

Pyrolysis of Poly(vinyl Chloride)

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Synopsis

A pyrolysis-gas chromatography-mass spectrometric technique has been developed to study the thermal degradation of poly(vinyl chlorides) polymerized at different temperatures. Hydrogen chloride and benzene evolution during successive stages of pyrolysis have been quantitatively determined and correlated to the tacticity and molecular weight of the polymer. It was found that lowering the temperature of polymerization and molecular weight depresses benzene evolution and increases char weight but does not affect the HCl yield. It is suggested that the syndiotactic *trans* microstructure favored at low temperature of polymerization yields polyenes which cannot cyclize to form benzene. As the molecular weight decreases, the increase in number of vinyl chain ends facilitates pyrolytic crosslinking and char formation.

INTRODUCTION

It is well known that thermal degradation of poly(vinyl chloride) (PVC) evolves HCl, and the dehydrochlorination proceeds along the polymer chain resulting in the formation of a conjugated polyene which is responsible for the dark color of the degraded polymer.¹ The initial reaction is believed to be the elimination of a chlorine atom adjacent to a carbon-carbon double bond or at a tertiary C-Cl bond which is weaker than a secondary C-Cl site.² Stromberg,³ in studies of the thermal degradation of PVC at 400°C for 30 min under vacuum, identified approximately 25 hydrocarbon products after stripping the resin of HCl at temperatures up to 350°C for 30 min.

Otani and Ishikawa⁴ pyrolyzed PVC at 425°C in a nitrogen atmosphere and studied the resulting degradation products by infrared and ultraviolet spectroscopy. They found that PVC of higher syndiotacticity produced shorter-chain alkyl-substituted aromatics. Thinius et al.⁵ showed by gas chromatography the presence of saturated and unsaturated hydrocarbons up to C₈, benzene, toluene, and other aromatic materials during the decomposition of PVC in air. In addition, they reported traces of chlorinated hydrocarbons, formaldehyde, and certain other oxygenated species. Noffz et al.,⁶ using pyrolysis chromatography with capillary columns, demonstrated that the hydrocarbon degradation products consisted mainly of aromatic compounds, while a volatile aliphatic hydrocarbon fraction was too complex to be identified. Wolley detected by gas chromatography of the thermal decomposition product of PVC approximately 75 organic