

EFFECT OF STRUCTURE OF CHLORINATED VINYL POLYMERS ON SMOKE EVOLUTION

BY

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Recent reports have appeared concerning pyrolytic gas chromatographic studies for a series of polymers, including halogenated vinyl polymers.¹⁻³ However, few workers have related polymer structure and pyrolysis studies to smoke. Our interest in this thermal degradation of chlorinated vinyl polymers has led us to a study of polymer structure and the structural relationships of the decomposition products produced upon burning and their subsequent smoke evolution. We have attempted to answer certain questions, including: (a) Why do certain vinyl polymers evolve increasing amounts of smoke as the amount of chlorine is increased? (b) Does the structure of the polymer being chlorinated have any effect on evolved smoke? (c) Is there an optimum chlorine content at which smoke is reduced?

To answer the above questions it was necessary: (1) to demonstrate that the major pyrolysis products from the thermal degradation of a vinyl polymer can be related to the smoke evolved from that polymer; (2) to demonstrate that total chlorine content of a polymer is less significant as regards fire retardancy and smoke generation than the structural location of the chlorine atom on the polymer chain; and (3) to provide information and insight regarding smoke-evolution properties of chlorine-containing vinyl polymers. To attain the above objectives, four polymer systems were studied: polyethylene (PE), chlorinated polyethylene (CPE), poly(vinyl chloride) (PVC), and chlorinated poly(vinyl chloride) (CPVC). Initially, these polymers were pyrolyzed using gas chromatographic technique and the major decomposition products were identified. Then, the smoke evolution from a series of these polymers was measured using the Rohm and Haas XP2 Smoke Density Chamber. Finally, relative smoke values were determined for these decomposition products using the NBS Smoke Density Chamber. These data were then used for our evaluation of the effect of structure on the smoke-evolution properties of chlorinated and unchlorinated vinyl polymers.

1. Gas Chromatographic Pyrolysis Studies. Most vinyl polymers decompose thermally by radical fragmentation of the polymer chain.² Many types of combustion fragments have been trapped and identified. Boettner and co-workers have analyzed the volatile combustion products of certain vinyl plastics.³ The main decomposition products are carbon dioxide, carbon monoxide, methane, hydrogen chloride, and benzene, which is the most abundant hydrocarbon for PVC. No oxygen-containing compounds were found.

The thermal decomposition of PE, CPE, PVC, and CPVC has been studied at the Armstrong Research and Development Center using pyrolytic gas chromatography.⁴ Representative pyrograms for PE and CPE are shown in Figure 1. No aromatic pyrolytic decomposition products were found with PE. The components in the 3 peak spikes are α,ω -diolefin, α -unsaturated olefin, and saturated paraffin, in order of elution from the column. Mass-spectrographic analysis of the pyrolytic decomposition products of PE has shown that low-molecular-weight, essentially straight-chain, fragments are formed.⁵ These are essentially hydrocarbon fuel-type molecules known to produce little or no smoke on burning. Aromatic molecules were not found and, therefore, the polymer is not expected to evolve appreciable smoke on burning. Substituting a chlorine for hydrogen in PE substantially changes the decomposition products and increases the smoke density. Tsuge and co-workers have investigated chlorinated polyethylenes by pyrolysis gas chromatography.⁴ They found that as the chlorine/carbon ratio increased, the amounts of aromatic hydrocarbons, such as benzene, toluene, styrene, and naphthalene, increased. At a Cl/C ratio of 0.74 (66.8% Cl) chlorinated aromatics, such as chloro- and dichlorobenzenes, were found in appreciable amounts while the yields of unsubstituted aromatics were reduced. We have found that PE requires a higher degree of chlorination than PVC before the pyrolytic yield of unsubstituted aromatic compounds is

reduced. PVC is substituted at some random block methylene groups pound formation: alcohol), poly(v. products similar

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PVC develo: obscuration. I: the maximum sm: reduce the smok: graphically in: slightly obsc: the chlorine c: test. PVC chl: is equivalent: Poly(vinyliden: dicted for PVC: total smoke in: total smoke is