

Thermal and Oxidative Degradation of Polymers

In recent decades synthetic polymeric materials, because of their unique physical properties, have rapidly replaced more traditional materials such as steel and nonferrous metals, as well as natural polymeric materials such as wood, cotton, and natural rubber. However, one weak aspect of synthetic polymeric materials compared with steel and other metals is that these materials are combustible under certain conditions. Thus the majority of polymer-containing end products (for example, cables, TV sets, electric appliances, carpets, furniture) must pass some type of regulatory test to help ensure public safety from fire. However, traditional pass/fail tests have not provided any information regarding the relationship between flammability properties and the physical and chemical characteristics of polymeric materials. Such information is needed to develop more fire-safe materials, a need that has accelerated because of European environmental concerns about the use of halogenated flame retardants (because of potential formation of dioxins in the incineration of spent end products). The paper *Effects of Weak Linkages on the Thermal and Oxidative Degradation of Poly(methyl methacrylate)* [1] is one of a series published on this topic by the members of the Materials Fire Research Group at NBS/NIST from 1985 to 1994 [2-11]. These

papers report a new approach that studies the effects of molecular-level structure of polymers on their thermal stability and flammability properties instead of a traditional global thermal-balance approach. This series of studies is built upon the pioneering work on thermal degradation of polymers conducted at NBS from the late 1940s to early 1970s [12].

Providing the technical basis for industrial clients to design less flammable materials requires unfolding the structural features that determine thermal stability. This paper [1] reports a study of the thermal and oxidative degradation mechanisms of an acrylic polymer in atmospheres of nitrogen and air by measuring the change in the sample mass while various specially polymerized samples were heated from 80 °C to 480 °C. Thermal degradation of the acrylic polymer, polymerized using a free-radical method, proceeds in three steps of mass loss: the first and easiest (scheme 1 in Fig. 1) is initiated by scissions of head-to-head linkages at about 160 °C (representing one type of defect at the polymer backbone); the second (scheme 2) by scissions at the chain-end initiation from vinylidene ends at around 270 °C; and the last (scheme 3) by random scission within the polymer chain (at the weakest bonds).

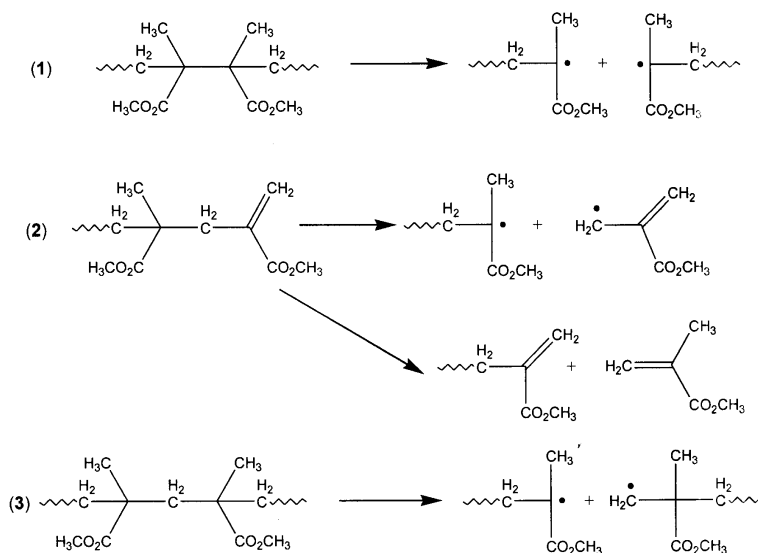


Fig. 1. Three chain scission steps leading to thermal degradation in acrylic polymers.

The first two mass loss steps were not observed with ionically polymerized samples, which indicates that the first two steps are caused by the defects in the polymer. Although the existence of head-to-head linkages could not be demonstrated, the vinylidene ends in the polymer were detected by the ^1H NMR spectrum. No significant differences were seen in the thermal or oxidative degradation of the acrylic polymer when it was polymerized with the free-radical method using two common initiators. It was found that gas-phase oxygen traps polymer radicals resulting from chain scissions at head-to-head linkages, and no mass loss was observed from this step in air. Similarly, oxygen traps radicals generated by end initiation, but mass loss is only delayed to slightly higher temperatures, presumably because of a slight gain in the thermal stability of the oxygen-trapped polymers compared with end initiation.

This series of studies involved not only experimental observations, but also theoretical calculations in which kinetics equations were solved for each polymer chain. Detailed thermal degradation models were developed based on random initiation, depropagation of free radicals, and termination of free radicals; calculations were made with the assumption of steady-state free radical concentration [4], and without that assumption [5]. The kinetic rate constants for each reaction were derived by comparing experimentally measured molecular weights of polymer samples collected at various temperatures and exposure times with the theoretically calculated results [6]. The final paper of the series on thermal degradation investigated the behavior of primary radicals generated from random scissions by measuring evolved degradation products with a mass spectrometer [9].

The influence on thermal stability by the above-discussed defects in the polymer have been studied and published [7,8,10]. The results show that a higher thermal stability increases piloted-ignition delay time and gasification rate of the polymer, but initial molecular weight does not affect ignition delay time. On the other hand, initial molecular weight of the polymer has significant effect on flame spread rate because low molecular weight materials will flow more readily when heated. The physical and chemical roles of the condensed phase in the burning process of polymeric materials were published as a summary of this series of studies [11].

The molecular-level study of the thermal degradation and flammability properties of polymers described above was pursued further by Marc Nyden and coworkers at NIST. They used molecular dynamic simulations of thermal degradation of polyethylene to identify factors that might be effective in reducing polymer flammability by promoting the formation of residual

char [13]. The results predicted that the formation of cross-linking, for example by exposure of polyethylene to ionizing radiation, enhanced further cross-linking when the polymer is burned. An increase in ignition delay time was observed for irradiated polyethylene samples compared to unexposed samples. A similar approach has been pursued by Charles Wilkie at Marquette University, Richard Lyon at the FAA Technical Center, and James McGrath at Virginia Polytechnic Institute and State University.

Because of the increasing demand for non-halogenated flame retardant additives for polymeric end products, this molecular-level study has been extended to include flame retardant mechanisms of polymers containing small quantities of inorganic flame retardant additives. As a result of advances in nanoscale science and technology, molecular-level studies of the effects of trace additives in clay-polymer nano-composites are demonstrating enhanced physical properties with simultaneous improvements in the flammability properties of polymers. This contrasts with the traditional approach, which improves the flammability but often degrades mechanical properties.

The study described in this paper involved the synthesis of specific polymers, analytical characterization of the synthesized polymers, and careful thermogravimetric analysis. Two different groups, the Materials Fire Research Group at NIST and Department of Chemistry at Osaka University, contributed their own expertise to this highly collaborative undertaking. The group at Osaka University synthesized and characterized all polymer samples used in the study, while the group at NIST performed the thermogravimetric analyses.

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James E. Brown joined the Polymer Division of NBS in 1956 as a research chemist, moved to the Fire Science Division in 1975, and retired in 1996. Koichi Hatada, a professor in the Department of Chemistry at Osaka University, was known internationally for his work on

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