied, but not as intensively as the plastics formation previously mentioned (69, 70).

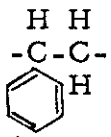
Only one reference (75) has been found which describes curing (polymerization) of an adhesive through irradiation. According to the patent description, irradiation of an adhesive formulation in situ results in an adhesive bond. However, graft polymerization may be considered a special case of adhesive formation because in the process one polymer is caused to grow and bind on another (48).

2. Irradiation of Polymers

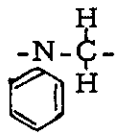
The influence of radiation on the engineering properties of plastics and elastomers has been exhaustively studied. At present it is possible to predict

in general terms the behavior of polymeric materials under irradiation. The materials may be categorized in accordance with the two main effects that predominate: degradation of the polymer by breakage of the bonds in the main chain, or fusion of main chains through crosslinks. In the first category are such substances as cellulose, polyisobutylene, polymethyl methacrylate (lucite), polyvinyl chloride, and polytetrafluoroethylene. In the second category are gutta percha, neoprene, nylon, polyethylene, polystyrene, polyvinyl acetate, and polyvinyl alcohol (98). A special case is that of Thiokol (87) which is both cleaved and crosslinked at nearly equal rates. The response of these materials toward radiation may be modified by additives, e.g., p-benzoquinone protects polymethyl methacrylate from radiation damage (87, 90, 94, 96, 97).

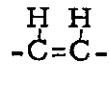
Polymers have been evaluated for their stability against radiation-induced cleavage. A rough ranking system has been evolved (85) which relates polymer cleavage stability to the structure of the repeating monomeric unit. These monomer structures are shown below in decreasing order of stability.



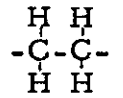
(styrene)



(aniline formaldehyde)

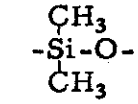


(many)

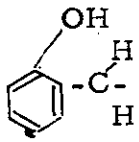


(polyethylene)

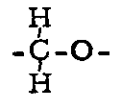
(nylon)



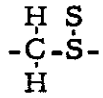
(silicone rubber)



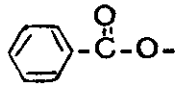
(phenol formaldehyde)



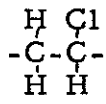
(polyether)



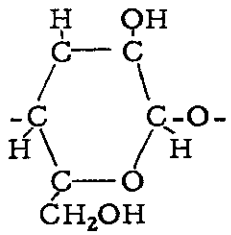
(Thiokol)



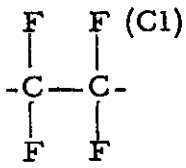
(Dacron)



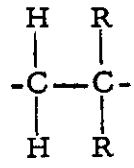
(polyvinyl chloride)



(cellulose)



(Teflon)



(polymethyl methacrylate, butyl rubber, poly-alpha methyl styrene)

The range of stability covered by these materials is indicated by the following data:

Polystyrenes show less than 50% reduction in shear, impact, and tensile strengths after exposures of 3×10^{10} rad. Lucite (polymethyl methacrylate) shows 50% reduction in shear and impact strength after 10^8 rad exposures and a 50% reduction in tensile strength after a 5×10^7 rad exposures.

Radiation-caused reactions of pure plastic materials are often modified by fillers, plasticizers, and other additives which are frequently used in commercial formulations. Because of this, the entire plastic composition must be considered in practical applications.

Although the physical changes in plastics and elastomers under the action of radiation have been carefully measured and catalogued (84, 87, 92, 95, 99, 121, 142, 157, 158, 179), and although the changes are explained descriptively as being caused by chain degradation or crosslinking, there is little knowledge of the basic chemical changes.

From several studies (94, 110, 153, 157, 158, 179), we have learned that, under radiation, polyethylene:

1. evolves gas

2. crosslinks to form a three-dimensional structure of greater rigidity (melts at higher temperature and is resistant to chemical attack)

3. loses the original vinylidene linkage and forms a vinyl linkage at a faster rate

4. crosslinks at a rate one-third of this rate of dehydrogenation (unsaturation)

5. forms one crosslink for every 5×10^7 ergs of radiation absorbed.

Lesser amounts of information have been collected for other plastics.

It has not been possible to formulate a mechanism which suitably accounts for crosslinking of all polymers which undergo this reaction. Partial mechanisms have been offered, however.

Elastomers have been exposed to radiation in cold vulcanization attempts and in the course of engineering tests seeking radiation-resistant materials for construction. For radiation resistance, natural rubber is currently the best material available. It is able to withstand 5×10^8 rad (85, 206, 216, 219, 220, 222, 225).

No published information has been found which describes the behavior of adhesives under irradiation other than the curing process described by a patent which was mentioned previously.

IV Bibliography, with Abstracts

1. Polymerization by Irradiation

A. General Studies

1. Allen, P. E. M., J. M. Downer, G. W. Hastings, H. W. Melville, P. Molyneux, and J. R. Urwin.

   New methods of preparing block copolymers. Nature 177, 910-912 (1956).

2. Anon.

   The next frontier. Chem. Week 76, 48-50, 52, 54 (1955).

Radiation catalysis is developing into an exciting new tool for industry. Diamond Alkali Co. and Standard Oil Development Co. are constructing facilities to carry out research plans.

Gamma irradiation causes some types of chemical reactions not as yet fully understood, but may be useful in the future, e.g.:

1. Some monomers radiated at -18°C do not polymerize, but do explode when elevated to room temperature.

2. Irradiation may permit better control of the end product of polymers consisting of a mixture of hypothesized addition isomers (e.g. 1,2- and 1,4-butadiene) by initiating reaction at low temperatures.

3. Heat-sensitive monomers may now be polymerized by use of gamma radiation.

3. Anon.

   Radiation countermove. Chem. Week 77, 52, 54 (1955).

Naval Research Laboratory has prepared high-density, high-melting polymers of high purity and unusual physical qualities, using gamma ray irradiation of ethylene, acrylonitrile, vinyl acetate, acrylic acid, vinyl ethers such as butyl and methyl methacrylate, silicones and polyester precursors such as glycol, and dibasic acids. Yields are said to be substantially quantitative. Irradiated polyethylene is reputed to be a slightly denser, slightly higher-melting product than the new crystalline polyethylenes.

4. Anon.

Pipe dream coming true. Chem. Week 77, 84 (1955).

Pilot plant tests show that gasoline can be produced by radiation under milder conditions than those of conventional processes.

Studies also indicate that gamma radiation accelerates the reaction, gives higher yields than present cracking processes, requires less heat.

Esso also reports it has used gamma rays to produce new lube oil additives. Butyl rubber was broken down by irradiation, the degradation products examined as potential oil additives. Company scientists say that as yet none of the new compounds has been fully evaluated.

5. Anon.

Britain plans to harness spent elements for production. Nucleonics 14, No. 1, 13 (1956).

When the U. K. power program gets under way, radioactive waste products from Britain's atom power plants are likely to be used on a large scale for the industrial manufacture of a number of already-existing materials and some entirely new materials. Specific projects contemplated include manufacture of polyethylene plastic from ethylene gas simply by exposing it to radiation, thus eliminating complex chemical reactions for making the raw plastic. One hundred thousand curies of fission products are sufficient to make 1,000 tons of polyethylene at a radiation cost of 1.5 cents per curie. Other plastics, such as methacrylate, styrene, and fumarates, could be manufactured this way.

6. Anderson, L. C., and J. J. Martin

Polymerization by gamma rays. Modern Plastics 32, No. 7, 94-7, 210 (1955).

An analysis of the economic feasibility of radiation-induced polymerization based on the rate of reaction of cobalt-60-catalyzed polymerization of ethylene. A price of 10 cents/curie was picked from a range of 0.05 cents to five dollars/curie. It was noted that there are some differences in the structure of radiation-catalyzed polymers and that such polymers contain no catalyst fragments.

7. Ballantine, David S.

The initiation of chemical reactions by gamma and other ionizing radiations. Technical Information Service, AEC Report No. TID-8005, (Feb. 1956).

An introduction to industrial radiation chemistry. Emphasis is placed on the advantages of radiation induced polymerization for:

a. low temperature radical initiation

b. use of lower pressures

c. solid state polymerization

d. different molecular weights of polymer

e. different polymer characteristics

f. external catalyst.

8. Ballantine, David S., A. Glines, P. Colombo, and Bernard Manowitz.

Progress report on fission products utilization. VI. The effects of gamma radiation on vinyl polymer systems. U. S. Atomic Energy Commission Report BNL-294 (T-50) 18 p.

Investigations were carried out on the emulsion polymerization of styrene (I), the polymerization of 1-vinylpyrrolidinone (II), fluorocarbon monomers (III), and acrylamide (IV) in the solid state, as well as on the effects of cobalt-60 gamma rays and electrons (V) from a Van de Graaff accelerator on polyethylene (VI). The radiation-induced emulsion polymerization of (I) is more efficient than bulk polymerization. The molecular weights and reaction rates are larger by about one order of magnitude. Polymerization of (II) is sufficiently rapid to be of commercial significance. Desired K-values are obtained by varying the monomer concentration and nature of solvent.

9. Behr, J., R. B. Mesrobian, A. J. Restaino, D. S. Ballantine, A. Glines, and D. J. Metz.

G values of gamma-ray initiation of vinyl polymerization and their relation to graft copolymer formation. J. Polymer Sci. 19, 219-224 (1956).

10. Callinan, T. D.

Gamma radiation cures resins. Electronic Equipment 4, 14-17 (1956).

An account of Naval Research Laboratory studies to determine the radiation dosage required to polymerize commercial resins suitable for embedding such electronic components as resistors, capacitors, and transistors. Resins such as Paraplex-P-43, Laminac 4116, Laminac 4134, Laminac 4128 were used.

11. Callinan, T. D.

Polymer synthesis by gamma radiation, J. Electrochem. Soc. 103, 292-6 (1956).

Monomers were polymerized successfully by the action of gamma rays to high molecular weight solids without elevated temperatures or catalysts. Styrene, ethylene, methyl-styrene, acrylonitrile, and methyl methacrylate were among the monomers polymerized. Low molecular weight polyester sirups were solidified into hard transparent solids without the use of the usual catalysts and accelerators. Some chemical and physical properties of these polymers were determined. Observed values were compared with the properties of polymers obtained by thermal and catalytic activation. Radiation energies required for causing polymerization were determined.

12. Chen, W. K. W., R. B. Mesrobian, D. S. Ballantine, D. J. Metz, and A. Glines.

Studies on graft polymers derived by ionizing radiation. Preprint. Polymer Research Institute, Polytechnic Institute of Brooklyn.

Studies are presented on the preparation of graft copolymers by gamma-ray irradiation of various polymer-monomer combinations. The following graft copolymers have been prepared and evaluated for specific applications: (1) vinyl carbazole grafted to polyethylene to produce a higher temperature dielectric material; (2) styrene grafted to polyethylene and sulfonated to produce a cation exchange membrane of high mechanical strength, low resistivity, and high permeaselectivity; (3) styrene surface-grafted to polytetrafluoroethylene for modification of adhesive properties; (4) acrylonitrile grafted to polydimethylsiloxane to increase the solvent resistance of the latter.

13. Fukada, Eiichi.

New polymers by irradiation. Kagaku (Science) 25, 554-8 (1955).

A review with 25 references.

14. Hobbs, L. M., D. E. Brown, and D. W. Pletcher

Effects of cobalt-60 on formation and degradation of polymers. Bull. Am. Phys. Soc. 29, 14 (1954).

15. Hopwood, F. L., and J. T. Phillips.

Polymerization of liquids by irradiation with neutrons and other rays. Nature 143, 640 (1939).

Of the different methods - determination of changes in color, refractive index, viscosity, streaming polarization, density, etc. - observing the rate of polymerization following the changes in density consequent on irradiation by means of a volume dilatometer was most convenient. The sources of radiation sometimes were placed inside the bulb of the dilatometer.

The liquids investigated so far, in addition to methyl methacrylate, include styrene, vinyl acetate, and a ketone. The expulsion of dissolved substances which had been deliberately added, for example, ceresin, indole, etc., was often strikingly shown during the polymerization.

16. Hopwood, F. L., and J. T. Phillips.

Some effects produced by the irradiation of liquids and gels with alpha, beta and gamma rays and neutrons. Proc. Phys. Soc. (London) 50, 438 (1938).

During an investigation of some of the effects of neutrons on substances of biological importance, it was found desirable to re-investigate some of the effects due to alpha, beta, and gamma rays which had been observed in some cases before the neutron was discovered. The following studies were made:

1. decomposition of dilute solutions of hydrogen peroxide by gamma rays and neutrons
2. liquefaction and re-gelation following irradiation of a gel
3. effect of gamma rays and neutrons on the formation of Liesegang rings
4. developability of silver grains in a photographic emulsion bombarded by alpha particles
5. turbidity of irradiated protein solutions
6. polymerization of unsaturated hydrocarbon compounds.

It has been found that styrene and vinyl acetate can be polymerized at room temperature by alpha rays and gamma rays acting either in conjunction with neutrons or alone. The polymerization is demonstrated by the increase in viscosity of the liquids, streaming polarization, and solidification.

17. Joliot, J. F.

Polymerization. Fr. 966, 760 (October 18, 1950).

Substances such as methyl or ethyl methacrylate, styrene, and acrolein, alone or with plasticizers and/or catalysts, are exposed to a beam of rapid neutrons, such as produced by a radium salt or by a mixture of radiothorium and beryllium. Radon or any other source may be mixed with the monomer, and the polymer may then be used for treatment of cancer.

18. Lawton, E. J., W. T. Grubb, and J. S. Balwit.

A solid state polymerization initiated by high energy electrons. J. Polymer Sci. 19, 455-458 (1956).

Hexamethylcyclotrisiloxane monomer polymerizes when exposed to high-energy electrons. The greatest yield of polymer occurs when the monomer is irradiated in the solid state. Above the crystal melting temperature, the yield of polymer is almost zero for equal radiation. The polymer obtained is crosslinked. This is unlike the polymerization of acrylamide in which there is extensive polymerization in both the solid and liquid states by high-energy electrons.

19. Magat, Michael.

New aspects of polymerization kinetics. Bull soc. chim., France, 535-41, 1956.

An address about kinetic schemes of polymerization, termination reactions, steady-state hypothesis, "normal" polymerization reactions, "abnormal" polymerization reactions, and induction of polymerization by ionizing radiations. 20 references.

20. Martin, J. J.

Use of radiation to promote chemical reactions. Chem. and Eng. News 33, 1424-28 (1955).

Radiation does not function exactly like a catalyst, since it supplies energy to the system. This energy may go to at least two places: it may be used to overcome the potential barrier and start some chain reactions which cause the system to proceed to its normal equilibrium point, or it may supply free energy to the reaction in such a way that the reaction will proceed away from its normal equilibrium point. Reactions which are of the chain type and which suffer a loss in free energy are more promising than those which take place with an increase in free energy. In considering any

particular reaction for promotion by radiation, one should study the thermodynamics involved so that conditions of temperature, pressure, and concentrations may be adjusted to give a negative free energy change, and thus set up the possibility of a chain reaction.

21. Metz, Donald J.

Production of graft copolymers by gamma rays. Preprint copy. Brookhaven National Laboratory, Upton, New York, Jan. 15, 1956.

The grafting of various vinyl monomers to polymers has been studied, with emphasis placed on grafting monomers to films of polyethylene and "Teflon." In some cases the kinetics of the reaction have been partially studied and some ideas as to the effect of film thickness and dose rate have been tentatively drawn from the data. Some of the mechanical and electrical properties of a few of the products formed have been studied. In some cases there are indications that these materials have properties which are superior to those of the initial films employed.

22. McGarry, F. J.

Review of plastics developments in 1953-1954. Mechanical Eng. 77, No. 4, 318-19 (1955).

Perhaps the most provocative single development which has occurred in the plastics field in the past year is the recognition and study of the effects produced in polymer materials by various forms of atomic radiation. As an example, the apparent cross-linking of polyethylene, with a consequent elevation of its softening temperature, constitutes a highly beneficial effect, but numerous cases of material degradation have also been observed. The existence of the latter action does not, however, negate the possibility that radically altered plastics may be obtained by this process in the near future.

23. Nikitina, T. S., and Bagdasar'yan, Kh. S.

Distribution of absorbed energy in radiational polymerization. Sbornik Statei Radiosionnoi Khim., Akad. Nauk S. S. S. R. 183-95 (1955).

Kinetics of polymerization of methyl methacrylate, styrene, and vinyl acetate either en masse or in solutions with ethyl acetate, benzene, and carbon tetrachloride were examined under gamma radiation from cobalt 60. The rate of polymerization in styrene or methyl methacrylate systems in carbon tetrachloride rises through a maximum in respect to combination

of the solution; such curves cannot be explained by primary radical formation from the initial components. Equations are derived for formation of primary radicals in 2-component mixtures, by taking into account a redistribution of the absorbed radiant energy. The equation is well supported by experimental data which are shown graphically. The yields of primary, initiating radicals per 100 e.v. of absorbed energy are: styrene, 0.4; methyl methacrylate, 3.5; vinyl acetate, 5.0. The capture of radicals was attained in some of the runs by the use of diphenylpicrylhydrazyl.

24. Roche, Arthur F.

Polymerization. Catalysts and inhibitors. High energy radiation. Part II. Ind. Eng. Chem. 47, 1904-05 (1955).

This is a brief review touching upon the economic feasibility of the use of radiation; emulsion polymerization of styrene by gamma irradiation: polymerization of vinyl pyrrolidone (possibly commercial) particularly in solid state solutions; polymerization of fluorocarbons; solid state polymerization of acrylamide, which is of interest because of the radiation-induced frozen-in radicals; polymerization of styrene and methyl methacrylate in solution by the use of beta rays from a mixture of strontium 90 and yttrium 90; the polymerization of benzene by 1.5-Mev electron irradiation; catalysis of ethylene by gamma radiation; and gamma-ray polymerization of acrylamide.

25. Watson, John H. L.

Crystalline alpha-ray-acetylene reaction products. Radiation Research 3, 121-6 (1955).

Crystalline deposits resulting from alpha particle bombardment of acetylene at a pressure of 35 mm mercury at 27°C were examined by electron microscopy and electron diffraction. A known activity of radon, enclosed in a thin-walled glass bulb, served as the alpha-particle source. Crystalline products were not obtained when there was an intimate mixture of the reacting gas with the radon. The deposits were collected directly upon prepared electron-microscope specimen screens and examined as deposited without further manipulation. Photographs of deposits magnified to 12,000 and 37,000 diameters are given. Identification of the product was not possible from the data obtained. Crystalline deposits are also obtained with carbon monoxide and acetylene monochloride under the same experimental conditions.

B. Thermosetting Materials

26. Byrd, N., R. B. Mesrobian, D. J. Metz, and R. Zand.

Gamma ray polymerization of acrylamide in the solid state. Quarterly Report No. 6(Final) July 1, 1952 to Jan. 31, 1954. Report of new polymerization methods. 7 p. Illus. Brooklyn Polytechnic Institute. AD-28235

Experiments are described which demonstrate that crystalline acrylamide undergoes polymerization upon irradiation with gamma rays from an intense cobalt 60 source. Below its melting point the monomer shows little or no tendency to polymerize thermally. Samples of the polymer were prepared and rate curves were obtained at 5°, 35°, and 55°C.

27. Collinson, E., F. S. Dainton, and G. S. McNaughton.

Molecular and radical yields of aqueous acrylamide solutions irradiated with radiation of 50 and 220 kv. J. Chim. Phys. 52, 556-69 (1952).

In a neutral, degassed aqueous solution, acrylamide is polymerized by x-rays, forming a soluble polymer of high molecular weight. The velocity R_p is given by $R_p = (G_i I/k_t)^{\frac{1}{2}} K[m_1]$ moles/liter/sec., where K is the overall rate constant, and m_1 is moles/liter. The degree of polymerization, DP, is proportional to m_1 and to I^{-a} where $a<0.5$, I is the intensity of radiation in 100 ev/liter/sec. G_i is the starting yield equal to the number of chains initiated by 100 ev; k_p/k_t = 5.2 liter$^{1/2}$ mole$^{-1/2}$ sec$^{-1/2}$. $E_p - E_{t/2} = \sim 2$ kcal.

28. Henglein, A., and R. Schulz.

Effect of gamma rays on solid acrylamide. Z. Naturforsch. 9b, 617-18 (1954).

Acrylamide crystals gradually exhibit a yellowish opaqueness when irradiated by intense gamma rays. Solution in water yields a viscous solution and a strongly swollen residue (5-10% of total amount of polymer). The reaction rate is smaller by approximately a factor of 100 than the one in aqueous solution and the reaction takes place in vacuo as well as in an oxygen atmosphere. An average degree of polymerization (of the water soluble part) of about 4×10^3 is reported at 7×10^3 roentgens/hour. Polymerization at low temperature indicates that not all radicals are deactivated during irradiation; some induce a considerable post-irradiation effect. About 50% of the amount of acrylamide employed is so polymerized. The gel part of the polymers formed is probably crosslinked.

29. Mesrobian, R. B., P. Ander, D. S. Ballantine, and G. J. Dienes.

Gamma ray polymerization of acrylamide in the solid state. J. Chem. Phys. 22, 565-6 (1954).

Polymerization in the solid state by ionizing radiation is not reported in the literature; the purpose of this note is to describe some experiments which demonstrate that crystalline acrylamide undergoes polymerization upon irradiation with gamma rays from an intense cobalt-60 source. Below its melting point the monomer shows little or no tendency to polymerize thermally.

30. Restaino, A. J., R. B. Mesrobian, H. Morawetz, D. S. Ballantine, G. J. Dienes, and D. J. Metz.

Gamma ray initiated polymerization of crystalline monomers. J. Am. Chem. Soc. 78, 2939-43 (1956).

Acrylamide, methacrylamide, methylene-bis-acrylamide, vinyl carbazole, vinyl stearate, acrylic acid, methacrylic acid, and potassium, calcium, and barium acrylates have been polymerized in the solid state by irradiation with gamma rays. The molecular weight of the polyacrylamide obtained at low conversion was constant over a 270-fold variation of radiation intensity and in the temperature range 20 to 65°C, but increased slightly with the energy of the radiation. The polymerization rate, however, was linear with field intensity, independent of the energy of radiation and had an overall activation energy of 4.7 kcal/mole. Irradiation of acrylamide at -179° produced "frozen-in" radicals in concentrations of the order of 10^{-4} molal. In the polymerization of vinyl stearate the temperature dependences of rate and molecular weight exhibit a discontinuity on passing through the melting point of the monomer. With barium acrylate there is no significant variation in polymerization rate between 10 and 65°. Crystalline maleic anhydride, an allylamine hydrochloride and picrate, and stilbene did not polymerize upon exposure to gamma rays.

31. Schulz, Rolf, A. Henglein, H. E. v. Steinwehr, and H. W. Bambauer.

Polymerization of crystalline acrylamide through radiation. Angew. Chem. 67, 232 (1955).

Gamma rays permit polymerization of acrylamide at room temperature in the solid state. Unreacted monomer was extended by treating with alcohol for 20-40 hours. Crystallographic and x-ray examination of the fractions were made. Gamma radiation gave a polymer which retained

externally the crystal form of the monomer. The polymerization process is considered a special case of replica polymerization.

32. Schulz, R., G. Renner, A. Henglein, and W. Kern.

Gamma ray polymerization of acrylamide. Investigation of the radical polymerization of acrylamide. Makromol. Chem. 12, 20-34 (1954) (in German).

Different methods of radical-polymerization of acrylamide in solution and in bulk are described. The gamma-ray induced polymerization yields products of extremely high molecular weight. The polymerization induced by Fenton's Reagent, on the other hand, leads to products of low intrinsic viscosity. Ultrasonic waves polymerize the monomer and depolymerize the polymer. The viscosity of a pure polymer and its fractions plotted against the concentration show that these polyacrylamides in aqueous solution are homeopolar molecular colloids.

C. Thermoplastic Materials

33. Ballantine, D., and B. Manowitz.

The polymerization of vinyl monomers by intense gamma radiation. BNL-229 (T-35) Office of Technical Services, Department of Commerce, Washington, D. C. (March 1955).

34. de Bataafsche Petroleum Maatschappij, N. V.

Irradiation-catalyzed polymerization of vinyl compounds. Brit. 697, 289 (Sept. 16, 1953). See U. S. 2,666,025.

35. Bensasson, Rene, and Annette Prevot-Bernas.

Radiochemical polymerization of acrylonitrile in solution and the spatial distribution of active primary centers. J. Chim. Phys. 53, 93-5 (1956).

Kinetic studies of the polymerization of acrylonitrile (with gamma rays as initiators) show that the active primary centers are uniformly distributed. Solutions of water and acrylonitrile (7 mole % water; 99.2 mole % water), pure acrylonitrile, and a solution of dimethylformamide and acrylonitrile (70 mole % dimethylformamide) are polymerized. The percentage conversion in 24 hours of each solution is measured with 5 or more different radiation intensities.

36. Buckley, G. D., and L. Seed.

(to Imperial Chemical Industries) Brit. 714,843 (Sept. 1, 1954) Patent for the catalysis of ethylene polymerization by x and gamma rays.

37. Callinan, T. D.

Polymer synthesis by gamma radiation. J. Electrochem. Soc. 103, No. 5, 292-6 (1956).

Monomers have been polymerized successfully by the action of gamma rays to high molecular weight solids without employment of elevated temperatures or catalysts. Among the monomers polymerized were ethylene, styrene, methylstyrene, acrylonitrile, and methyl methacrylate. Low molecular weight polyester syrups have been solidified into hard transparent solids without the use of the usual catalysts and accelerators. Some chemical and physical properties of these polymers have been determined. Observed

values are compared with the properties of polymers obtained by thermal and catalytic activation. Radiation energies required for causing polymerization have been determined.

38. Chapiro, A.

On the polymerization of vinylic compounds initiated by gamma rays. I. J. chim. phys. 47, 747-63 (1950).

The kinetics of gamma ray initiated polymerization of styrene in various diluents has been studied. The addition of small quantities of diluent to the monomer generally produces an acceleration of the polymerization, due to the fragility of the diluent molecules to gamma rays; styrene itself is very stable.

39. Chapiro, A.

On the polymerization of vinylic compounds initiated by gamma rays. II. J. chim. phys. 47, 764-75 (1950).

The study of the polymerization by gamma rays reported for styrene, has been extended to methyl methacrylate, acrylonitrile, vinyl acetate, vinyl chloride, methyl acrylate, and butadiene.

40. Chapiro, A.

Polymerization by gamma rays. Compt. rend. 228, 1490-92 (1949).

A 20-cc ampul of monomeric styrene, pure or in solution, was placed 4.5 cm from 100-400 millicuries of radium wrapped in 1 mm lead foil. The progress of polymerization at 120°C, followed by dilatometry, was 0.015 g % polymer per curie-hr exposure. The percentage converted was linear with exposure time; for pure styrene less than 5% polymerized and for styrene in methyl alcohol less than 15% polymerized, and was proportional to the square root of the radiation intensity. The reaction involves free radicals since polymerization was blocked by 1% benzoquinone. The speed of polymerization was 2.8 times as rapid when the styrene was in solutions that were 20 mole per cent of any of the first 6 primary alcohols. With larger concentrations of alcohol the speed was less, probably because of precipitation of the polymer. Styrene in solutions 20 mole per cent with primary or secondary amines, acetone, propionitrile, benzene, or cyclohexane, was polymerized faster than when pure, the hydrocarbons being least effective.

41. Chapiro, A.

Polymerization by gamma rays. II. Compt. rend. 229, 827-9 (1949).

If the polymer formed is soluble in the solution, the speed of polymerization of styrene under the previously described conditions is about constant in the range 25-80 mole % diluent. For more dilute solutions, the speed of polymerization is much less. Diluents of this type in order of increasing efficiency for accelerating polymerization are benzene, ether, acetone, and carbon tetrachloride. For cyclohexane, the speed of polymerization increases regularly to solutions with 92% diluent. In more dilute solutions the speed of polymerization drops rapidly to zero. For all these solutions the intrinsic viscosity decreases regularly with increased dilution.

42. Chapiro, A., C.H. Cousin, L. Landler, and M. Magat.

The study of polymerization initiated by nuclear radiation. Rec. trav. chim. 68, 1037-68 (1949).

The following monomers were studied: styrene, acrylonitrile, butadiene, methyl methacrylate, and vinyl acetate. The addition of the following compounds were studied: carbon tetrachloride, alcohols, butylamine, diethylamine, acetone, aniline, ether, cyclohexane, heptane, and benzene.

43. Chapiro, A., M. Magat, Annette Prevot-Bernas, and Jeanne Sebban.

Radiochemical polymerization of vinyl monomers. J. chim. phys. 52, 689-98 (1955).

In the light of recent results, some fundamental aspects of the radiochemical polymerization of vinyl compounds were re-examined: the nature of the primary centers; their distribution in space; influences of intensity, solvents, polymer present, and temperature, on the kinetics of the reaction. It is shown that the priming is made with free radicals and that everything occurs for polymerization as if their distribution in space (in a stationary state) were uniform.

44. Chapiro, A., and Eva Migirdicyan.

Upon the polymerization of methyl methacrylate by means of gamma rays. J. chim. phys. 52, No. 5, 439-440 (1955).

The experimental conditions were identical to those of our former experiments: dilatometers filled and sealed under vacuum were placed at variable distances from a 25-curie source of cobalt-60 and a 0.275-curie source of radium, respectively. The progress of the reaction was checked by measuring the degree of contraction of the solution, and the final degree of conversion was checked by weighing the polymer obtained. In order to avoid complications resulting from gel effects, the reaction was stopped at conversions below 7%. The conversion was a linear function of time. All

irradiations were performed at 19°C. The mean molecular weights of the polymer were deduced from the viscosities measured in chloroform at 25°C using the reaction of Baysal and Tobolsky.

45. Chapiro, A., and Philippe Wahl.

The reaction rate-intensity relation in the polymerization of styrene by gamma rays. Compt. rend. 238, 1803-5 (1954).

Earlier experiments were extended to higher dose rates (0.29-370 roentgen/minute, cobalt 60 and radium at 19°); the proportionalities of percentage of polymer/hour to the square root of intensity and degree of polymerization to the reciprocal square root of intensity were verified. The rate law expressing proportionality to intensity established by Manowitz, et al., is believed to be erroneous, probably as a result of: (a) inaccurate reasoning in regard to the spread of the experimental data and, (b) of the limited intensity range investigated.

46. Dainton, F.S.

Polymerization as a guide to track distribution. J. Chem. Phys. 48, 182-83 (1951).

Vinyl compounds in dilute aqueous solution are readily polymerized by the indirect action of ionizing radiation absorbed by the water. The initiating step is the reaction with the monomer of a fraction of the H and OH radicals formed in the primary radiochemical act to create the appropriately substituted ethyl radical, which then grows by the usual type of radical propogation reaction. Using D_2O as a solvent and utilizing infrared analysis of the end groups of the polymer so formed, it can be shown that H and OH can each start polymerization chains.

47. Doucerain, J.

Polymers. French 982,463 (June 11, 1951).

Monomers, such as acrylic and methacrylic esters, styrene, and aminoplasts, are polymerized successively in zones which are small enough to ensure complete polymerization. When the polymerization agent is a form of radiation, shields with appropriate apertures can be used.

48. Fox, M., and P. Alexander.

After effects in the polymerization of aqueous solutions of methacrylic acid initiated by x rays. J. chim. phys. 52, 710-717 (1955).

Oxygen-free aqueous solutions of methacrylic acid are readily polymerized by x rays. At concentrations of monomer below 7.5%, the rate of polymerization is proportional to the concentration of monomer. The rate decreases to a minimum at a 65% solution of monomer (limit of solubility). A mechanism involving a chain termination produced by radiation

is used to explain the decreasing polymerization rate. Polymerization continues for several days after irradiation at a rate proportional to the sum of the monomer and polymer concentrations (distinguished from the Trommsdorf effect, observed when the polymer is in a gel-like form). The polymer, formed by irradiation, is capable of initiating the polymerization of methacrylic acid even after exposure to air.

49. Garrison, W.N.

The polymerization of unsaturated hydrocarbons by ionizing radiations. J. Chem. Phys. 15, 78 (1947).

The polymerization of ethylene by ionizing radiations (such as alpha-particles) can be explained in terms of both ionic and free-radical mechanisms, either of which can be initiated by ethylene ions.

50. Hauptschein, Murray, and Joseph M. Lesser.

The copolymerization of highly fluorinated olefins with ethylene oxide. J. Am. Chem. Soc. 78, 676-9 (1956).

The copolymerization of perfluoropropene and trifluorochloroethylene with ethylene oxide has been effected and studied in the presence of ultraviolet light or di-t-butyl peroxide (DTBP) as the initiators. Vinylidene fluoride did not copolymerize with ethylene oxide using DTBP as the initiator, but the conversion to vinylidene fluoride homopolymer has been shown to be increased greatly by the presence of ethylene oxide. Perfluoropropene and vinylidene fluoride in the presence of DTBP react with ethyl ether to form telomers.

51. Hayward, J.C., Jr.

Polymerization of ethylene initiated by gamma radiation. NYO-3313 (June 1955) 277 p. Contract AT(30-1)-1173. Atomic Energy Commission, Oak Ridge, Tenn.

Initial rates of the polymerization of ethylene initiated by gamma radiation have been obtained between 0.1 and 60% per day at temperatures between 80 and 460°F, pressure between 1/2 and 21 atmospheres, and a radiation intensity of the order of 100,000 roentgens/hour. The initial rates corresponded to ion-pair yields between 5 and 2,500 and to G values (number of molecules of ethylene polymerized per 100 electron volts) between 20 and 10,000. The product is generally a liquid; however, a white waxy solid was obtained at room temperature and the higher pressures. The reaction is homogeneous and is strongly inhibited by a trace concentration of oxygen. Furthermore, the effect of saturation electric field on the rate of polymerization at 80°F and 2 atmospheres is small, if not completely negligible. A simplified version of a free-radical polymerization mechanism is presented, according to which the ion neutralization energy is ineffective in the initiation of ethylene polymerization. Furthermore, the chain-transfer process by which the liquid product is formed at elevated temperatures is

suppressed by an increase in pressure. The initial radiation yields and the nature of the products obtained are generally consistent with the type of mechanism postulated.

52. Hayward, J.C., Jr., and R.H. Bretton.

Kinetics of the ethylene reaction initiated by gamma radiation. Chem. Eng. Progr. Symposium Ser. No. 13 50, 73-88 (1954).

Initial rates of the reaction initiated by gamma radiation have been derived from total-pressure measurements on a batch system of ethylene subjected to a radiation intensity of about 100,000 roentgens/hour. Initial rates from about 0.1 to 60% per day, and corresponding ion-pair yields from about 6 to 3300, were obtained at temperatures between 80 and 460°F and at pressures between 1/2 and 21 atmospheres. The reaction is homogeneous and is strongly inhibited by traces of oxygen. The product was generally a liquid; however, a white waxy solid was obtained at room temperature and the higher pressures.

53. Kline, G.

The year 1955 in review. Modern Plastics 33, 135, 136, 138, 140, 142, 144, 149, 150, 152, 154, 156, 234-37 (1956).

It is the use of irradiation for catalysis of polymerization and modification of the properties of thermoplastics by crosslinking that occupies most of the research effort today. A survey of plastics manufacturers indicates that several have installed their own radiation sources and facilities, generally using cobalt 60 as a gamma ray source. Numerous reports have described the results obtained in the irradiation of polyethylene, polystyrene, methyl methacrylate, and other polymers and monomers.

54. Landler, I., and M. Magat.

The polymerization of styrene induced by slow neutrons. Compt. rend. 226, 1720-1 (1948).

A solution of styrene in ethyl bromide was exposed to slow neutrons. The neutrons were capable of inducing styrene polymerization through formation of atmospheric bromine, hydrogen, and free radicals. The extent of polymerization appeared to depend upon the quantity of neutrons, although no exact relationship was found. Atmospheric bromine was found to promote the polymerization, and the polymer contained combined radioactive bromine. The relative efficiencies of bromine and hydrogen atoms for the production of secondary centers was 2:1.

55. Landler, I., and M. Magat.

Preliminary results of styrene polymerization initiated by slow neutrons. Bull. Soc. Chim. Belges 57, 381 (1948).

The Szilard-Chalmers effect (on ethyl bromide) was used to initiate the polymerization of styrene.

56. Lewis, John G., Joseph J. Martin, and Leigh C. Anderson.

Syntheses. Polymerization of ethylene. Chem. Eng. Prog. 50, No. 5, 249-254 (1954).

A white, solid polyethylene was produced by irradiation of ethylene with cobalt-60 gamma rays. The yield was small until about 0.5 x 10 roentgen equivalent physical (megarep) had been applied; then it increased rapidly to about 2,500 g-mols reacted/(metric ton/(megarep)) at about 3 megarep, and remained nearly constant to 7 megarep, the highest dosage used. A considerable induction period was required for polymerization. Solution viscosities, melt viscosities, densities, and tensile strengths of the products are tabulated.

57. Lewis, John G., Joseph J. Martin, and Leigh C. Anderson.

Polymerization of ethylene by gamma radiation. Program of the American Institute of Chemical Engineers International Congress on Nuclear Engineering. p. 62 (1954).

58. Majury, T.G.

Polymerization of methyl methacrylate by pulses of high-energy electrons. J. Polymer Sci. 15, 297-304 (1955).

Methyl methacrylate, vinyl acetate, styrene, and diethylene glycol-bis (allyl carbonate) were subjected to irradiation by very intense micro-second pulses of electrons of 3-Mev energy. The methacrylate underwent a prolonged, slowly decaying polymerization beginning immediately after irradiation. In a typical run, a dose of 1.5×10^5 rep delivered in 12 pulses resulted in 1% polymerization after six hours and 5% polymerization after 50 hours.

59. Mund, W. and J.A. Herman.

Comparison quantitative des effets radiochimiques en phase liquide et en phase gazeuse. Academie Royal de Belgique Classe des Sciences Bulletin 37, 333-340 (1951).

60. Mund, W., J.A. Herman, and G. Verfaillie.

La polymerisation due chlorure de vinyle sous l action des rayons alpha. J. chim. phys. 35, 656-668 (1949).

Experiments on the polymerization of vinyl chloride. The results are interpreted through a free radical mechanism.

61. Mund, W., M. van Meerssche, and J. Momigny (Louvain).

On the radiochemical polymerization of vinyl chloride under constant pressure. Bull. Soc. Chim. Belg. 62, 109-118 (1953).

62. Mund, W., M. van Meerssche, and J. Momigny.

Influence of various factors on the isobaric radiochemical polymerization of vinyl chloride. Bull. Soc. Chim. Belges 62, 645-52 (1953) (in French).

In the radiochemically induced gaseous polymerization of vinyl chloride, the radiochemical reaction velocity is proportional to the radius of the reaction chamber and to the square of the pressure, and diminishes with increasing temperature. Inert gases are effective by increasing the number of collisions. Oxygen is consumed in terminating chains, but appears to give rise to the production of a catalyst which is itself consumed at a rate proportional to the radiochemical velocity.

63. Peebles, L.H., Jr.

The kinetics of vinyl acetate polymerization in benzene. Abstracts of Symposium on Applications of Radioactivity in the Rubber and Plastic Industries. Page B-4 (Oct. 1954).

The mechanism and kinetics of polymerization of vinyl acetate in the undiluted state and in benzene solution are discussed.

64. Rexer, Ernst.

Accelerated polymerization by radiation with gamma- and x-rays. Reichsber. Physic (beihefte Physik Z.) 1, 111-19 (1945).

The polymerization of methyl methacrylate at room temperature under the action of a radium preparation is determined. Polymerization occurs not only during, but after radiation. In both cases, the reaction is auto-catalytic, though much less rapid in the latter.

65. Seitzer, Walter H.

Initiation of polymerization by beta radiation. Dissertation Abstr. 14, 2214 University of Michigan (1954).

Polymerization of styrene and methylmethacrylate in solution was induced by the use of beta rays from a mixture of strontium-90 and yttrium-90. The reaction was induced by free radicals formed by the action of the beta particles on the solvent. Carbon tetrachloride was one of the most efficient, cyclohexane less efficient, and benzene least efficient. Beta radiation seems to be about one-tenth as effective as gamma.

66. Seitzer, Walter H., R.H. Goeckermann, and A.V. Tobolsky.

Beta ray initiation of polymerization of styrene and methyl methacrylate. J. Am. Chem. Soc. 75, 775 (1953).

The rates of beta-ray-induced polymerization of styrene (I), methyl methacrylate (II), and an equimolar mixture of I and II were determined at 30.5°C. The source of the beta particles was an equivalent mixture of anhydrous strontium-90-chloride and yttrium-90-chloride, which gave a spectrum of electrons with a maximum energy of 2.24 Mev. Air is a powerful inhibitor of both beta-ray-induced and thermal polymerization. The composition of the copolymer formed from beta-ray initiation indicates that a free-radical mechanism is operative. In the case of (I), 0.19% of the absorbed radiant energy is effective in producing radicals, and 2.3% in the case of (II).

67. Seitzer, Walter H. and A.V. Tobolsky.

Interaction of beta particles with organic liquids in the presence of vinyl monomers. J. Am. Chem. Soc. 77, 2687-92 (1955).

Solutions of common organic liquids with vinyl monomers (either styrene or methyl methacrylate) were exposed to a point source of beta particles, and the resulting rates of polymerization were measured for several monomer concentrations. An expression was derived which relates rate of chain initiation to the measured rate of polymerization in terms of the average absorption coefficient for the beta particles. The number of radical chain starters produced in the various organic liquids per 100 electron-volts of energy absorbed was thereby calculated. The halogen-containing solvents were the most sensitive to beta radiation among those tested. Fewer halogen atoms per molecule gave less sensitivity. Iodine atoms were more sensitive than bromine atoms. Hydrocarbons were the least efficient, the aromatics being less efficient than the aliphatics. Other functional groups, such as esters and ethers, had about the same level of efficiency as was found to exist with single halogen atoms.

68. Schmitz, John V., and Elliott J. Lawton.

Initiation of vinyl polymerization by means of high-energy electrons. Science 113, 718-719 (1951).

Difunctional vinyl monomers, such as tetraethyleneglycol dimethacrylate (TEGMA), polymerize much more than monomers containing only one double bond. Thus, irradiation of 1 ml samples, in air, with 2.5×10^6 equivalent roentgens accumulated in 17.5 seconds, produced only 1% of high polymer from methyl methacrylate. Similar irradiation of TEGMA produced a solid polymer in which 45% of the double bonds had been utilized, as measured by heat evolution. The electrons appeared to function as catalysts in initiating chain growth; the number of bonds reacting per ion pair was of the order of 10 in the former case and 500 in the latter. In the polymerizations

studied, the conversions were increased by either an increase in the dose or an increase in the length of time employed to administer the same dose.

The polymerization of cross-linking monomers initiated by high energy electrons was found to be dimensionally specific and could be used to form shaped objects in a pool of monomer.

D. Elastomers

69. Anon.

Reprieve in rubber. Chem. Week 77, 78-80 (1955).

The use of high energy radiations opens up new avenues of process research, i.e., the possibility of using both radiation and heat, the use of new synthetics which would require less dosage for vulcanization, and the use of sensitizers with radiation. However, such catalysts as organic disulfides and t-butyl hydroperoxide have not substantially boosted the process's efficiency in early tests.

70. Bernstein, I.A., E.C. Garmer, W.G. Rothchild, and F.F. Spaulding.

Studies on the gamma-radiation-induced polymerization of acrylonitrile. J. Chem. Phys. 21, 1303 (1953).

The effects of cobalt-gamma radiation on the polymerization of acrylonitrile monomer have been investigated in order to determine the feasibility of utilizing the pure monomer as a visual-indicating chemical dosimeter.

71. Collinson, E., and F.S. Dainton.

X-ray and gamma ray induced polymerization of aqueous solutions of acrylonitrile. Aberdeen University Press, Ltd., No. 12 (1953).

72. Dainton, F.S.

Effect of gamma and x rays on dilute aqueous solutions of acrylonitrile. Nature 160, 268-269 (1947).

The immediate effect of the absorption of high energy radiation by water is the ejection of electrons from the water molecules lying along the tracks of the rays. Weiss proposed that the activated water consists of a hydrogen atom and hydroxyl radical, possibly formed by direct dissociation of water or by electron capture and ion breakdown processes.

In order to test this view, types of reactions known to be brought about by neutral entities such as H or -OH, but unaffected by high concentrations of H or OH ions, were tested in dilute aqueous solution under irradiation by x rays or gamma rays. A polymerization chain-reaction was felt to be best. The monomer selected was acrylonitrile, the polymerization of which in aqueous solution can be initiated by OH radicals.

73. Mund, W., Ch. Guidée, and J. Vanderauwera.

Kinetics and products of the polymerization of isobutylene

by alpha rays. Bull. Classe Sci., Acad. Roy. Belg. 41, 805-15 (1955) (in French).

Alpha rays of radon gas initiate the polymerization of isobutylene in a reaction maintained at constant pressure by addition of the monomer as the polymerization progresses.

74. Prevot-Bernas, Annette.

Polymerization in the homogeneous and heterogeneous phase; dimethylformamide solutions of acrylonitrile. Compt. rend., 237, 1686-8 (1953).

The effects of the precipitation of the polymer on the reaction rate of the radio-polymerization of acrylonitrile solution were studied. The purified and deaerated solutions were irradiated with gamma rays of a 275-mc radium source (0.86 roentgen/min). The progress of the reaction was followed by dilatometry.

E. Adhesives

75. Brophy, John J., and Robert R. Perron.

Adhesive bonding processes. U.S. 2,668,133 (Feb. 2, 1954).

Curing a polymerizable adhesive by radiation, i.e., high-speed electrons, offers a rapid method of bonding that causes no significant rise in the temperatures of the adherends. Suitable sources of radiation are the microwave cavity electron accelerators and the dc electron accelerators. Satisfactory bonds to leather have been obtained with adhesives of the polyester, natural rubber, and synthetic-rubber types. Damage to the leather by heat is averted by subjecting it to radiation.

F. Miscellaneous Materials

76. Ballantine, D., A. Glines, and B. Manowitz.

Gamma-ray-initiated polymerization of N-vinylpyrollidone. U.S. Atomic Energy Commission Report BNL Report 2275 (1955).

It has been found that K value (which is an empirical constant related to viscosity) can be controlled by variation of monomer concentration, gamma ray intensity, and solvent composition. The K value increases with increasing monomer concentration and decreases with increasing intensity. K values are lower when nonaqueous solvents are used and rate simultaneously decreases. Temperature has little or no effect on K value.

The rate of polymerization was found to depend on monomer concentration to the first power and intensity to the half power. Rate of polymerization increases with temperature, going from 9.3%/min at 30°C to 17.8%/min at 69°C.

77. Ballantine, D.S., and B. Manowitz.

Status report on the gamma-ray-initiated polymerization of N-vinylpyrollidone. Progress Report on Fission Products Utilization VII. U.S. Atomic Energy Commission Report BNL Report 317, (T-53) (1954).

Gamma radiation from cobalt 60 has been used to polymerize N-vinylpyrollidone in an attempt to produce a polymer that might have use as a blood plasma expander of better quality than the commercial polymer. A study has been made of the effect of monomer concentration, temperature, gamma ray intensity, and solvent composition on the polymerization rate and average molecular weight.

78. Ballantine, D.S., and B. Manowitz.

Studies on the use of radiation as a catalyst for chemical reactions. Progress Report on Fission Products Utilization. VIII. BNL 389(T-73) (May 1956).

Polyvinylpyrollidone, equivalent to material produced commercially by peroxide catalysis, has been prepared by gamma irradiation of dilute aqueous solutions of the monomer, N-vinylpyrollidone. The kinetics of the reaction indicate that the rate of polymerization is a function of monomer concentration to the first power and intensity to the one-half power. The molecular weight, expressed as an empirical K value, increased with monomer concentration, decreased with increased intensity, and varied widely with the solvent used.

79. Heiks, Ray E.

Your future in nuclear energy. Chem. Week 18, 45-56 (Feb. 18, 1956).

An article covering: (a) The new markets springing up as a result of the advancement of this new industry (radiation-resistant materials for use in construction and in other applications where materials are subjected to a radiation atmosphere, chemicals involved in the reprocessing of fuel elements, decontamination materials, and agents for disposal of radioactive wastes); (b) Consideration of nuclear power as a new processing industry; the applications of nuclear power (in control applications, in radioisotope work, in commercial chemical processes); (c) The part that research has played and will play in the utilization of nuclear power in chemical processes; (d) Consideration of radiation sources; (e) The outlook for nuclear energy.

2. Irradiation of Polymers

A. General

80. Anon.

Plastics: boost heat resistance. Iron Age 174, 77-78 (1954).

In addition to temperature resistance, irradiation also increases corrosion resistance, since the plastic becomes less soluble in many liquids. Also, parts are easily fabricated, whereas costlier halo-polycarbons, also high temperature resistant, must be made by pressure molding.

It is possible that radioisotopes may be used, although control of this type of radiation would be more difficult and the use of generators involves no residual activity.

Stress-cracking is much reduced by irradiation of polyethylene.

81. Anon.

Why do polymers crosslink. (Report on 127th Nat'l ACS Meeting - Polymer Chem. Div.). Polymer Chem. 33, 1655-56 (1955).

Crosslinking of polymers by ionizing radiation results in increased tensile strength, reduced solubility, and increased abrasion resistance. Degradation is a competing reaction:

1. Impinging radiation causes molecules to ionize
2. then to split into free radicals and, finally,
3. to be raised to activated states.

These three events can occur in sequence from a single impact, and the result is an area in the polymer (called a spur) with molecules or molecular fragments at various levels of excitation.

Free radicals combine to form the desired crosslinks, or activated molecules can stabilize themselves by having fragments -- hydrogen or low molecular weight hydrocarbons -- split off, resulting in the undesired degradation.

82. Anon.

Science 122, 915 (1955).

For doses up to 10^8 roentgens, polyethylene tape and Formex wire enamel undergo discernible decreases in their resistance to short-time voltage breakdown. Cellulose acetate shows little change under the same conditions, and polyvinyl chloride shows some distinctly favorable alterations after

irradiation. Mica-and-glass tape, impregnated with silicone resin (an inorganic insulator) is virtually unaffected even at radiation levels up to 10^{10} roentgens.

83. Bennett, James F.

A guide to selection of organic materials suitable for radiochemical work. U.S. Atomic Energy Commission Report UCRL-2666, Technical Information Service, Oak Ridge, Tenn. (July 12, 1954).

Organic materials were tested at the Radiation Laboratory to determine their suitability for radiochemical operations. Any effects of irradiation, corrosive atmospheres, and temperature variables are listed.

84. Bopp, C.D., and O. Sisman.

Radiation stability of plastics and elastomers. U.S. Atomic Energy Commission Report ORNL-1373, Office of Technical Services, Department of Commerce, Washington, D.C. (July 1953).

The changes brought about by pile radiation, pile radiation with increased gamma component, cobalt-60 and gold-198 gamma on nine commercial elastomers sealed in aluminum cans containing air, 11 commercial elastomers sealed under helium, plasticized natural rubber, special formulations of natural rubber and Neoprene W, and 21 commercial plastics comprising synthetic fibers are reported. Measurements on the effect of oxygen, aging after irradiation, change in specific volume, and radiation-induced gassing are included. The radiation stability of the materials tested is linked to their structure.

85. Bopp, C.D., and O. Sisman.

The effect of high energy radiation on the vibration characteristics of high polymers. Abstracts of papers, 127th Meeting of American Chemical Society, Cincinnati, Ohio (March 29 to April 7, 1955).

The vibration characteristics were measured for certain irradiated elastomers and vinyl chloride polymers. The very small displacements used fulfill the assumptions made in the elasticity theory for calculating the dynamic Young's modulus and the viscous modulus. For vinyl chloride polymers the direction of the radiation-produced change in Young's modulus is governed by the pre-irradiation rigidity of the polymer. For the more rigid polymers, it is increased; for the less rigid polymers, it is decreased.

86. Bopp, C.D., and O. Sisman.

Radiation stability of plastics and elastomers. Nucleonics 13, No. 7, 28-33 (1955).

Data on how radiation affects plastics and elastomers show a rough relationship between radiation stability and Young's modulus. Generally, mineral-filled and rigid plastics are most stable. Natural rubber resists damage better than the synthetics. Addition of butyl rubber (which softens when irradiated) to natural rubber (which hardens) gives a product with irradiated strength inferior to that of natural rubber.

87. Bopp, C.D., and O. Sisman.

How radiation changes polymer mechanical properties. Nucleonics 13, (10) 51-55 (1955).

Ordinary elasticity, high elasticity, and viscous flow are the mechanisms of deformation of solid polymers. Qualitatively, the effect of radiation on the mechanical properties of polymers can be described by considering the effect of crosslinking and cleavage on these mechanisms. Crosslinking tends to impede viscous flow. The equilibrium value of Young's modulus for high elasticity is directly proportional to the concentration of crosslinks, but for ordinary elasticity the sensitivity of the Young's modulus is less for the more rigid materials. Cleavage reduces the yield stress for viscous flow and decreases the equilibrium value of Young's modulus for high elasticity. The Young's modulus for ordinary elasticity is again insensitive for the more rigid materials.

The changes in the mechanical properties of irradiated plastics and elastomers depend upon the rates of crosslinking and cleavage. These rates are governed by the polymer's chemical structure and the strength of the van der Waals forces. For uncrosslinked polymers, the change in Young's modulus is a measure of the crosslinking rate of the less rigid materials. Sensitivity to chain cleavage has been correlated with chemical structure for the materials studies.

88. Bopp, C.D., O. Sisman, W.K. Kirkland, and R.I. Towns.

Radiation stability of plastics and elastomers. Solid State division semiannual progress report. U.S. Atomic Energy Commission Report ORNL 1606, (August 31, 1953).

89. Bopp, C.D., O. Sisman, R.I. Towns, and W.K. Kirkland.

Dynamic properties of irradiated elastomers. U.S. Atomic Energy Commission Report ORNL 1677, 55-60 (Feb. 1954).

90. Bopp, C.D., O. Sisman, R.I. Towns, and W.K. Kirkland.

Radiation stability of plastics and elastomers. Solid State division quarterly progress report. U.S. Atomic Energy Commission Report ORNL 1506, (Feb. 10, 1956).

Dose rates and ozone effects are discussed.

91. Burr, J.G., and W.M. Garrison.

The effect of radiation on the physical properties of plastics. U.S. Atomic Energy Commission Report AECD-2078, (December 6, 1943).

Changes in tensile strength and electrical resistivity as a result of beta and gamma irradiation are presented for 25 different plastics and synthetic rubbers.

92. Charlesby, A.

The crosslinking and degradation of paraffin chains by high-energy radiation. Proc. Roy. Soc. (London) A222, 60-74 (1954).

n-Paraffins and polyethylene polymers have been subjected to radiation in a pile. The paraffins studied are C_7, C_{10}, C_{12}, C_{24}, C_{28}, C_{32}, and C_{36}. For the paraffins there is a decrease in their melting points until for a certain radiation dose they no longer melt at temperatures of 160°C or above. At this dosage the paraffin turns into an insoluble gel. The energy required to form a crosslink is independent of the chain length. From data on butane and methane this is extended to include n = 1. Earlier studies on deuteron and alpha bombardment of paraffins are now explained in terms of crosslinkages. For the polyethylene polymers, it is shown that for every crosslink formed, about 0.35 C-C bond in the main chain is fractured. Similar values are found for methane and butane. The greater susceptibility to fracture of the C-H bond compared with the C-C bond when subjected to radiation is in contrast to thermochemical data. There is evidence that the process of polymerization of saturated hydrocarbons under radiation occurs by a stepwise process, each link formed requiring a separate activation. The energy required per crosslink appears to be approximately independent of the physical state of the irradiated paraffin.

93. Charlesby, A.

Effect of molecular weight distribution on gel formation by high energy radiation. J. Polymer Sci. 14, 547-553 (1954).

The effect of exposing long-chain polymers to high-energy radiation is either to produce crosslinking or chain degradation. Changes in some of the properties are outlined. The formation of gel in many polymers offers a possibility for obtaining information regarding the initial molecular weight distribution. Results of a mathematical analysis of the amount of gel formed for various degrees of crosslinking are given. From the shape of the gel crosslinking curve, the ratio of z average, z + 1 average, etc., to weight-average molecular weight can be deduced. Formulae for the changes in the molecular weight of the sol are also given.

94. Charlesby, A.

How radiation affects long-chain polymers. Nucleonics 12, No. 6, 18-25 (1954).

Properties of many long-chain polymers can be modified considerably by exposure to high-energy ionizing radiation. The changes are far greater than those produced when most nonbiological materials are exposed to a similar amount of radiation, as a change of only one chemical bond of many hundreds can profoundly influence a material's physical properties even though the chemical structure is affected very little.

This article is concerned with the behavior of irradiated long-chain polymers of the thermoplastic type. The effect of radiation on polymerization of unsaturated monomers and on thermosetting resins of the urea-formaldehyde type is not considered.

95. Charlesby, A.

Effect of ionizing radiation on long-chain olefins and acetylenes. Radiation Research 2, 97-107 (1955).

Irradiation of unsaturated hydrocarbons (olefins and acetylenes) results in crosslinking similar to that observed for the equivalent saturated molecules (paraffins). The presence of the unsaturated bond does not appear to result in any chain reaction, with the exception of ethylene, although in this case chain reaction proceeds with far greater difficulty than for other monomers such as styrene and methyl methacrylate.

The ease of crosslinking depends on the position of the unsaturated bond. When near the center of the molecules, the bond behaves very much like a saturated bond in the corresponding paraffin; whereas, when it is at the end, the radiation energy required per crosslink is reduced from 32 ev (for the paraffin) to 19 ev (in the olefin) and 13 ev (in the acetylene).

The average energy per crosslink varies little with the length of the irradiated molecule.

The presence of two double bonds (in a diene molecule) reduces the energy per crosslink compared with molecules with only one double bond, but the difference is not great, certainly insufficient to indicate the occurrence of any chain reaction.

In addition to crosslinking, changes in isomerism of olefins take place under irradiation. Both trans and cis structures are converted into a mixture containing about 35% trans, after 10 units of radiation. There is very little change in unsaturation.

96. Charlesby, A.

Atomic radiation treatment of polymers. Research 8, 288-94 (1955).

Radiation from atomic piles consists of a mixture of corpuscular radiation -- fast electrons, neutrons, protons, and heavier particles; and of electromagnetic radiation -- x rays or gamma rays. When any of these forms of high-energy radiation pass through matter, energy is transferred to atoms of the irradiated material, resulting in the production of displaced atoms, free electrons, ions, and excited molecules. These may react with each other and with other molecules to produce conventional chemical changes and/or changes not achieved by ordinary chemical techniques.

97. Charlesby, A.

Irradiation of long-chain polymers. Chem. Engr. Prog. 51, 476-7 (1955).

Two major effects have been observed in long-chain polymers exposed to high-energy radiation. The first is termed crosslinking and corresponds to the formation of bridges or links between molecules, such links consisting of new primary bonds. As a result, a specimen is transformed from an assembly of separate linear or branched molecules, held together by weak secondary forces, into a 3-dimensional network, each atom linked to the others by primary bonds. The whole specimen now consists of a single gigantic molecule which cannot be melted, and whose properties depend on the density of these links. It is therefore possible to modify, to any desired extent, the physical properties of such materials merely by varying the radiation dose.

98. Charlesby, A.

Irradiation of polymeric substances. Brit. 732,047 (June 15, 1955).

High-molecular natural and synthetic substances with a chain structure, consisting largely of carbon atoms having an average of 1.5 carbon atoms directly attached thereto, were irradiated with high-energy sources, e.g., high-energy neutrons, gamma rays, x rays, protons, electrons, or alpha-particles. Prolonged irradiation caused undesirable changes. However, if shorter irradiation times were used, useful changes in physical properties took place. Effects obtained with polystyrene, polyvinylchloride, nylon, Neoprene, gutta percha, smoked rubber, polyvinyl acetate, rubber hydrochloride, and polyvinyl alcohol are described.

99. Charlesby, A.

Some radiation effects in long-chain polymers. Plastics Inst. Trans. 23, 133-8 (1955).

A discussion on the effects of atomic pile radiation in producing heat- and solvent-resistant products by crosslinking polyethylene, polystyrene, polyvinyl alcohol, polyvinyl acetate, nylon, silicones, Neoprene, rubber, and rubber hydrochloride. Polymethyl methacrylate, polyisobutylene, and polytetrafluoroethylene decomposed when exposed to such radiation.

100. Charlesby, A., and P. Alexander.

Crosslinking of polymers in aqueous solution by gamma rays. J. chim. phys. 52, 694-709 (1955) (in French).

The effect of x and gamma rays on a number of vinyl polymers in aqueous solutions has been studied. Certain polymers (such as polymethacrylic acid) deteriorate at all concentrations, while others deteriorate only if they are irradiated at concentrations less than, or equal to, 0.5%, but they are crosslinked, and separate in the form of a gel, if the concentration is higher. The influence of different factors on the crosslinking of polyvinylpyrrolidone is described. Several theoretical interpretations have been developed in the case where intermolecular bonds result from the interaction of an activated molecule with an ordinary molecule and in the case where the molecule of the polymer is broken into two fragments with active extremities which can then produce reticulation. The experimental results are in agreement with the second mechanism designating the "end linking." This case is developed in detail.

101. Coleman, J.H., and D. Bohm.

A method for increasing the electrical resistivity of insulators under ionizing radiation. J. Applied Phys. 24, 497-8 (1953).

Measurements on good insulators under beta radiation indicated that the induced specific volume resistivity decreased for a definite period of time, reached a minimum, and then actually increased until physical degradation resulted in surface leakage.

102. Davidson, W.L.

Elastomeric materials as shielding compounds for nuclear reactors. U.S. Atomic Energy Commission Report AECU-1952, (April 1, 1952).

Studies are reported on the evaluation of commercial elastomers and plastics to replace water as a neutron shield, with attendant saving in weight. Elastomers loaded with heavy fillers are also evaluated for use as total shields.

103. Durup, J.

Radiochemical degradation of high polymers. I. Theoretical study of the variation of mean molecular weights in numbers, in weights, viscometric, and of type Z. Measurement of the number of chain cleavages. J. chim. phys. 51, 64-73 (1954).

On the hypothesis that cleavages occur with equal probability at any bond of any chain, Durup considers the variation in the distribution of molecular masses during an infinitesimally small time, and compares this

distribution to a continuous distribution. A study is made of the variation of the limiting index of viscosity, as well as of other physical quantities, with the number of chain cleavages. Experimental application to the degradation of polystyrene by gamma radiation is given as an example.

104. Jones, Samuel S.

How radiation affects important materials. Gen. Elec. Rev. 57, No. 4,6-11 (1954).

A discussion is given of the effects of gamma radiation from a concentrated cobalt-60 source on various materials. Some fundamental conclusions are drawn, e.g., materials in which electrons are free to move (metals) and which are not particularly associated with any one atom do not suffer much. Otherwise, the effects can be drastic. Some rubbers become hard and brittle, others oily or tacky. Usually plastics suffer by rupture of large molecules. Glasses discolor, but their physical properties are not strongly affected. Lubricants can be profoundly changed.

105. Gauthier, J.

Some new industrial applications of x rays in the control of phenolics, thermoplastics, and rubber. J. ind. chim. Belge. 14, 205-10 (1949).

106. Karpov, V.L.

The action of nuclear radiation on high polymeric compounds. Conference on Peaceful Uses of Atomic Energy, Academy of Sciences U.S.S.R. p. 3-22 (July 1-5, 1955) Moscow, Publishing House of the Academy of Sciences of the U.S.S.R. 378 p. (1955).

A study of the changes in mechanical properties, solubility, and molecular weight taking place under irradiation showed that, depending on the molecular structure of the polymer, one of the following two types of process prevails: "crosslinking" or destruction. Crosslinking dominates in polyethylene, polyvinylchloride, natural rubber, and polyvinylbutyral; destruction in polyisobutylene, polymethylmethacrylate,polyvinylacetate, polyvinyl alcohol, thermovulcanizate of polybutadiene, and polytetrafluoroethylene. The gases evolving during the irradiation of various polymers were investigated.

107. Leeser, D.O.

How nuclear radiation affects engineering materials. Materials and Methods 40, 110-20 (1954).

The effects of various radiation intensities on the mechanical and physical properties of metals (stainless steels, carbon steels, nickel, nickel alloys, zirconium, Tantalloy, tungsten, Tantung G, tantalum and cobalt alloys), and nonmetals (elastomers, electric insulators, plastics, and oil)

are given. Results are tabulated. The mechanisms of radiation damage and test procedures are discussed.

108. Levy, P.W., and G.J. Dienes.

Research on radiation effects in insulating materials at Brookhaven National Laboratory. ONL symposium Report ACR-2. Conference on Effects of Radiation on Dielectric Materials, Washington, D.C. pp. 39-50 (Dec. 1954).

Research work in progress at Brookhaven National Laboratory on radiation effects in insulating materials is described. This work is concentrated on high melting inorganic oxides, compounds of mixed ionic and covalent bonding, and organic high polymers.

109. Mannal, C., C.A. Bruch, and R.F. Loenig.

Atomic radiations change materials. Power 99, 94-96, 196, 198, 200 (1955).

A general article dealing with types of radiation, how they affect matter in general, the effect on nonmetals and structural metals.

110. Miller, A.A., E.J. Lawton, and J.S. Balwit.

The radiation chemistry of hydrocarbon polymers: polyethylene, polymethylene, and octacosane. J. Phys. Chem. 60, 599-604 (1956).

Polymethylene, polyethylene and octacosane were irradiated with high-energy (800 kv) electrons. Crosslinking, changes in unsaturation, and gas evolution were measured. The only type of unsaturation formed is trans-vinylene, which is produced in approximately equal yields in all three hydrocarbons. About 40% of the hydrogen evolved comes from this reaction, the remainder from crosslinking. Volatile hydrocarbons result from C-C scissions near the chain-ends and at the short branches in polyethylene. The results indicate that in the unbranched hydrocarbons, polymethylene and octacosane, permanent C-C scissions do not occur at random throughout the hydrocarbon chain. In polyethylene the evidence is not as clear, but the tentative conclusion is that some main-chain cleavage leading to methyl end-groups may occur. Radiation yields (G values) for crosslinking, vinylene unsaturation, gas evolution, and a general mechanism for crosslinking of these hydrocarbon structures are presented.

111. Mincher, E.L.

Summary of available data on radiation damage to various nonmetallic materials. Report No. KAPL-731 (April 2, 1952). General Electric Co. Declassified in 1955.

Data on effects of pile radiation on organic and inorganic materials are summarized. The effects of gamma radiation on the viscosity

of lubricants, beta and gamma radiation on the tensile strength and electrical resistivity of plastics and synthetic rubbers, and neutron radiation on the electrical properties of ceramic insulators are tabulated.

112. Muller, F.A., and H.G. Nordlin.

The effects of ionizing radiation on the electrical conductivity of the high-quality insulating materials. Presented at Conference on Electrical Insulation, National Research Council, Lennox, Mass. (Oct. 2 to 4, 1952).

Some of the effects of high-energy radiation on the conduction properties of several low-loss plastics have been measured.

Conductivity was found to increase with increasing irradiation rate, being proportional to a power function of the rate. The exponent is different for different materials but always within the range between about one-half and one. Radiation-induced changes in conductivity in these materials do not occur instantaneously. The increase when irradiation is begun is more rapid than the recovery after irradiation is stopped.

113. Namur, Paul.

Irradiation of plastics by high-energy particles. Kunststoffe 45, 421-4 (1955).

A review.

114. Newhall, R.G.

Applications of plastics in radiation research. Technical Report No. 2. Western Plastics 2, 21 (1955).

Plastics used or considered for use in establishments carrying out radiation research are discussed, and their area of application in the design and set-up of such establishments is examined.

115. Ryan, John W.

Effect of gamma radiation on certain rubbers and plastics. Nucleonics 11, No. 8, 13-15 (1953).

Samples of polyethylene, nylon, Koroseal, Buna-N, Neoprene and natural rubber were exposed to gamma flux of 10^{11} photons/square centimeter second (fission product spectrum) for 6 months. The stress-elongation relation showed a steep increase for all of the irradiated samples. The hardness remained either identical (polyethylene, nylon) or was higher than in the controls. The "compression set," defined as $(t_o-t)/t_o$, where t_o is the original thickness and t the thickness after compression, yielded larger values than comparable unirradiated sets. No cracks appeared in the material, but a loss of flexibility and luster could be observed. Koroseal and Neoprene evolved chloride ions and corroded the aluminum containers. An appreciable

growth in the amount of crosslinkage was indicated that accounted for the decrease of plastic flow and increase in elastic modulus and hardness. Gas evolution also occurred.

116. Ryan, J.W.

Theory of the changes in physical characteristics of plastics caused by radiation. Soc. Plastics Eng. Journal 10, No. 1, 11, 40-1 (1954).

It is evident from recent and past work in this field that an increase in the high temperature characteristics of polymers can be anticipated. The principal mechanisms of radiation adsorption by gamma and x rays are the Compton, pair-production, and photoelectric effects. In addition to the processes initiated by free radicals, there is proposed a "Functionality Series" such that the highest functional group tends to transmit energy received from the interaction with a photon to a lesser transmitting group where it selectively decomposes.

117. Sisman, O., and C.D. Bopp.

Radiation stability of plastics and elastomers. U.S. Atomic Energy Commission Report ORNL-1373 (July 23, 1953).

118. Sisman, O., C.D. Bopp, W.K. Kirkland, and R.L. Towns.

Radiation stability of plastics and elastomers. Solid State Division Semiannual Progress Report, U.S. Atomic Energy Commission Report ORNL-1606, 86-93 (1954).

119. Sisman, O., C.D. Bopp, R.L. Towns, and W.K. Kirkland.

Dynamic properties of irradiated elastomers. Solid State Progress Report, U.S. Atomic Energy Commission Report ORNL-1677, 55-60 (Feb. 1954).

120. Sun, K.H.

A general survey of effects of atomic radiations on high polymers. Abstracts Symposium on Applications of Radioactivity in the Rubber and Plastic Industries Abst. B-3, Pub. by Tracerlab, Inc. (Oct. 6-8, 1954).

Since high polymers are covalent substances, the effect of radiation is largely caused by ionization and electronic excitation. These processes cause instantaneous excitation, instantaneous flow of electrons, breaking and rearranging of chemical bonds, and formation of free radicals, resulting in initiation of chemical reactions. Resulting phenomena include: (1) gas liberation, (2) double bond formation degradation, (3) polymerization, (4) crosslinking, (5) vulcanization, (6) vitrification, and (7) hydrogenation. As a result, physical property alterations occur.

Understanding of the damaging effects of radiation has resulted in the development of radio-resistant polymers. Studies of beneficial effects provide a new experimental variable or tool unique in itself. Already, high polymers of better physical or chemical properties have been achieved.

A brief review of various radiation sources is given.

121. Sun, K.H.

Effects of atomic radiation on high polymers. Modern Plastics, 32, 141-144, 146, 148, 150, 229-233, 236-238 (1954).

This is a review; it covers the following topics: atomic radiation, penetration of radiation, units of radiation, radiation sources, physiochemical changes, phenomenological changes, primary changes, secondary changes, and applications of radiation.

122. Sun, K.H.

Effects of atomic radiation on high polymers. ONL Symposium Report ACR-2, Effects of Radiation on Dielectrics Materials, Washington, D.C. 103-121 (1954).

When atomic radiation passes through ordinary matter, the energy is dissipated largely through ionization and electronic excitation, a small fraction through atomic displacement and lattice disturbance, and, usually, an even smaller fraction through transmutation. For different kinds of radiation and matter, the effects differ primarily in degree rather than in kind.

As high polymers are covalent substances, the effect of radiation is largely caused by ionization and electronic excitation. These processes cause instantaneous flow of electric current, breakage and rearrangement of chemical bonds, and formation of free radicals. Consequently, chemical reactions are initiated. The phenomenological results include gas liberation, double-bond formation and elimination, degradation, polymerization, crosslinking and vulcanization, vitrification, hydrogenation, etc.

123. U.S. Technical Services Office

High energy radiation of polymers, a literature review. PB Report No. 111529 (1953).

124. Wall, L.A.

Atomic radiation and polymers. Soc. Plastics Eng. Journal 12, No. 3, 17-20 (1956).

A review.

125. Wall, Leo A.

Factors influencing the behavior of polymers exposed to high-energy radiation. J. Polymer Sci. 17, 141-2 (1955).

The relative stabilities of radicals formed by radiation have been advanced as an important factor in determining the direction of the radiation effect (i.e., crosslinking or degradation). This presents additional factors to be considered.

Heats of polymerization and pyrolytic behavior of certain high polymers are compared with the effects observed upon exposure of the polymers to radiation. Polymers degraded by radiation have heats of polymerization and are interpreted as the presence of large steric repulsions operating between substituent groups. Therefore, it might be suspected that in degrading polymers chain bonds once broken would have difficulty in reforming, and that the structure of radicals formed would be favorable for disproportionation.

126. Wall, L. A., and M. Magat.

Degradation of polymers by gamma rays and neutrons. J. chim. phys. 50, 308-16 (1953).

Degradation of solid polymers by irradiation in a pile and degradation of polymers in solution irradiated by gamma rays have been studied with the aid of the viscometric method. It was found in the first case that, by varying the structure of the polymers, either augmentation or diminution of the molecular weights can be obtained. It was also shown that, according to the type of polymer, the measured intrinsic viscosity can be modified by dissolving the polymer in solvents containing inhibitors. This is considered proof of the existence, in the solid polymer after irradiation, of immobilized free radicals. In the case of gamma rays, the presence of oxygen is necessary to the degradation when the solutions of high polymers are irradiated. An after effect is observed which can be eliminated by the addition of an inhibitor following the period of irradiation.

127. Wall, Leo A., and M. Magat.

Effects of atomic radiation of polymers. Modern Plastics 30, 111-12, 14, 16, 76, 78 (1953).

The effects on solid polymers of exposure to atomic pile radiation, and degradation of solutions by exposure to gamma rays from radium, have been studied by use of viscosity methods. In the first case variation of the structure of the polymer has been shown to cause both increases and decreases of molecular weight. It has also been demonstrated that, depending on the type of polymer, the measured intrinsic viscosity can be varied by the use of inhibitor-containing solvents in carrying out the measurement. This is taken to be evidence of immobilized free radicals within the solid polymer after exposure.

B. Thermoplastic Materials

128. Alexander, P., and A. Charlesby.

Energy transfer in macromolecules exposed to ionizing radiations. Nature 173, 578-579 (1954).

Experiments with synthetic polymers provide direct evidence for energy transfer in saturated macromolecules of different constitution.

Polymethyl methacrylate is degraded at random by gamma and pile radiation. From the simple function relating molecular weight to radiation dose, it was computed that one main-chain bond was broken for every 61 ev of energy absorbed. This energy is used for main-chain break and associated reactions, such as decomposition of the ester side-chain. When films of polymer containing 10% of allyl thiourea, aniline, or di-meta-tolylthiourea were irradiated, 143, 152, and 227 ev, respectively, had to be taken up by the system before a main-chain bond was ruptured. This protective effect, occurring in a system where the action of the radiation is direct, is now being studied in detail.

129. Alexander, P., and A. Charlesby.

Radiation protection in copolymers of isobutylene and styrene. Proc. Roy. Soc. A230, 136-145 (1955).

The effect of ionizing radiations on copolymers of isobutylene and styrene were studied. Molecules consisting only of isobutylene units degrade under radiation, whereas the styrene polymer crosslinks. In the copolymer the styrene units offer protection against radiation to the neighboring isobutylene units. An estimate of the extent of this protection is given.

130. Alexander, P., A. Charlesby, and M. Ross.

The degradation of solid polymethylmethacrylate by ionizing radiation. Proc. Roy. Soc. (London) A223, 392-404 (1954).

When polymethylmethacrylate in the solid form is irradiated in the atomic pile, or with gamma radiation, two reactions predominate: (a) breakdown of the main chain, and (b) decomposition of the side-chain with evolution of gases. The first was followed by changes in viscosity. A linear relationship is obtained between R and $1/M_V$ where R is the dose and M_V is the viscosity molecular weight. The degradation is thought to proceed by random rupture of main-chain C-C bonds by rearrangement of the excited polymer, and 61 ev are absorbed per fractured bond. For each main-chain rupture approximately one ester side-chain is also decomposed.

The cage effect is thought to prevent direct dissociation, and reaction occurs by rearrangement of the molecule to give relatively stable entities. Added substances reduce the amount of degradation. (Possibly by transfer of energy from the excited polymer molecule.) This is only possible if the excited molecules have an appreciable life before decomposition.

Viscosity measurements on irradiated polymethylmethacrylate in the solid form offer a possible means of measuring high-energy radiation doses in the range of about 1 million roentgens and up.

131. Alexander, P., and M. Fox.

Polymerization and depolymerization by x rays. Effects of protective agents. J. chim. Phys. 50, 415-22 (1953).

Polymethacrylic acid in aqueous solution is degraded by x rays in the presence of oxygen, and evidence is presented that the HO_2 radicals are responsible for the rupture of the C-C bond in the polymer chain. Experiments with a synthetic polyphosphate indicate that the P-O bond is not easily ruptured by the radicals produced in aqueous solution by the ionizing radiation. The addition of amines, sulfides, and indole derivatives attenuates the degradation. The polymerization of polymethacrylic acid in aqueous solution by x rays was also studied, and certain protective substances were found that greatly reduce the amount of polymer formed.

132. Alexander, P., and M. Fox.

Degradation of polymethacrylic acid by x rays. Trans. Faraday Soc. 50, 605-12 (1954).

The number of breaks in the main chains in aqueous solution was proportional to the quantity of x rays and the effect was brought about by free radicals formed as a result of the ionization of water. The polymer was more readily degraded when expanded, but there was no difference between the random coil and condensed particle. Oxygen was necessary for the degradation to take place, and as hydrogen peroxide did not decompose the polymer it was believed that HO_2 radicals were responsible for the chain scission. Hydrogen peroxide enhanced the degradation and, at a concentration greater than 10^{-6}M, the amount of degradation was almost exactly doubled (i.e., 500 roentgens in the presence of hydrogen peroxide caused the same drop in viscosity as 1000 roentgens alone). Hydroxyl radicals may react with polymethacrylic acid, but the reaction product did not decompose in such a way as to break up the polymer chain.

133. Anon.

Crosslinking of polythene in the atomic pile. Brit. Plastics 26, 79-81 (1953).

134. Anon.

Polypropertied polymers. Ind. Eng. Chem. 45, 11A, 13A (1953).

Variations in the heat stability, solubility, and mechanical properties of polyethylene can be obtained by changing the radiation dosage. Although the nominal melting point for polyethylene is approximately 115°C,

samples which have been irradiated for short periods can be taken up to 250°C or above without losing their shapes.

Irradiation has been found not only to produce crosslinking in polyethylene, but also to reduce the degree of crystallinity present at room temperature.

Irradiated polyethylene suffers only a surface attack when immersed in boiling sulfuric acid; in aqua regia at 100°C the attack is also confined to the surface.

135. Anon.

Crosslinked polyethylene. Chem. Eng. News 32, 1392 (1954).

Irradiated polyethylene is offered in narrow film form by GE's chemical division under the name Irrathene. This material has greater heat and chemical resistance than normal polyethylene; superior properties result from bombardment of polyethylene with high-energy cathode rays from million-volt electron generators.

136. Anon.

Atom smasher: new process tool. Chem. Eng. 63, 114-116 (1956).

Bradley Containers, at Maynard, Mass., is using a 2-Mev Van de Graaf particle accelerator to sterilize pharmaceutical packages, either filled or empty, and to irradiate injection-molded, mass-produced polyethylene items.

137. Anon.

New products using nuclear techniques. Atomic Energy Newsletter 14, 4 (1955).

Carbon black reinforcing filler has been added to polyethylene which has then been irradiated. The resulting product has superior properties. Before irradiation, the filled polyethylene was stiff, brittle, and had no desirable physical properties. The irradiated, filled material is said to have a tensile strength in the upper temperature ranges that is five to eight times that of the unfilled, irradiated material. It is not stiff or brittle and has improved tear strength and "cut through" qualities at both normal and elevated temperatures.

138. Anon.

Discuss two polyethylenes. Plastics Technology 1 (10), 637 (1955).

A new material, Irrathene 210 (a polyethylene), which is available in the film form, shrinks 40-50% when exposed to temperature of

150°C (an advantage in packaging operations). In general, the tensile strength of irradiated polyethylenes becomes lower through temperature resistance and crosslinkage. Polyethylene is actually upgraded by irradiation, but this process must be carried out after molding through the use of an electric generator.

139. Anon.

New developments in irradiated polyethylene. Materials and Methods 41 (2), 104-5 (Feb. 1955).

Essentially, irradiation converts polyethylene from a thermoplastic to an infusible material. Irradiated polyethylene exhibits no stress-cracking. Although its solvent resistance is only slightly improved at ordinary temperatures, it is much improved at elevated temperatures. There seems to be evidence that elevated temperature dielectric strength is also improved. Irradiated polyethylene becomes elastomeric at elevated temperatures. Irradiation does not significantly improve room temperature strength or toughness, and the advantages offered by irradiated polyethylene are pretty much confined to elevated temperature applications. Whereas ordinary polyethylene melts at about 230°F, irradiated polyethylene can be used continuously at this temperature and it maintains form stability (under no load) at temperatures as high as 350°F. However, injection-molded parts that have been irradiated tend to warp as a result of relief of molding stresses (as do nonirradiated parts).

140. Ballantine, D.S.

Irradiation of plastics. Paper presented at the S.P.E. Technical Conference, 12th Annual Meeting, Cleveland, Ohio (Jan. 18-20, 1956).

The effects of radiation on polystyrene, nylon, acrylic, polyethylene, and other plastics are discussed, with particular reference to its effects on polyethylene. A variety of graft copolymers has been produced by irradiation of polymers in the presence of a monomer.

141. Ballantine, D.S., G.J. Dienes, B. Manowitz, P. Ander, and R.B. Mesrobian.

Evaluation of polyethylene crosslinked by ionizing radiation. J. Polymer Sci. 13, 410-14 (1954).

Samples of pure polyethylene film of 4 mil thickness, and rod of 1-inch diameter, obtained from Bakelite Corporation, were used. The source of ionizing radiation was a cobalt-60 gamma source.

142. Baskett, A.C., and C.W. Miller.

Electron irradiation of polythene. Nature 174, 364-5 (1954).

The material was irradiated with electrons of a 4-Mev travelling-wave linear accelerator (500 w, 125 microamp). The beam had a

nearly uniform spread over an area of 20 square centimeters at a distance of 70 centimeters from the window; likewise, the effects of the radiation throughout the sample varied only 10% over most of the electron range. Gel fractions (with 0.4% solution fraction) from lightly-crosslinked polymers indicate, on further irradiation, an increase in solubility (chain scission). The limiting soluble fraction is 2.4-2.8% -- appreciably less than that expected for pile radiation on the basis of an exponential distribution of original molecular weight. The obtained value of 0.18-0.20 for beta (ratio of main-chain scissions to atoms crosslinked) can be applied to estimate the gel fraction which would arise if no scission occurred. The original molecular weight calculated from this information indicates a wide distribution.

143. Bockhoff, F.J., and J.A. Neumann.

A new material: irradiated polyethylene. Chem. Eng. 62, 228, 230, 232, 234 (1955).

Irradiated polyethylene can be produced by the bombardment of conventional polyethylene with extremely high-energy electrons. This treatment results in a transformation of properties, in that polyethylene is changed from an easily fusible thermoplastic to a thermoset material which retains form stability at temperatures as high as 400°F. A definite increase in certain mechanical properties is also noted and these improvements are retained at elevated temperatures. Solvent resistance is increased, and the phenomenon of stress-cracking is completely eliminated. Yet, within proper dose limits, irradiated polyethylene retains all of the traditionally desirable properties of conventional polyethylene, i.e., toughness, flexibility, impact resistance, and complete inertness in most chemical environments.

144. Campbell, J.B.

Irradiated polyethylene. Materials and Methods 40, 91-95 (1955).

When polyethylene, ordinarily thermoplastic, is bombarded by high-energy electrons, it becomes a new, infusible material. The first commercially available irradiated polyethylene is General Electric's Irrathene 101, which is only lightly crosslinked to preserve the flexibility and toughness of the conventional plastic. It is presently available only in the tape form.

145. Chapiro, A.

Action of x rays on polymers in the solid state. I. Crosslinking of polyethylene. J. chim. phys. 52, 246-58 (1955).

The course of crosslinking of polyethylene under irradiation by x rays was studied by means of the fusion point. An apparatus is described for measurement of curves of stretching, at a constant load, as a function of the temperature, and for determination of the temperature at which small plates of polyethylene rupture. Yield of crosslinking for different intensities of radiation for irradiation under vacuum or nitrogen and in the air were

studied. For the latter, 3 types of curves, depending on radiation intensity, resulted. Above 400 roentgens/minute, about 2.5×10^6 roentgens are necessary to render polyethylene infusible. Below 100 roentgen/minute, oxidative degradation occurs. In the absence of air, polyethylene becomes infusible after a dose of 10^6 roentgens, regardless of intensity of radiation. The results lead to the following radiochemical output: G air linkages = 0.75 linkage by 100 e.v.; G vacuum linkages = 1.9 linkages by 100 e.v.; G_R = 5.1 primary radicals by 100 e.v.

146. Chapiro, A.

Relative radiochemical efficiencies of mixed radiation from the atomic pile and of gamma rays. Compt. rend. 239, 703-5 (1954).

The relative efficiencies of mixed radiation from the Zoé (heavy water) pile and of gamma radiation from cobalt-60 in their effects on several chemical systems are described. Included are comparisons for reduction of ferric o-phenanthroline, oxidation of ferrous sulfate, crosslinking of polyethylene, and the degradation of methyl polymethacrylate. The effects of position in the pile and capture cross section are discussed

147. Charlesby, A.

Crosslinking of polythene by pile radiation. Proc. Roy. Soc. A215, 187 (1952).

148. Charlesby, A.

Swelling properties of polystyrene crosslinked by high-energy radiation. J. Polymer Sci. 11, 521-29 (1953).

149. Charlesby, A., and J.C. Bevington.

The mechanisms of radiation-induced changes in high polymers. British Atomic Energy Authority. Unclassified Report AERE, M/M 85 (1954).

150. Charlesby, A., and N.H. Hancock.

The influence of crosslinking on the elastic modulus of polyethylene. British Atomic Energy Authority AERE M/R-1060 (1952).

The effect of Young's modulus, E, is studied when polythene is crosslinked by pile irradiation. Dynamic and static measurements of E are given at various temperatures and for varying degrees of crosslinking. At room temperature, E decreases at first with increasing crosslinking, resulting in a more flexible polymer. With further crosslinking E increases rapidly, as a glass-like amorphous structure is produced.

Pile radiation of polythene destroys crystallinity and produces crosslinking. At room temperature the former effect predominates up to about 8% crosslinking. As a result, a more flexible material is produced. Beyond this point the crosslinked material becomes more rigid and glass-like.

151. Charlesby, A., and N.H. Hancock.

The effect of crosslinking on the elastic modulus of polythene. Proc. Roy. Soc. A281, 245-255 (1953).

(see above)

152. Charlesby, A., and M. Ross.

Breakdown of methyl methacrylate polymer by high-energy radiation. Nature 171, 1153 (1953).

Polymethyl methacrylate (Perspex) shows rapid breakdown after relatively short radiation doses. The nature of the changes produced is complex and appears to vary with the temperature as well as the radiation dose.

153. Charlesby, A., and M. Ross.

The effect of crosslinking on the density and melting of polythene. Proc. Roy. Soc. A217, 122-35 (1953).

The density of polythene was studied in relation to temperature and the degree of crosslinking produced by pile irradiation. Crosslinking results in a progressive reduction in the percentage of crystalline material at room temperature. The transition temperature corresponding to melting in ordinary polythene is only very slightly decreased with increasing crosslinking, so that the temperature at which all crystalline structure vanishes is little affected.

154. Cole, Q.P.

Effect of irradiation on polyethylene coatings. Gordon Research Conference on Organic Coatings. (July 15, 1954).

155. Cole, Q.P.

Property changes in polyethylene induced by radiation. Abstracts of Papers, 127th Meeting of the American Chemical Society, Cincinnati, Ohio (March 29 to April 7, 1955).

Irradiation of polyethylene with high-energy electrons causes the formation of crosslinks, with resultant gelation of a portion of the polymer. The size of this portion and the consequent changes in the behavior of the polyethylene are a function of the irradiation dose. The relationships between irradiation dose and several properties in the irradiated material have been studied.

156. Dole, M., and C.D. Keeling.

Long-range migration of chemical activity in the solid state. J. Am. Chem. Soc. 75, 6082 (1953).

A study of the chemical effects of irradiation in vacuo on solid polyethylene in the heavy-water pile showed that the concentration of vinylidene groups decreases linearly with radiation time, while the concentration of trans-vinylene groups increases simultaneously. There is in this type of polyethylene only one vinylidene group per 2300 C atoms, yet one vinylidene group is eliminated for every 3.6 mols of H evolved. In explanation, long-range migration of chemically active centers in the polyethylene is postulated.

157. Dole, M., C.D. Keeling, and D.G. Rose.

Pile irradiation of polyethylene. J. Am. Chem. Soc. 76, 4304-11 (1954).

The comparison of evolved gases, stress-strain relations, tensile strength, bromine absorption, infrared absorption, extent of gel formation, and the viscosity of solutions were measured on polyethylene (I) irradiated in heavy water in vacuo and in air. The vinylidene groups disappeared from (I) as hydrogen was evolved and vinylene groups were formed. About 70-80% of the hydrogen evolved formed unsaturated compounds and about 20% produced crosslinkages that gave pronounced changes in the stress-strain properties without significant changes in the tensile strength. The rapid initial decrease in vinylidene concentrations is explained as a long-range migration of chemically active centers.

158. Dole, M., C.D. Keeling, and D.G. Rose.

How polyethylene crosslinks. Chem. Engr. News 32, 1342 (1954).

Polyethylene molecules are long hydrocarbon chains similar to much-elongated paraffin hydrocarbon molecules. They are essentially saturated straight chains, although there is some branching and each molecule is thought to contain one unsaturated vinylidene group. Neutrons and gamma rays cause the ejection of hydrogen atoms from the chain, leaving an active free radical center. Irradiation also brings about inactivation of the vinylidene groups. Since there is only about one/2300 carbon atoms in the chain, the statistical probability of a group being affected is only two in 2300. It was found that one group disappeared for every 3.6 molecules of hydrogen evolved -- each hydrogen atom representing one reaction in the chain.

159. Feng, Paul Y.

Electrical conductivity of solid dielectrics under beta radiation: radiation chemical effects in polystyrene. Thesis (Washington University, St. Louis, Mo.) (1954).

160. Feng, Paul Y.

Radiation chemical effects in polystyrene. Abstracts of Papers of the 126th Meeting of the American Chemical Society, New York, N.Y. (September 12 to 17, 1954).

Irradiation of polystyrene by beta particles is found to cause degradation if air is present but further polymerization if air is excluded. Bombardment of polystyrene by deuterons in a helium atmosphere caused extensive crosslinkage. The data obtained in studies of the radiation chemical effect in polystyrene show that the rate of polymerization depends on the square root of the radiation intensity. In the presence of air the rate of degradation varies somewhere between the square root and the first power of the radiation intensity.

161. Feng, Paul Y., and Joseph W. Kennedy.

Electrical and chemical effects of beta radiation on polystyrene. J. Am. Chem. Soc. 77, 847-51 (1955).

The electrical conductance of polystyrene, polyethylene, and Teflon under beta irradiation has been studied by investigation of the potentials produced by the passage of beta rays through the dielectrics. The potentials agree with values calculated from the assumption that the dielectric conductance is proportional to the concentrations of radiation-produced ions, and that these ions disappear by bimolecular reaction. Irradiation of polystyrene causes degradation if air is present, the rate depending on something between powers of 1/2 and 1 of radiation intensity. In the absence of air, irradiation causes further polymerization, the rate varying with $(\text{intensity})^{1/2}$. Bombardment of polystyrene in a helium atmosphere by deuterons causes extensive crosslinkage.

162. Field, F.H.

Electron impact studies of the vinyl ion and radical. J. Chem. Phys. 21, 1506 (Sept. 1953).

The change produced in the optical absorption of various substances has been suggested as a means of measuring high doses of ionizing radiation. The darkening of red-dyed polymethyl methacrylate (Perspex 400) was found to be linear with ray dosage up to 3×10^5 roentgens. Silver-activated glass was recently suggested for measuring gamma and beta doses between 10^3 and 10^6 rep. A saturation of absorption with increasing dosage was found at about 2×10^6 rep.

163. Fowler, J.F., and F.T. Farmer.

Conductivity induced by x rays in polyethylene terephthalate: a possible insulator for radiological apparatus. Nature 175, 590-91 (1955).

Measurements of the conductivity induced by x rays in Melinex (polyethylene terephthalate sheet) have been made using the dc amplifier techniques. The specimens consisting of sheets of Melinex film 0.03 mm in thickness were placed in a chamber that could be evacuated. The magnitudes of the static and induced conductivity upon temperature and dose-rate, and the shape of the decay curve after irradiation, were determined.

164. Fowler, J.F., and F.T. Farmer.

Conductivity induced in insulating materials by x rays. Nature 173, 317 (1954).

Measurements of the conductivity induced in insulating materials by x rays and gamma rays have shown the existence of a long-period decay, and more recent investigations have shown that the electron trapping mechanisms which apply to photoconductivity also apply to these materials. This general picture may make it possible to elucidate the energy level distribution of the material.

165. Fowler, J.F., and F.T. Farmer.

Conductivity induced in polytetrafluorethylene by x rays. Nature 174, 136 (1954).

The equilibrium induced current i is related to the dose rate R by the general relationship $i \propto R^{\Delta}$, where Δ is a characteristic of the material. For polytetrafluoroethylene over the range R equals 2 to 65 roentgens/min and between 20° and 110°C, Δ equals 0.63 ± 0.08 with the higher values at the lower temperatures. This is in contrast to Perspex and some specimens of amber, but is comparable to polythene.

166. Fowler, J.F., and F.T. Farmer.

Conductivity induced in unplasticized Perspex by x rays. Nature 175, 516-17 (1955).

The conductivity induced in unplasticized Perspex (polymethyl-methacrylate) by x rays differs markedly from that induced in ordinary plasticized Perspex: (1) the time-constant of recovery after irradiation is very long for unplasticized Perspex, and (2) the equilibrium induced current i_x is related to the dose rate R by the general formula $i_x \propto R^{\Delta}$, where Δ equals 0.55 ± 0.05 for unplasticized but is nearly unity for the plasticized Perspex. These properties place unplasticized Perspex in the same class of behavior as polyethylene, polytetrafluoroethene, and polystyrene.

The range of dose rates was 2.64 roentgens/minute and the range of temperature 20-80°C for plasticized and 20-100°C for unplasticized Perspex.

167. Gilfillan, E.S., and L. Linden.

Effects of nuclear radiation on the strength of yarns. Textile Research J., 25, 773-7 (1955).

Two competing physical changes take place in an irradiated fiber: one is crosslinkage of the polymer chains, which tends to strengthen the fiber; the other, chemical degradation, which tends to break the chains and to some extent destroy the crosslinkage previously formed by the radiation, thereby weakening the fiber. Gamma radiation seriously weakened the cellulosic fibers and nylon, but had no visible effect on the strength of the type 81 nylon. Neutron irradiation weakened all of the fibers tested. For the same amounts of neutron irradiation, the cellulosic fibers were weakened sufficiently to make it impractical to test them.

168. Goodwin, P.A.

Applications of irradiated polyethylene. Modern Plastics 32, 102 (1955).

Most of the development work on the irradiation of plastics in the Chemical and Metallurgical Division of General Electric Company is centered on Irrathene, an irradiated polyethylene. It is still limited to use in tapes and films. There are 2 grades: Irrathene 101 and 201. Irrathene 101 is similar to the conventional polyethylene but does not melt at temperatures as high as 350°F and has outstanding resistance to stress-cracking in a broad range of chemicals. It is slightly crosslinked, sufficiently to make it non-melting without loss of flexibility or toughness. Irrathene 201 was developed especially for electrical insulation and contains an oxidation inhibitor which will permit its continuous use at 125°C (or even higher in special applications).

169. Goodwin, P.A.

Irradiated 201 -- irradiated polyethylene. A new form of electrical insulation. Paper presented at Symposium on Electron Beam Radiation, Wisconsin (March 21-22, 1955).

170. Goodwin, P.A., and J.W. Wetzel.

Irradiated polyethylene. General Electric Review 58, 48-51 (1955).

Polyethylene requires only a relatively small dose of radiation to make it non-melting and insoluble in organic solvents at elevated temperatures. Processing problems include such things as difficulty in manipulating the polymer in and out of the radiation source and the ability to focus and control the source. Polyethylene has many of the most desirable plastics properties: excellent dielectric characteristics, low specific gravity, toughness and flexibility even at frigid temperatures, and resistance to moisture and many chemical agents. Irradiation enhances these qualities without degrading the material. It doesn't melt or crack when stressed in the presence of active liquid environments.

171. Great Britain Department of Atomic Energy.

Changes in some physical properties of polyethylene by pile irradiation at 80°C. A.E.R.E. Report M/R 1401 (1954).

By subjecting polyethylene to the effect of ionizing radiation it is possible to produce a series of amorphous crosslinked materials which will not melt or dissolve in organic solvents and which vary from very flexible to almost glass-hard. When the temperature of irradiation is raised, crystallinity disappears at a lower radiation dose, and a more flexible crosslinked material is produced. If these materials are heat-treated in a vacuum after irradiation, the initial drop in Young's modulus when they are heated can be largely eliminated. The percentage of crystallinity in polyethylene, and the Young's modulus of amorphous non-irradiated polyethylene, were studied.

172. Henley, E.J.

How crosslinking works. Modern Plastics 32, 98-101 (1955).

Physical properties of plastics depend upon molecular types and constructions. Irradiation can produce large, linked molecules and hence, property changes. Physical properties of plastics depend upon the following:

1. the number of atoms per molecule
2. the electronic forces between the constituent atoms
3. the arrangement of the molecules in space.

Polyethylene is used as an example.

173. Kaindl, K.

Effect of radiation on high polymers, particularly on polyethylene. Osterr. Chem.-Ztg 56, 164-71 (1955).

This is a review.

174. Karpov, V.L., and B.I. Zverev.

Disordering processes in crystalline polymers under action of nuclear radiations. Sbornik Rabot Radiatsionnoi Khim., Akad. Nauk S.S.S.R. 215-22 (1955).

Gamma irradiation (cobalt-60) or fast-electron-beam impact on polyethylene specimens leads to increase of the amorphous state of the polymer at the expense of the crystalline pattern. Tabulation of this effect in respect to dosage is made. The results are interpreted by formation of free radicals and their recombination reactions.

175. Kebely, F.T.

Plastics in some atomic radiation applications. Western Plastics 2, 23-24 (1955).

The degree of radiosensitivity of a plastic is a major factor in its selection for use in atomic radiation installations. Among the more resistant plastics are the phenolics, polyethylene, and some of the polystyrenes. Polyethylene undergoes some improvement in some of its qualities as a result of irradiation, i.e., becomes tougher and more resistant to thermal deformation as a result of crosslinking.

176. Keeling, C.D.

Irradiation of polyethylene (in the heavy-water pile). Dissertation Abstr. 14, 1938 (1954) University of Michigan.

177. Lawton, Elliott, J., J.S. Balwit, and A.M. Bueche.

Properties of irradiated polyethylene. Effect of initial molecular weight. Ind. Eng. Chem. 46, 1703-10 (1954).

178. Lawton, E.J., A.M. Bueche, and J.S. Balwit.

Irradiation of polymers by high-energy electrons. Nature 172, 76-77 (1953).

The effects of high-energy electrons on the solubility, swelling, gas evolution, and physical properties of a large number of polymers were investigated. The polymers investigated fell into two classes: those that became degraded and those that became crosslinked as a result of irradiation. The radiation-induced changes in the properties of polyethylene, nylon, and polydimethylsiloxane were investigated in detail. The amount of crosslinking appeared to be proportional to the amount of irradiation. Physical properties and solubility were changed. The efficiencies for crosslinking were found to vary widely from polymer to polymer.

179. Lawton, E.J., P.D. Zemany, and J.S. Balwit.

Gases liberated during the high voltage electron irradiation of polyethylene. J. Amer. Chem. Soc. 76, 3437 (1954).

The pressure of the noncondensable gas, hydrogen, increased linearly with the amount of irradiation. The number of crosslinks, as determined by swelling and tensile measurements, was found to increase nearly linearly with irradiation.

Loss of hydrogen and volatile compounds is accompanied by a loss in weight of the sample. As the supply of these gases is decreased by increased crosslinking and unsaturation, the amount of gas evolved per given irradiation dose is decreased.

180. Little, K.

Irradiation of linear high polymers. Nature 170, 1077 (1952).

The initial effect of high-energy radiation is to break down bonds (some ionic, the majority covalent). The radicals formed can react in a number of ways: (1) in the presence of oxygen, they can form low-molecular-weight compounds and carboxyl end-groups; (2) in the absence of oxygen they can form low-molecular weight compounds; (3) they can reform the original bonds; or (4) they can combine in other ways.

181. Little, K.

Some effects of irradiation on nylon and polyethylene terephthalate. Nature 173, 680 (1954).

Irradiation of nylon 66 under anaerobic conditions with 5×10^{18} neutrons/sq. cm. (plus associated gamma rays), 50 times the dose which first affected solubility, did not cause crosslinking. On the contrary, the amount of hydrogen evolved decreased with dose. Groups of atoms were broken off with subsequent formation of lower molecular weight fractions. X ray diffraction indicated that the crystallites were unaffected. Complete loss of strength occurred after doses high enough to disrupt the crystallites.

182. Mayburg, S., and W.L. Lawrence.

The conductivity change in polyethylene during gamma irradiation. J. Applied Phys. 23, 1006-1011 (1952).

The effect of cobalt-60 gamma irradiation on the direct current conductivity of polyethylene has been determined up to an intensity, I, of 4000 roentgens/hour at room temperature.

183. Meyer, R.A.

Conductivity of polyethylene and Teflon during irradiation at low temperatures. Abstrs. of papers presented at the Conference on Effects of Radiation on Dielectric Materials, Washington, D.C. ONR Symposium Report ACR-2 p. 93-96 (Dec. 1954).

This investigation has been undertaken to attempt to determine experimentally whether the conductivity change is dependent on the type of material being irradiated, total dose, or flux, and whether the charge carriers are electrons or ions.

184. Miller, A., E.J. Lawton, and J.S. Balwit.

Effect of chemical structure of vinyl polymers on cross-linking and degradation by ionizing radiation. J. Polymer Sci. 14, 503-4 (1954).

For a polymeric chain composed only of saturated C-C linkages, crosslinking under the influence of ionizing radiation will occur if the polymer contains at least one alpha hydrogen atom, whereas those polymers

without this hydrogen atom degrade. Mechanisms for crosslinking and degradation are proposed.

The following are given as examples of polymers that will crosslink: polyethylene, -methylene, -propylene, -styrene, -acrylic acid, -methylacrylate, -acrylamide, and -vinyl methyl ketone. Examples of polymers that will degrade are the following: polyisobutylene, - -methylstyrene, -methacrylic acid, -methyl methacrylate, and -methacrylamide.

185. Muller, F.A.

Electrical conductivity by ionizing radiation in some polymeric materials. Presented at Seminar on the Effects of Ionizing Radiation, Evans Signal Laboratory. Belmar, New Jersey (1953).

Conductivity does not immediately increase to a new value. In the case of polyethylene, it takes more than one hour to reach its ultimate value. Conductivity sometimes decreases with time after having reached a peak value (as in Teflon, and as slightly indicated for polyparachlorostyrene). It is rather surprising that the polar materials have lower conductivity than the nonpolar ones. One of the characteristics displayed is the rapidity with which the conductivity approaches its peak. In this respect, Kel-F is better than polyethylene or polystyrene, but poorer than polyvinylchloride or polyparachlorostyrene. For this reason the latter two materials would make better insulators for high intensity dosimetry than Kel-F.

186. Neuman, J.A., and F.J. Bockhoff.

The new polyethylenes and their impact on fabricated parts. Modern Plastics 32, 117-22 (1955).

187. Nordlin, H.G., D.K. Kell, and C.H. Mayhew.

Ionization-chamber insulating material. Final report July 15, 1951 to July 15, 1953. Contract DA 36-039-sc-5424, Signal Corps Procurement Agency, Squier Signal Laboratory, Fort Monmouth, N.J. (Published October, 1953).

Measurements of polarization current, radiation-induced conductivity, and irradiation after-effects were made on a wide variety of dielectric materials. Polar materials such as PVC, polyparachlorostyrene, and polychlorotrifluoroethylene were characterized by a high dielectric absorption and low radiation-induced conductivity. The nonpolar materials such as polystyrene and polytetrafluoroethylene had a low dielectric absorption and were affected to a much greater degree by high-energy radiation. A great increase in the purity of polystyrene resulted in an increase in the radiation-induced conductivity and a decrease in the dielectric absorption.

188. Nordlin, H.G., F.A. Muller, and C.H. Mayhew.

Ionization-chamber insulating material. Quarterly Rept. No. 7, Jan. 15 to April 15, 1953. Progress

Rept. No. 15. Contract DA 36-039-sc-5424 22 p. Ill. (May, 1953). Signal Corps Procurement Agency, Squier Signal Laboratory, Fort Monmouth, N.J.

Measurements of polarization, irradiation, and recovery conductivity were made on polyvinylchloride, Mylar and Dow Q541. The latter two dielectrics were obtained in the form of 0.00005-in. thick film. The effect of electronic equilibrium is discussed briefly.

189. Power Engineering.

Irradiated polyethylene used for hot-spot electrical insulation. Power Engineering 59, 85 (1955).

When polyethylene plastic is bombarded with beta radiation (or high energy electrons) its excellent insulating properties are moved up a notch on the temperature scale.

190. Price, C.C., R.E. Hughes, and Paul Yen-Hsiung Feng.

Soft x ray degradation of polystyrene in solution. Abstracts of papers. 128th Meeting of the American Chemical Society, Minneapolis, Minn. (Sept. 11-16, 1955).

The degradation of fractionated polystyrene by x rays (from copper K-α target) in benzene, carbon tetrachloride, and mixtures of both was studied. It was found that for a range of initial molecular weight of 2.9×10^5 to 4×10^3, the increase in the number of molecules caused by the x ray-induced degradation was approximately independent of the initial molecular weight for a given total dosage. For polystyrene having an initial molecular weight of 2.9×10^5, subjected to total dosage of approximately 4×10^5 rep, there was no detectable change when the solvent was benzene, but there was a significant decrease in molecular weight when the solvent contained as little as 3 mole percent of carbon tetrachloride. It was observed also that the radiation yield, in the case of solutions containing carbon tetrachloride, was very much higher than the radiation yields observed in the beta-induced reactions in solid samples of polystyrene.

191. Ross, M.

Changes in some physical properties of polyethylene by pile irradiation at 80°C. Atomic Energy Research Establishment (Great Britain) AERE Rept. No. M/R 1401, 7 p. Illus. (April 2, 1954).

Changes in the density, percentage of crystallinity, and Young's modulus of polyethylene, as a result of pile irradiation at about 80°C were studied. It is shown that increasing the temperature during irradiation makes possible the production of amorphous material after a shorter irradiation time, and that a wide variety of materials of varying density and different mechanical properties can be made. A new method of estimating the density of amorphous material in ordinary (nonirradiated) polyethylene is outlined.

192. Ross, M., and A. Charlesby.

The effect of pile radiation on polymethyl methacrylate ("Perspex")-I. Atomics 4, 189-94 (1953).

Unlike many other long-chain polymers, Perspex is broken up by high energy radiation in the atomic pile. Several of the changes produced are described, the most obvious being internal bubbling. The minimum radiation required for incipient bubbling depends on the temperature, e.g., 1.5-2 units at 70°C. Specimens exposed to shorter doses of radiation, although apparently unaffected, can be bubbled subsequently by heating. The suggested explanation of this phenomenon is the decomposition of the side-chains of the polymer, liberating gases, which, at a suitable temperature, can diffuse into bubbles. Polymer breakdown occurs when the internal gas pressure is sufficient to overcome the cohesive forces of the materials. Bubbles do not occur within a distance of 1 mm from the surface of the plastic.

193. Ryan, J.W.

Radiation of polytetrafluoroethylene. Modern Plastics 31, 152 (1953).

The mechanical deterioration of Teflon at high-level gamma radiation is accompanied by double-bond formation and evolution of fluorine.

194. Ryan, J.W.

Theory of the changes in physical characteristics of plastics caused by radiation. Soc. of Plastics Eng. Jour. 10, No. 4, (1954).

195. Ryan, S.W.

Decomposition of polytetrafluoroethylene by gamma rays. Industrie Plastiques Mod. 6, No. 6, 40 (1954).

The relation between dose (Y) in roentgens and γ (X) of fluorine evolved is $X = 3.78 \times 10^{-7} Y^{1.151}$.

196. Schneider, E.E.

Paramagnetic resonance of x rayed Teflon. J. Chem. Phys. 23, 98-99 (1955).

Paramagnetic resonance absorption at 23,700 Mc has been observed in x irradiated Teflon. The structure of the resonance has similarities to the structure found in x irradiated Lucite.

197. Schneider, E.E.

Paramagnetic resonance. Nature 168, 645 (1951).

Using the sensitive microwave apparatus described recently, operating at 9,500 Mc/sec, sharp paramagnetic resonance spectra have been obtained with a number of plastics after irradiation in a 200-kv x ray therapy set. The experiments were carried out with specimens (2 cm diameter x 0.3 cm) of colored polymethylmethacrylate and of clear uncolored Perspex. The observed intensities and widths of the resonance absorptions and their increase with x ray dosage (which was varied between 10^5 and 10^7 roentgens) are in accordance with the assumption that the magnetic centers are electrons produced as the result of irradiation and trapped in the plastic lattice.

198. Seed, L.

II. Ethylene polymerization-initiation by gamma rays (and gamma ray irradiation of polyethylene). Atomic Energy Research Estab. (Gt. Brit.) Rept. No. C/R 1231: 64-71 Disc. 91-3 (1953).

New observations during irradiation of polyethylene are: (1) a progressive increase in double bond ($R_1CH{:}CHR_2$) formation which indicates that 25% of the hydrogen evolution found by Charlesby arises as such (2) the low exponent (α + 0.3) of the dose rate R in the relation $E \propto R$ (E = effect, e.g., change in density, carbonyl content, double-bond increase).

199. Sheridan, L.W.

Balloon material evaluation. Tech. Report No. 2, Oct. 1 to Dec. 31, 1953. Contract AF 19(604)718. 11 p. Rep. No. 1263.

Burst-strength, toughness, and dimensional specifications were determined for 1-mil polyethylene films and for 1.5 and 2-mil laminated polyethylene films. Polyethylene-cellophane laminated film exhibited about 4 times the tensile strength of polyethylene. The film tested was composed of 2-mil polyethylene laminated to 0.6-mil cellophane. Samples of polyethylene films irradiated at 10×10^6 rep and 20×10^6 rep were tested for toughness and cold brittleness. The toughness of 2 samples of 1-mil film was increased 8.4% and 13.5% by low and high dosages, respectively.

200. Sheridan, L.W.

Balloon material evaluation. Tech. Rep. No. 2, Jan. 1 to March 31, 1954. Contract AF 19(604)718. 9 p. ill. Rep. no. 1286 (Pub. April 1, 1954).

Tests on samples of polyethylene film exposed to cathode radiation were completed. Tests were also conducted on a polyethylene-Mylar laminated film and a new type Saran film. Findings indicated that the film receiving less radiation will withstand colder temperatures without becoming brittle, but that the film subjected to greater radiation is tougher at room temperature.

201. Shultz, Allan R., and Frank A. Bovey.

Electron irradiation of polyacrylates and polymethylmethacrylate. Abstracts of papers presented at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio (March 29 to April 7, 1955).

Films of seven acrylate polymers and polymethylmethacrylate have been irradiated with electrons from a converted 800-kv resonant transformer x ray apparatus. Gel-content data have been examined according to recent theoretical treatments assuming random crosslinking and main-chain scissioning of polymers having a most probable molecular weight distribution. From these data and the weight-average molecular weights, M_{wo} of the polymers, the energy E_c, dissipated within each polymer during the formation of crosslinked unit, and the ratio B/a of main-chain scissions to crosslinked units formed were calculated.

202. Shultz, A.R., P.I. Roth, and G.B. Rathman.

Light scattering and viscosity study of electron-irradiated polymethylmethacrylate and polystyrene. Abstract of papers, 128th Meeting of the American Chemical Society, Minneapolis, Minn. (September 11-16, 1955).

A combination of light-scattering and intrinsic viscosity data reveals that no appreciable crosslinking occurs during the degradation of polymethylmethacrylate under a 1-Mev electron beam. The apparent energy dissipation per main-chain scission (E_d = 58 to 62 ev) determined by viscometry is therefore the true E_d in this instance. Calculated viscosity-molecular weight-radiation dose relations show conclusively that crosslinking does not proceed at the rate found in polyacrylates. Reactions leading to crosslinking of polyacrylates are either blocked or diverted by the methyl group present on the polymethylmethacrylate backbone.

203. Sisman, O.

Plastics in the atomic energy program. Plastics Tech. 1, 345-50 (1955).

Six years ago a systematic study was initiated to establish changes occurring in plastics subjected to high energy radiation and to establish the mechanisms involved in these changes.

204. Sisman, O., and C.D. Bopp.

Physical properties of irradiated plastics. Report ORNL-928, Office of Technical Services, Department of Commerce, Washington, D.C. (June 1951).

A series of graphs and charts are presented depicting quantitatively the changes in physical properties which various plastics undergo when subjected to radiation in the ORNL reactor. Tests were made of the

following properties: tensile properties, shear strength, impact strength, Rockwell hardness, change in weight, specific gravity, water absorption, light transmission and haze, volume resistivity, dielectric strength, and arc resistance.

205. Sisman, O., and C.D. Bopp.

Radiation stability of polymers. ONL Symposium Report ACR-2. Conference on Effects of Radiation on Dielectric Materials, Washington, D.C. (85-91) (Dec. 1954).

206. Sisman, O., C.D. Bopp, R.L. Towns, and W.K. Kirkland.

Radiation stability of plastics and elastomers. Solid State Division Quarterly Progress Report, ORNL 1506, p. 56-57 (1954).

207. Slovokhotova, N.A., and V.L. Karpov.

Chemical changes in polymeric substances under the action of ionizing radiations as studied by the method of vibration spectra. I. Action of fast electrons on polyethylene. Sbornik Rabot Radiasionnoĭ Khim. Akad. Nauk S.S.S.R. 196-205 (1955).

Examination of the vibrational spectra of polyethylene after exposure to a fast electron stream (10-40 Min; 275- and 415-kv electrons) showed that the structure of the polymer is severely altered; double bonds form, the branching of the chains increases, and the crystalline material tends to pass into the amorphous state. If the radiation is done in contact with air, oxidation also takes place, yielding carbonyl and ether groups.

208. Slovokhotova, N.A. and V.L. Karpov.

Chemical changes in polymeric substances under the action of ionizing radiations as studied by the method of vibration spectra. II. Action of gamma radiation on polyethylene. Sbornik Rabot Radiasionnoĭ Khim. Akad. Nauk S.S.S.R. 206-14 (1955).

Irradiated polyethylene shows in its infrared spectra an increased branching of chains and the presence of cross-linked units, along with the appearance of double bonds and HO, CO, and CO_2H groups. The products are deducible from probable free radicals formed in the radiation impact. In contact with air, the process also yields carbonyl compounds, while activated oxygen can participate in chain initiation reactions.

209. Sobolev, I., J.A. Meyer, V. Stannett, and M. Szwarc.

Permeability to gases of irradiated polyethylene. J. Polymer Sci. 17, 417-21 (1955).

Specimens cut from the same piece of polyethylene film are irradiated with a known dosage and their permeabilities measured. Using the data of Lawton, Zemany, and Balwit, the approximate concentration of crosslinks in each specimen may be calculated and therefore the changes in permeability may be directly correlated with the number of crosslinks.

210. Stark, K.H., and C.G. Garton.

Electric strength of irradiated polyethylene. Nature 176, 1225-26 (1955).

The electric strength of irradiated polythene has been measured for material crosslinked by exposure to 4-Mev electrons from a linear accelerator. Thin (1-mm) moulded disks of material (average molecular weight, 17,000) recessed to a thickness of about 50 microns were irradiated in vacuo with doses of 150-300 Mrad, and the electric strength was measured with direct voltage. Control results for normal material coincide with those of other investigations. The changes in electric strength resulting from irradiation unexpectedly resemble those of Young's modulus for similar material measured by Charlesby and Hancock. They are quite unlike those expected from the theory of intrinsic electric strength, which predicts for the crosslinked material a temperature fall more marked and a lower beginning temperature.

211. Stein, Richard S., Richard J. Volungis, and Tsi Tieh Li.

Some stress-birefringence studies of oriented crosslinked polyethylene. Abstracts of Papers, 128th Meeting of the American Chemical Society, Minneapolis, Minn. (September 11-16, 1955).

Simultaneous measurements of the stress and of the birefringence have been made on elongated samples of radiation-crosslinked polyethylene at temperatures between 30° and 180°C. These were made on samples in vacuo in a creep-type experiment. The material behaves as an essentially ideal rubber above 120°C and conforms to the Kuhn-Treloar theory of birefringence. The birefringence of the statistical segment is approximately 5.0×10^{-24} cc but varies with temperature between 120°C and 180°C. Comparing this with a calculated birefringence for a C-C bond unit of 5.9×10^{-25} indicates that a statistical segment consists of 815 bonds. The temperature variation of the statistical segment birefringence is consistent with a potential energy opposing bond rotation of 7 kcal. This would correspond to a chain having 6.9 bonds per segment.

212. Stirrat, J.R., and P.A. Goodwin.

Electron irradiated polyethylene. Electrochemical Society 107th Meeting, Cincinnati, Ohio. p. 12 (1955).

213. Todd, Audrey.

Pile irradiation of polyethylene terephthalate (Terylene). Nature 174, 613 (1954).

Work by Little on degradation of polyethylene terephthalate (I) by pile radiation was corroborated.

214. Wall, L.A., and D.W. Brown.

Chemical activity of polymethyl methacrylate previously exposed to gamma radiation. Abstracts of Papers, American Chemical Society, 127th Meeting, Cincinnati, Ohio (March 29 to April 7, 1955).

Recently it has been demonstrated that free radicals or atoms, when produced in frozen hydrocarbons or monomers at about 90°K, can be immobilized and stored for extended periods of time. Their existence in significant quantities can be demonstrated either spectrometrically or by polymer formation. It appears probable that solid polymers at room temperature, after exposure to high energy radiation, are also likely to contain active species in quantities capable of detection by chemical means.

215. Wall, L.A., and D.W. Brown.

Gamma irradiation of polymethyl methacrylate and polystyrene. Preprint, National Bureau of Standards, Washington 25, D.C.

The number of scissions produced in polymethyl methacrylate for a given dose of irradiation is decreased measurably by the presence of air, small amounts of benzene, and by lowering the temperature to -196°C. Irradiation in air produced labile structures in the polymer (probably peroxides) which decompose and cause further scissions. The decomposition of these structures is accelerated by traces of tert-butyl catechol, hydroquinone, and dimethyl aniline.

The crosslinking reaction in polystyrene caused by gamma irradiation is also decreased when temperatures are lowered to -196°C. Studies of partially deuterated styrenes show little correlation between crosslink formation and site of deuteration. This observation, plus the fact that crosslinks exceed the number of hydrogen molecules produced, suggest that the phenyl ring is involved in crosslinking. Comparison of the results with deuterated polystyrene and deuterated polyethylene indicates a difference between the two materials in the mechanisms of irradiation-induced processes.

C. Elastomers

216. Alexander, P., R.M. Black, and A. Charlesby.

Radiation-induced changes in the structure of polyisobutylene. Proc. Roy. Soc. A232, 31-43 (1955).

Polyisobutylene suffers random main-chain fracture when exposed to high radiation. Identical results are produced by electron and gamma radiation and the average energy absorbed per break amounts to 20 ev at 20°C. The unsaturation produced is proportional to the number of breaks. A new absorption band appears in the infrared at 11.25μ, which indicates that a vinyl double bond of the type $R_1R_2C{=}{=}{=}CH_2$ has been introduced. The gases evolved on irradiation have been analyzed. A chemical mechanism for the degradation has been proposed.

The energy per break varies with temperature, the relationship being somewhat similar to the inactivation behavior of ionizing radiation on certain biological systems.

The ultraviolet absorption spectrum is different for polymers which have been irradiated in vacuum or nitrogen from those irradiated in air, but the number of main-chain breaks is not affected by the surrounding gas.

217. Bueche, A.M.

An investigation of the theory of rubber elasticity using irradiated polydimethylsiloxanes. J. Polymer Sci. 19, No. 92, 297-306 (1956).

High-energy electrons were used to crosslink a series of polydimethylsiloxanes. Equilibrium tension measurements at low elongations were used to determine the number of chains between crosslinks as given by the kinetic theory of elasticity. After a rapid increase at low radiation dose, the number of chains was found to be proportional to the dose. The linear relationship between number of chains and dose, found at higher doses, and extrapolated to zero dose, has a positive intercept. This intercept was independent of the initial molecular weight of the polymer and was taken to be a measure of the effect of the maximum number of permanent entanglements in this polymer. The dependence of the number-average molecular weight of irradiated polydimethylsiloxane fluids on radiation dose was determined. The data were analyzed to find the efficiency of crosslink formation in this polymer. The number of chains between crosslinks produced by a given dose and determined by the kinetic theory was found to be only one-half the number to be expected from the measurement of the molecular weights of the irradiated fluids.

218. Charlesby, A.

The crosslinking of rubber by pile radiation. Atomic 5, 12-22 (1954).

Rubber becomes crosslinked when subjected to high energy radiation such as is present is atomic piles. This offers a means of studying the change in properties of rubber as the degree of crosslinking is varied without the use of chemical vulcanizing agents. The efficiency of crosslinking, variation of the gel fraction, and molecular weight of gel and sol fractions were studied.

219. Davidson, W.L.

Effect of pile bombardment on uncured elastomers. Rubber Chem. and Tech. 22, 138 (1949).

Previous work on the effects of ionizing radiations on hydrocarbons has established that four competitive processes are usually operative: (1) dehydrogenation, (2) condensation or polymerization, (3) hydrogenation (action of nascent hydrogen on any unsaturated matter present), and (4) decomposition (C-C cleavage). The chain-reacting nuclear pile offers an ideal means for subjecting relatively thick samples of such materials as natural rubber, butyl rubber, and polyisobutylene. Use of the pile allows one to draw the following conclusions: (1) Uncured natural rubber undergoes a slight curing action when exposed to pile radiations. (2) Polyisobutylene samples are appreciably degraded by pile radiation. (3) The same effects as noted in (1) and (2) are greatly enhanced by secondary alpha particles, produced by an (n, alpha) reaction on boron (milled into the elastomer). However, even a 2-hour bombardment of natural rubber yields a product greatly inferior to sulfur vulcanizates. (4) Pile bombardment does not introduce measurable unsaturation in polyisobutylene and decreases the unsaturation in natural rubber only slightly. (5) A typical butyl rubber stock is permanently degraded by pile irradiation, showing, on cure, reduced tensile strength compared with that of a control sample. (6) Natural rubber shows a weak but measurable radioactivity days after bombardment, probably because of its mineral content. Polyisobutylene is not appreciably active.

220. Davidson, W.L., and J.G. Geib.

The effects of pile bombardment on uncured elastomers. J. Applied Phys. 19, 427-33 (1948).

The work of previous investigators on the effects of ionizing radiations and particles is reviewed briefly. Eight compounds were studied: 3 uncured natural rubbers and 1 cured, 3 uncured polyisobutylene, and 1 butyl rubber, uncured and cured. The stocks were milled to 0.1-inch thickness and cut into 20-inch squares. They were exposed at the center of the pile for various times up to 2 hours. After exposure, Goodrich plasticity values were determined. The latter showed little change. The results indicate that uncured natural rubber undergoes a slight curing action; polyisobutylene is appreciably degraded. These same effects are greatly enhanced by secondary alpha particles, produced by an (n, a) reaction on B milled into the elastomer. But a 2-hour bombardment of natural rubbers yields a product greatly inferior to S vulcanizates.

221. Eisler, S.L.

Evaluation of rubber for ordnance use. Report No. 5, High Energy Radiation of Polymers, A Literature Review. ASTIA AD 24914, 16 p. (November 1953).

222. Gehman, S.D., and L.M. Hobbs.

Changes in elastomers due to radiation from cobalt-60. Rubber World 130, 643-6 (1954).

An experimental study was made of the effects of intense gamma radiation from cobalt-60 on the physical properties of elastomers and plastics. The results are of essential importance (1) in judging the resistance of different types of elastomers to radiation, and (2) in studying methods of compounding to obtain maximum resistance to radiation. Intense radiation may affect the physical properties of elastomers either beneficially or adversely, depending on the type of elastomer and the degree of exposure.

223. Hamlin, Horace C.

Rubber - a vital factor in the modern air weapon. Rubber World 132, 601-7, 614 (1955).

A review and discussion of present developments and the needs for elastomeric products for the construction of bomb-bay and cabin seals, fuel tanks and sealants, coatings, O-rings for fuel, lubrication, and hydraulic systems, fuel and oil hose, accumulators, diaphragms, and wire and cable coverings capable of service at -80 to 500°F. Some preliminary results on the effects of exposure of different elastomers (natural rubber, polybutadiene, butadieneacrylonitrile copolymer, Neoprene GN, Hypalon S-2, Hycar-4021, and Thiokol (OST) to nuclear radiations, and experiments on the vulcanization of elastomers by exposure to cobalt-60 gamma radiation, are described with graphical data. The properties of Poly-FBA and Kel-F elastomers pertinent to the service requirements under discussion are outlined and the need for far better elastomers is emphasized.

224. Hamlin, H.C.

Rubber - a vital factor in the modern air weapon. Armed Forces Chem. J. 10, No. 1, 34-9 (1956).

A discussion of problems involving rubber, solutions, effect of atomic radiation on rubber, vulcanization by gamma radiation, polymer research, Poly-FBA, Kel-F elastomer, and the part of the Air Force Research Program has in relation to these problems.

225. Hobbs, L.M., S.D. Gehman, and D.E. Brown.

Effects of gamma radiation on elastomers. 1943-17-P, University of Michigan Progress Report No. 7, 199 (1954).

226. Hobbs, L.M., D.W. Pletcher, and D.E. Brown.

Effects of gamma radiation on rubber and on polymerization. COO-196, 158 AEC Report, University of Michigan (1953).

227. Jackson, Wallace W., and Denver Hale.

Vulcanization of rubber with high-intensity gamma radiation. Rubber Age 77, 865-71 (1955).

Techniques for vulcanizing elastomers by exposure to gamma radiation of high intensity are described and illustrated. The sources of radiation were cobalt-60 and spent uranium reactor fuel elements. No heat or chemical vulcanizing agent was used. The elastomers included natural rubber, GR-S, Neoprene, a butadiene-acrylonitrile copolymer, polyisobutylene, and a polyacrylic ester polymer. Different types of carbon black and inorganic fillers were tested. Numerous properties, including tensile strength, extensibility, modulus, hardness compression set, swelling, and extractability of plasticizer, of the vulcanizates were tested, and the results are tabulated and discussed.

228. Jackson, Wallace W., and Denver Hale.

Vulcanization of rubber with high-intensity gamma radiation. (Period Covered: May 1954 to March 1955). Wright Air Development Center, Materials Lab., Wright-Patterson AFB, Ohio. WADC-TR-55-57, 36 p. (April 1955).

Techniques of vulcanizing both natural and synthetic rubber polymers, using high-intensity gamma radiation, are described. Evaluation of this technique shows considerable promise in developing elastomers for specialized uses.

229. Warrick, E.L.

Effects of radiation on organopolysiloxanes. Ind. Eng. Chem. 47, 2388-2393 (1955).

Organopolysiloxane elastomers vulcanized by high energy radiation show superior high-temperature performance and parallel in properties, a number of radiated organic polymers. Siloxanes containing large amounts of phenyl substitutions may be good construction materials around high-energy radiation sources.

D. Miscellaneous

230. Ryan, John W.

Effect of pile radiation on electrical insulation. Modern Plastics 31, 148-58 (1954).

An investigation of oil-modified phenolic varnish, silicone resins, phenolic glass laminates, and paper and tape impregnated with silicone have shown that most insulating materials become embrittled and craze or crack when subjected to in-pile radiation. It is postulated that crosslinkages are formed upon the recombination of free radicals produced by the radiation. It was shown that for use in high-level in-pile radiation equipment, an aromatic type of insulation material is desirable.