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THERMAL AND OXIDATIVE DEGRADATION OF AROMATIC AND HETEROCYCLIC POLYMERS

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by Leo A. Wall

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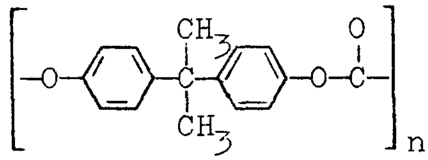
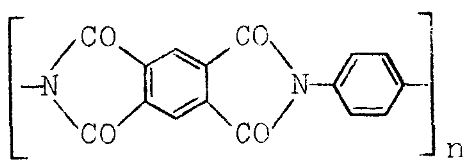
THERMAL AND OXIDATIVE DEGRADATION OF AROMATIC AND HETEROCYCLIC POLYMERS

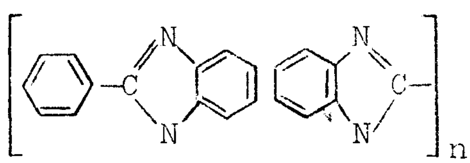
The most successful and complete investigations of polymer degradation have been those on linear polymers which on degradation gave unique chemical products capable of being analyzed by many techniques. The processes of degradation were overwhelming those of bond ruptures. With the aromatic polymers now of great interest and importance it can be presumed that bond formation is the key to their degradative mechanisms. A cursory survey of the characteristics of degradation will show that in all types of degradation, thermal oxidative, radiative, and photo, the more aromatic content in the material the more char-like, insoluble, or intractable the products become. There is of course some bond ruptures that lead to volatile products capable of conventional analysis by mass or infrared spectroscopy and other methods.

On the other hand what is of great importance is the determination of the mechanisms of the solid state reactions leading to the intractable and carbon-like residue. To this end we looked for an aromatic polymer that was soluble and characterizable in its initial state and only gradually became insoluble. This would permit measurements to be made of the degree of insolubility and permit a quantification of the "crosslinking" process.leading to char. Thus beside studying H-film and PBI we have made trial experiment on the polycarbonate "Lexan".



During the past six months we have: 1) Completed construction of a new thermogravimetric apparatus capable of both isothermal and non-isothermal thermogravimetry up to 1000°C. At present this apparatus is being tested, calibrated and adjusted. 2) Acquired a mass spectrometer and are designing and preparing apparatus for using it to monitor the volatile products as the degradations proceed. 3) Have carried out a series of experiments on the polycarbonate which have given interesting results which should be ready for presentation within the next six months. 4) Carried out a series of pyrolyses up to 600°C in air and in vacuum or H-film,





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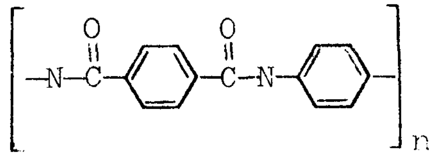

FUTURE PLANS

Study the thermal and oxidative degradation of aromatic and heterocyclic polymers by means of thermogravimetric techniques and other methods, DSC, NMR, ESR, etc., where feasible.

With the use of specially prepared or synthesized samples we plan to test the effect of: a) surface to volume ratio, b) catalytic or inhibiting additives, including trace metals, organics and metallo-organics and c) the chemical structure of the polymers.

PUBLICATIONS ON THIS 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. "On the Measurement of Random Chain Scission by Stress Relaxation", by Hyuk Yu, Polymer Letters 2, [4], 631 (1964).
4. "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, 825 (1946).

5. "Stress Relaxation of γ-Irradiated Fluorocarbon Elastomers", by T. Yoshida, R.E. Florin, and L.A. Wall, J. Polymer Sci. 3A, 1685 (1965).

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

7. "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 (1966).

8. "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 (1966).

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

10. "Pyrolysis of Vinyl and Vinylidene Fluoride Polymers--Influence of Prior Gamma Irradiation", by L.A. Wall, S. Straus, and R.E. Florin, J. Polymer Sci. 4, [2], 349 (1966).

11. "The Mechanism of the Radiolytic and Pyrolytic Initiated Depolymerization of Polytetrafluoroethylene", by R.E. Florin, M.S. Parker, and L.A. Wall, J. Research NBS 70A, [2], 115 (1966).

12. "Polymerization and Pyrolysis of Poly-1,2-dihydronaphthalene", by L.A. Wall, L.J. Fetters, and S. Straus, Polymer Letters 5, [8] 721 (1967).