HIGH-TEMPERATURE POLYMERS

edited by

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SYMPOSIUM ON HIGH-TEMPERATURE POLYMERS:
SYNTHESIS AND DEGRADATION

Held at the Western Regional Meeting of the

AMERICAN CHEMICAL SOCIETY

Los Angeles, California, November 18–20, 1965

Introduction

The papers included in this Symposium Issue are part of a continuing "experiment" that was initiated several years ago by the Polymer Group, Southern California Section of the American Chemical Society. In an effort to bring together the rapidly growing West Coast community of polymer chemists and plastics engineers, a series of symposia on specific polymer subjects was initiated. The first symposium, *Adhesives and Adhesion,* was held in November 1964; the second, recorded here, *High-Temperature Polymers: Synthesis and Degradation,* was presented in November 1965; and the third symposium, *Block Copolymers,* is scheduled for June 5, 1967, at the California Institute of Technology. These one-day symposia have been designed for maximum interplay between the participants. Several general introductory lectures were presented in the morning sessions, and a series of concise papers were given in the afternoons. An extensive discussion period was allowed for each paper and, in the case of the High-Temperature Polymers Symposium, an evening panel discussion was held. Although the quality of such meetings cannot be judged from attendance records, the presence of 250 persons at the first symposium and 400 at the second probably has some significance.

The reader of the literature in the polymer field will recognize that the papers in this issue contain information which has been outdated since the papers were given in 1965. Therefore, the authors and editors would like to consider this volume more as a progress report than as the final word on the subject of synthesis and degradation of high-temperature polymers. Several earlier "progress reports" may already be familiar to the reader (*1–6*). A later report (*7*), which has been amplified to include a "classification" of thermally stable polymers (*8*), has been given by Prof. Herman Mark. The present papers have been grouped in three categories, although some overlap of subject matter does occur: organic polymers, inorganic polymers, and polymer degradation.

Professor Marvel's introductory paper describes his investigations of polyaromatic heterocyclic polymers. The poly(bis-benzimidazobenzophenanthrolines), poly(quinoxalines), and poly(imidazopyrrolones) exhibit unusual thermal stability, and several papers published since the symposium amplify this observation (*9,10*). The work of Delman, Stein, and Simms demonstrates a much-needed approach to the understanding of the stability of macromolecules; i.e., the synthesis and characterization of model compounds and low-molecular-weight oligomers. The favorable stability of poly(3-aminobenzaldehyde) would warrant further investigation. Bilow and Miller have demonstrated that the thermal stability inherent in polyphenylene can be obtained in a tractable polymer although not without some sacrifice to yield, and a decreasing thermal stability with decreasing molecular weight. The approach to a tractable polyphenylene has been further expanded by the recent report of Millward (*11*). Dobinson and Preston, in their abbreviated text recorded here, show quite conclusively the changes in thermal stability of copolyamides in going from aliphatic to single- and multiple-ring aromatics and finally to fused-ring aromatics.

Inorganic polymers have been the subject of several monographs in the past few years. These are included in the bibliography that accompanies the introductory lecture by J. R. Van Wazer. The study of inorganic polymers, as ably analyzed by Van Wazer, has changed from that of hypothesis and speculations to a field in which precise physical methods are used for measuring molecular structure and physical properties. An excellent example of such an approach is the paper by Eisenberg, wherein viscoelastic behavior of certain polyelectrolytes has been quantized. The polymers described by Green and Mayes appear to be more organic than inorganic; at least their synthesis follows an organic approach. The thermograms in this work should be examined carefully and compared with the earlier ones of Marvel.

The introductory paper on thermal decomposition of polymers by Friedman and the accompanying papers by Conley and Shulman are representative of the current studies in this field. As a result of this symposium, and the discussions of these latter papers, a continuing dialog has developed on the subject of standardization of polymer samples and/or thermal analysis techniques. Two recent manuscripts might be mentioned in this regard (*12,13*).

As chairman of the symposium, I would also like to express my particular thanks to three additional invited participants on the panel who helped to enliven the discussions of these papers: Dr. A. J. Barry (Dow Corning), Dr. L. A. Wall (National Bureau of Standards), and Dr. E. E. Magat (Dupont).

REFERENCES

1. S. M. Atlas and H. F. Mark, *Angew. Chem.*, **72,** 249 (1960).
2. *High Temperature Resistance and Thermal Degradation of Polymers,* S.C.I. Monograph 13, Macmillan, New York, 1961.
3. J. D. Aitken, R. Sheldon, and G. B. Stapleton, *Brit. Plastics,* **34,** 622 (1961); **35,** 39 (1962).
4. *Proceedings of the Battelle Symposium on Thermal Stability of Polymers,* Dec. 1963.
5. F. T. Wallenberger, *Angew. Chem.*, **3,** 460 (1964).
6. V. V. Korshak and Ye. S. Krongauz, *Usp. Khim.*, **33,** 1409 (1964).
7. H. F. Mark, *J. Polymer Sci.*, **9C,** 1 (1965).
8. H. F. Mark, IUPAC Symposium on Macromolecular Chemistry, Tokyo, 28 Septempber 1966; *J. Polymer Sci.* (in preparation).
9. R. L. Van Deusen, *Polymer Prints,* **7**(2), 528 (1966).
10. J. K. Stille and E. L. Mainen, *Polymer Letters,* **4,** 39 (1966); **4,** 665 (1966).
11. B. B. Millward and R. J. Roberts, in *SAMPE 10th National Symposium on Advanced Fibrous Reinforced Composites,* Nov. 1966.
12. J. H. Flynn and L. A. Wall, Investigation of Polymer Pyrolysis with Thermogravimetry, *J. Res. NBS* (in press).
13. M. G. Church, Evaluation of New Polymers, *Brit. Government Rept. KS/1/-0183/C.B.43A*(2).

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Symposium on High-Temperature Polymers
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Thermally Stable Polymers with Aromatic Recurring Units

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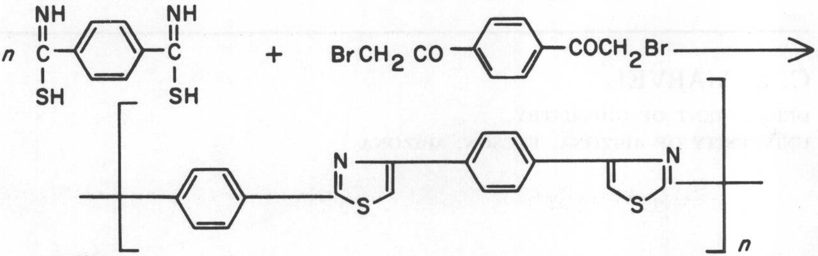
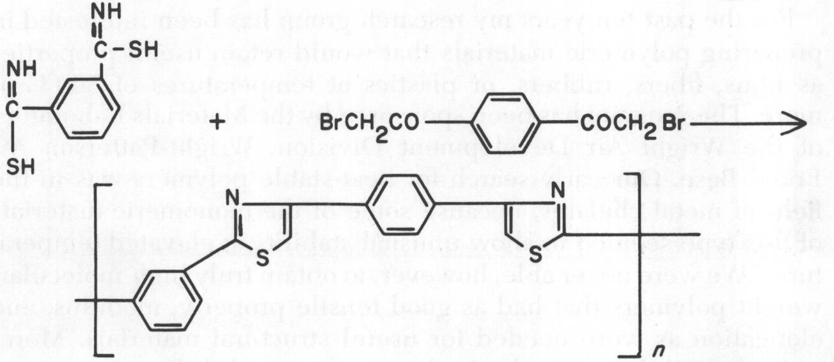
For the past ten years my research group has been interested in preparing polymeric materials that would retain useful properties as films, fibers, rubbers, or plastics at temperatures of 500°C or more. The program has been sponsored by the Materials Laboratory of the Wright Air Development Division, Wright-Patterson Air Force Base. Our early search for heat-stable polymers was in the field of metal chelates, because some of the monomeric materials of this type seemed to show unusual stability at elevated temperatures. We were never able, however, to obtain truly high-molecular-weight polymers that had as good tensile property, modulus, and elongation as were needed for useful structural materials. Moreover, the stability of the low polymers that we did obtain was never quite as good as we had hoped for.

We then turned to a study of aromatic systems. It is well known that such aromatic compounds as benzene, naphthalene, anthracene, pyridine, and quinoline are produced in the destructive distillation of such products as coal, bones, and other animal and vegetable materials. If formed at high temperatures, they can be expected to have some stability under these conditions. The best of our industrial polymeric materials are those which are long-chain molecules held together by covalent links, such as carbon-carbon bonds, carbon-oxygen bonds, and carbon-nitrogen bonds. It therefore seemed logical to try to synthesize polymers with recurring aromatic units joined together with covalent bonds.

Work on the synthesis of polyaromatic heterocyclic polymers in polycondensation reactions is underway in a number of laboratories. This field has been a very active one since 1961. In my laboratories we have been concerned with polythiazoles, polyoxadiazoles, polytriazoles, polybenzimidazoles, polyboroimidazolines, polytetraazopyrenes and, more recently, ladder-type polymers from aromatic tetraamines and aromatic dianhydrides.





Our polythiazoles were made by means of Erlenmeyer's synthesis (*1*) from bisthioamides and bisbromoacetylbenzene (*2*) in dimethylacetamide solution. We later learned that this work had been done earlier (*3*) in Japan with results very similar to those we obtained. In both instances polymers with molecular weights in the 5300 to 5400 range were obtained. The polymers were yellow to yellow-orange in color and soluble only in sulfuric acid or trifluoroacetic acid. When an aliphatic bisthioamide was used to give a mixed aliphatic-aromatic polymer chain, a slightly higher-molecular-weight polymer was obtained. It was soluble in formic acid and could be cast into a weak film. Thermogravimetric analyses (Fig. 1) showed that the polymer with aliphatic units degraded rapidly at 350 to 400°C in nitrogen but that the wholly aromatic

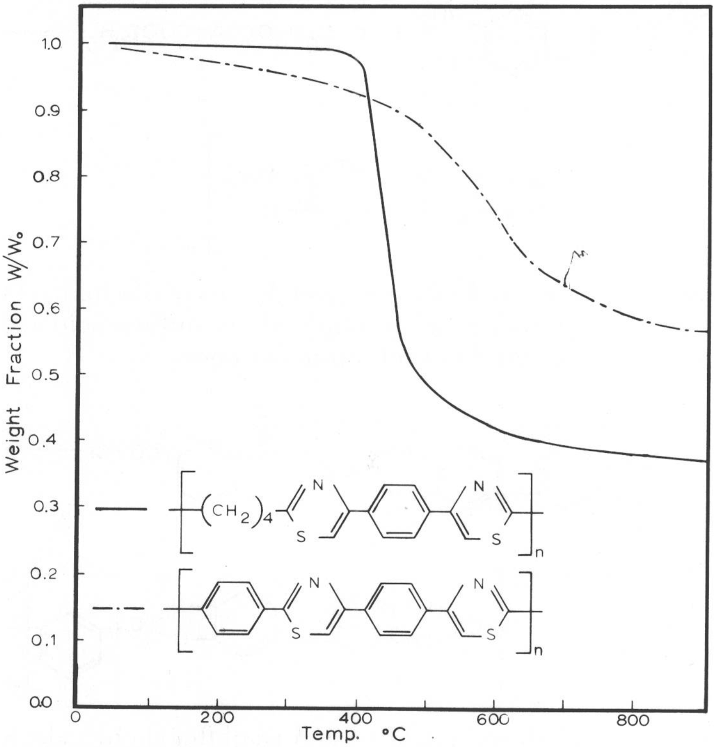
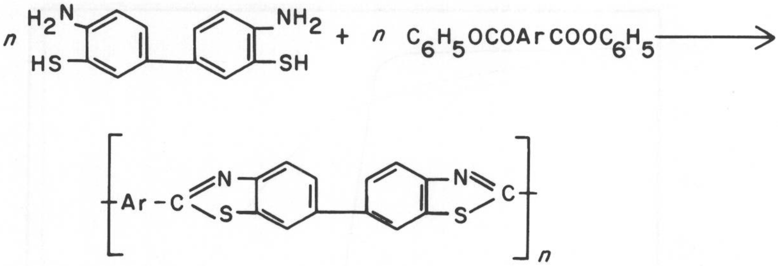


FIG. 1. Thermogravimetric curves of polythiazoles.

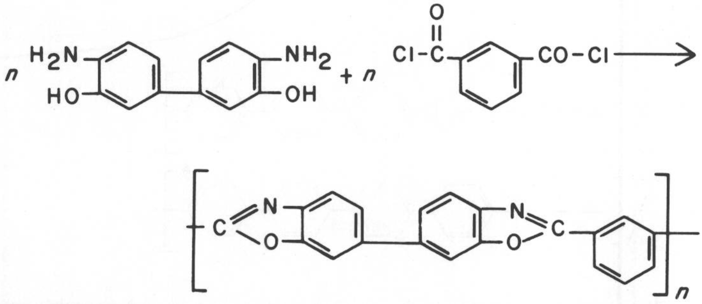
polymers held up well to 500 to 600°C and lost only 40% of their weight up to 900°C. This seems to be the case in most of the series we have studied. Aliphatic chains rarely withstand more than 400°C, whereas the aromatics are usually good up to 550°C or better.

As reported in a recent paper, Sheehan, Cole and Picklesimer (*4*) studied this polymerization reaction further and developed it to the state where by means of aliphatic bisthioamides they obtained high polymers with inherent viscosities as high as 5.83. From some of them fibers were drawn and films were cast. Some of the fibers had strengths of 2 to 3 g/den and the films had tensile strengths of up to 6800 psi.

Hergenrother et al. (*5*) prepared a series of polybenzthiazoles by condensing diphenyl esters of aromatic acids with bisorthoaminothiophenols and obtained polymers with remarkable thermal



stability both in air and nitrogen (weight loss of 6% up to 600°C in static air). The polymers are soluble only in sulfuric acid and have not yet been converted to useful films or fibers.



Using 3,3′-dihydroxybenzidine and isophthalyl chloride, Kubota and Nakanishi (6) have made polybenzoxazoles that are soluble in sulfuric acid and have inherent viscosities in the range of 1 to 1.2.