Meetings

Aromaticity: A Key to Polymers Stable at High Temperatures

Some important contributions to the current intensive search for polymers that are stable at high temperatures were presented and discussed at a symposium on new aromatic polymers held 27 April at the Polytechnic Institute of Brooklyn. A key point, pervading the entire symposium, was the desirability of employing aromatic structures for achieving high-temperature stability in polymers. An important concept, that of "post-fabrication polymer-modifying reactions," offered a significant solution to the difficult problem of fabricating these polymers. Novel approaches to the synthesis of aromatic polymers were also presented.

The symposium was devoted to four classes of linear aromatic polymers whose general mode of formation and structure are shown in Fig. 1. Numerous other important and related polymers, such as the polybenzimidazoles, the poly(phenylene oxides) and the Epon resins of high molecular weight could not be covered because of time limitations.

E. J. Vandenberg, chairman (Hercules Powder Company), observed that it was only within recent years that polymer chemists, spurred by the need for materials resistant to high temperatures, have taken maximum advantage of the excellent stability of aromatic systems in designing aromatic polymers. Some linear aromatic polymers, in which the aromatic nucleus is present in the main chain, have been known for many years to have outstanding and unusual properties and have acquired considerable industrial importance. Among these are poly(ethylene terephthalate), the Epon resins, and the polycarbonates.

A discussion of the chemistry and exciting commercial potential of the polypyromellitimides was presented by J. Idris Jones (National Chemical Laboratory, Teddington, England). These unique polymers are stable up to about 600°C. They not only have good oxidative stability but also extreme toughness, good mechanical and dielectric properties, good solvent resistance, and excellent flame and radiation resistance. These polymers were discovered independently by Jones's group, by E. I. du Pont de Nemours and Company (they form the basis of Du Pont H film), and by Westinghouse Electric Corporation. They are being developed by the two American companies.

The preparation of the polypyromellitimides involves a post-fabrication heat treatment. Pyromellitic anhydride reacts under mild conditions (under 50°C in dimethyl formamide) with an aromatic diamine in a mole ratio of 1:1 to form a solution of an intermediate of high molecular weight, polypyromellitamic acid. Films are then cast from this solution, and the film is heated to bring about an intramolecular cyclodehydration to form the insoluble, infusible polyimide. Examination of a wide variety of aromatic diamines revealed that the polyimide from 4,4′-diaminodiphenyl ether has the best combination of mechanical, electrical, and thermal properties. Polyimides based on aliphatic diamines and completely aromatic polyamides are much less stable.

Another group of outstanding high-temperature polymers, the poly(1,3,4-oxadiazoles), also involve an intramolecular cyclodehydration reaction which occurs after fabrication. A. H. Frazer (E. I. du Pont de Nemours and Company) showed that these completely aromatic, insoluble, infusible polymers, analogs of polyphenyl, can be made only by cyclodehydration at about 250°C on a film or fiber of an aromatic polyhydrazide. The intermediate, soluble polyhydrazide of high molecular weight, is prepared by the condensation of an aromatic dibasic acid chloride (1 mole) with hydrazine (1 mole) in hexamethyl phosphoramide solution at 0°C. The best polyoxadiazole is formed from the polyhydrazide derived from an equimolar mixture of the *p*- and *m*-phthalic acid chlorides. It is stable in air up to 450°C, resistant to attack by hot acid and bases, and soluble in concentrated H_2SO_4 with inherent viscosities up to 0.9. Fibers of such aromatic polyoxadiazoles show no change in properties up to 200°C and retain 60 percent of their room-temperature properties even at 300°C. Aliphatic polyoxadiazoles are somewhat less stable.

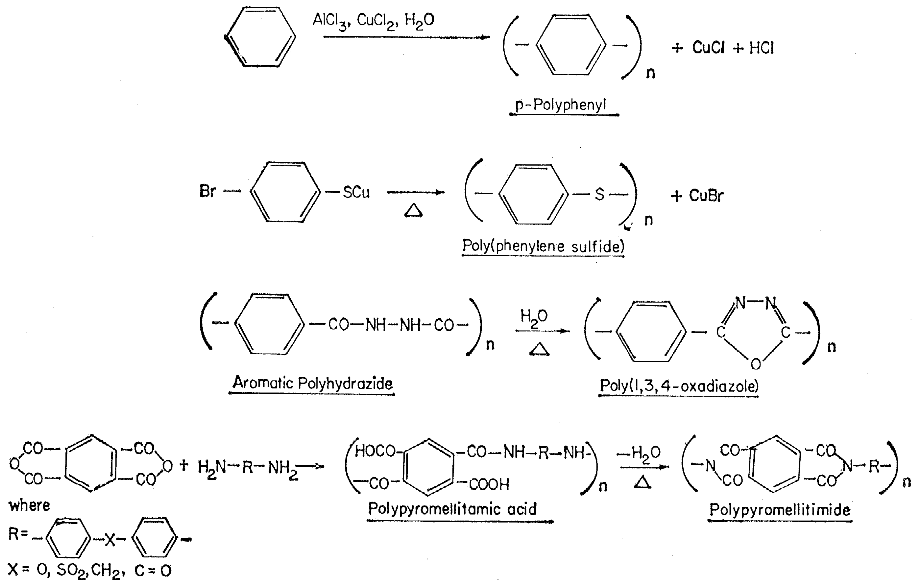

Fig. 1. General mode of formation and structure of four classes of linear aromatic polymers.

Both Jones and Frazer indicated that the solid-state, post-fabrication, cyclodehydration which was involved with their respective aromatic polymers appears to be solely intramolecular, and thus does not result in any cross-linking. With the polyhydrazides, the crystalline form changes during their conversion to polyoxadiazoles. This conversion is 5 to 10 times faster with an unoriented polyhydrazide than it is with a highly oriented polyhydrazide fiber.

An ingenious, direct polymerization of benzene to *p*-polyphenyl, the simplest linear aromatic polymer, was described by P. Kovacic (Case Institute of Technology). The remarkably mild polymerization conditions (70°C) involve treating benzene, in the presence of water, with a combination of aluminum chloride and cupric chloride, with ferric chloride, or with molybdenum pentachloride. The *p*-polyphenyl, whose structure was established with a variety of evidence, is highly insoluble; it has good thermal stability (up to 525°C), but its molecular weight is not known.

This unusual benzene polymerization to *p*-polyphenyl was described as an oxidative cationic polymerization of the aromatic nuclei. A co-catalyst, preferably water, is required. In the ferric chloride reaction a molar ratio of 1:1 of H_2O and $FeCl_3$ gives the most active initiating agent and highest polymer yield. The $AlCl_3$–$CuCl_2$ system gives fewer side reactions and the purest product. With biphenyl or *p*-terphenyl as monomers in place of benzene, only dimer or trimer is obtained.

Film-forming and fiber-forming poly (phenylene sulfide) of molecular weight greater than 20,000 shows promise in high-temperature laminates and adhesives (Robert W. Lenz, Dow Chemical Co.). This highly crystalline polymer (melting point up to 295°C) is thermally stable up to about 400°C (in air). Its use at high temperature, however, is somewhat limited by its melting point, unless it is cross-linked. This polymer has been cross-linked by protracted heating under nitrogen at 400°C. This treatment causes a weight loss, and the insoluble, infusible product has improved toughness, adhesive strength, and thermal stability. Although the chemistry of the heat treatment is obscure, this polymer is another example of a polymer which is favorably modified by treatment with heat.

The poly(phenylene sulfide) is formed by an aromatic nucleophilic substitution reaction at 250°C and involves a self-condensation of salts of *p*-halothiophenols, preferably cuprous *p*-bromothiophenoxide. Although solution polymerization in pyridine is most rapid, an unusual solid-state polymerization of the pure salt, below its melting point, is also feasible. For some of the *p*-halothiophenol salt polymerizations, an unusual phenomenon termed "preferential polymer formation" occurs. The end group of the polymer chain is more reactive than the monomer, and the reaction takes on some of the characteristics of an addition polymerization rather than the purely step-growth, condensation polymerization expected.

All of the aromatic polymers discussed are excellent insulators, showing no semiconducting behavior.

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Physical Anthropology

The American Association of Physical Anthropologists held its 32nd annual meeting in Boulder, Colorado, 2–4 May, and felt it set a record by having approximately 75 percent of the attending members present papers.

Considering that the study of man is such a broad subject, and that there was only one symposium scheduled (jointly with the Society for American Archaeology), the contributions were expectably diverse. The symposium covered quite a bit of territory—from the origin of Mongoloids to Eskimo–Aleut cultures. It was organized and chaired by William S. Laughlin (Wisconsin) who also summarized the results of recent fieldwork in the Aleutian and Kodiak Islands. Carter Denniston (Wisconsin) reported on the blood groups of three Koniag isolates from the standpoint of the microevolution of small populations. He showed that in spite of a complement of Caucasian genes in all three groups which was caused by admixture, the blood group frequencies are clearly "Eskimo," with high proportions of A_1, R_1, R_2, and M. The discussion by Charles F. Merbs (Wisconsin) dealt with patterns of osteopathology in 100 entire skeletons of Eskimos and Aleuts, particularly in respect to survival disadvantage in the local culture and environment. The disease loads on these isolates were found to be relatively light. There is a high frequency of skeletal anomalies, especially of the spine (spondylolysis, lower thoracic spina bifida, and so forth), and little evidence of trauma except for compression fractures of the vertebral bodies and dental ablation. Osteomyelitis is rare; Pott's disease is unknown from the prehistoric period; dental caries are virtually absent, although tooth wear and abscessing are common; and arthritic signs are concentrated primarily in the elbow and spinal joints with marked sexual dimorphism as far as involvement of the elbow is concerned.

Four papers from the general program illustrate the broad range of the subjects covered. Paul T. Baker and Joel M. Hanna (Pennsylvania State University) described racial differences in Lewis waves—the temperature fluctuations in the human extremities which occur when they are exposed to temperatures low enough to produce tissue damage. Working in the southern highlands of Peru, they found that the Indians have higher Lewis wave responses than whites. They believe that this represents a genetic rather than a cultural adaptation to altitude (actually to the cold of the Andes). On the other hand, they attribute to acclimatization the finding that the hands and feet of the Indians were warmer than those of whites under milder cold exposure.

Alice M. Brues (Oklahoma) reported investigations on the polymorphism of the ABO blood groups after she used a stochastic computer program. Natural selection has previously been suggested as the explanation of the persistence of the A and B genes, which are subject to continual loss as a result of maternal-fetal incompatibility reactions. Calculations which simulate genetic drift in combination with incompatibility and selection effects, show that a stable situation can be brought about by selection which favors all heterozygotes over all homozygotes and that any marked disturbance of this pattern results in a rapid decay of the polymorphism. It was concluded that an overall heterozygote advantage has prevailed over a