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POLYMER DECOMPOSITION INITIATED BY HIGH ENERGY RADIATION

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by Leo A. Wall

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The subject matter of this project is the kinetics and mechanisms of the chemical and physical changes occurring in polymers exposed to vacuum ultraviolet and gamma radiation at temperatures in the range from ambient (25°C) upward to 500°C. In addition to temperature and radiation, the conditions of exposure involve both vacuum and the presence of reactive gaseous atmospheres. Interpretation of results obtained with vacuum ultraviolet radiation is a rather formidable problem because of the large absorption coefficients and consequent inhomogeneous exposure within samples.

STATUS OF PRESENT RESEARCH

Progress in the past quarterly periods was along the following lines:

A. The article on the gamma ray initiated thermal depolymerization of polytetrafluoroethylene will shortly appear in the Journal of Research National Bureau of Standards. The mechanism is shown to consist of random initiation, termination by combination, at least 99.4%, and the kinetic chain lengths are short, 5 to 100 depending on temperature.

In order to improve our measurements for these gamma ray initiated studies, a new apparatus is being constructed and tested. It is anticipated that studies on other fluorocarbon polymers will be initiated shortly.

B. Several vacuum ultraviolet lamps, i.e., xenon resonance lamps, which previously failed by developing leaks at the complicated seal holding the lithium fluoride, now appear to be vacuum tight. After several trials, a lamp has been constructed which has held at 25°C and several polymers have been exposed to this lamp. At present we are testing the exposed polymers by solubility and swelling techniques, since it is anticipated that crosslinking should occur in the outskin. However, since all effects are expected to occur in the first 1000 Å layer of the sample, it is not surprising that so far all the samples appear to dissolve as readily as the unexposed samples.

C. A thermal decomposition study of anionically prepared polymers of 1,2-dihydronaphthalene was carried out. The polymer was investigated because references in the literature suggested that it had outstandingly thermal and radiolytic stability. It was found that the polymer was only slightly better than polystyrene, and unlike polystyrene appears to decompose exothermically. This exothermic process depends at least to some extent on the aggregation of the

polymer material. This work has been completed, written up and is now in editorial review.

D. During the past quarterly periods, an improved apparatus for isothermal and non-isothermal rates of volatilization measurements was constructed for use with both the vacuum ultraviolet and purely thermal studies. Attached is a description of the instrument.

STATUS OF PUBLICATIONS FROM THE PROJECT

1. "Pyrolysis of New Fluoropolymers", by S. Straus and L.A. Wall, SPE Trans. 4, [1], 56 (Jan. 1964).
2. "Pyrolysis of Polytrifluoroethylene. Influence of Gamma Radiation and Alkali Treatment", S. Straus and L.A. Wall, SPE Trans. 4, [1], 61 (Jan. 1964).
3. "Pyrolysis of Vinyl and Vinylidene Fluoride Polymers--Influence of Prior Gamma Irradiation", L.A. Wall, S. Straus, and R.E. Florin, manuscript accepted by J. Polymer Sci.
4. "Stress Relaxation of γ-Irradiated Fluorocarbon Elastomers", by T. Yoshida, R.E. Florin, and L.A. Wall, J. Polymer Sci. 3A, [5] 1685 (May 1965).
5. "On the Measurement of Random Chain Scission by Stress Relaxation", by Hyuk Yu, Polymer Letters 2, [4], 631 (1964).
6. "Effects of Composition and Irradiation on the Glass Transition Temperature of Methyl Methacrylate Styrene Copolymers", by M.S. Parker, V.J. Krasnansky and B.G. Achhammer, J. Appl. Polymer Sci. 8, [4], 1825 (July 1964).

7. "The Mechanism of the Radiolytic and Pyrolytic Initiated Depolymerization of Polytetrafluoroethylene", by R.E. Florin, M.S. Parker, D.W. Brown, and L.A. Wall, J. Research NBS, April-May 1966.

8. "Radiolytic Stress Relaxation of an Ethylene-Propylene Copolymer", by H. Yu and L.A. Wall, J. Phys. Chem. 69, [6], 2072 (June 1965).

9. "The Thermal Degradation Mechanism of Polystyrene", by L.A. Wall, S. Straus, J.H. Flynn, D. McIntyre, and R. Simha, J. Phys. Chem. 70, [1], 53 (Jan. 1966).

10. "The Effect of Gamma Irradiation on a Polyamide", by V.J. Krasnansky, M.S. Parker, and R.E. Florin, J. Phys. Chem. 70, [1], 40 (Jan. 1966).

11. "Kinetics of the Hydroxyl Radical in Aqueous Solution", by F. Sicilio, R.E. Florin, and L.A. Wall, J. Phys. Chem. 70, [1], 47 (Jan. 1966).

12. "Polymerization and Pyrolysis of Poly-1,2-dihydronaphthalene", L.A. Wall, L.J. Fetters, and S. Straus, presented at the 150th Am. Chem. Soc. Meeting, September 1965, Atlantic City, manuscript in editorial review.

13. Thermogravimetric Instrument, by S. Straus and L.A. Wall, copies attached.

FUTURE PLANS

Investigate:

1. Kinetics and mechanism of polymer, polytetrafluoroethylene, polyethylene and other, decompositions initiated by xenon resonance radiation (1475 Å),

2. at 25°C and

3. upward to 500°C.

4. Explore the effects of shorter wave length radiation by goint to krypton, argon or another rare gas resonance lamp.