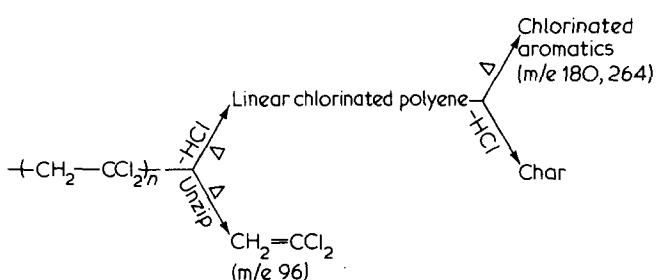


evolved from the decomposing polymer.

The effect of ZnCl_2 as a catalyst for the dehydrochlorination reaction of PVC is well-known⁷, so that these findings are not unexpected for PVdC. Furthermore, data in Figure 2b reveal the total absence of vinylidene chloride among the volatile decomposition products, whereas the chlorinated aromatic compounds appear unaffected.

According to Scheme 1, unzipping and dehydrochlorination are competitive processes, and the strong enhancement of the rate of HCl evolution caused by ZnCl_2 should, as a consequence, lower the rate of monomer evolution.



Scheme 1

Therefore, we can conclude that the absence of monomer observed is in agreement with the simple reaction mechanism proposed here for the thermal decomposition of PVdC.

ACKNOWLEDGEMENT

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Detection and identification of spin-trapped radical produced by ball-milling polyethylene powder with nitrosobenzene

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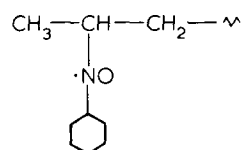
INTRODUCTION

When polymer powders such as polyethylene are fractured, scission of the polymer chain results together with production of a primary radical $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-CH}_2\text{-}\sim$. This primary radical converts to a secondary radical of the type $\text{CH}_3\text{-}\dot{\text{C}}\text{H-CH}_2\text{-}\sim$ at 77K by the movement of the unpaired electron away from the chain end^{1,2}.

Although this secondary radical is stable at 77K, it decays quickly at higher temperatures. Recently, the spin-trapping technique has been employed to stabilize unstable radicals in solution³ or in the gas phase⁴ by achieving an addition reaction of nitroso or nitron compounds (a spin trap) to the unstable radical to form a stable nitroxide radical (a spin adduct).

In this study, the spin-trapping technique was employed to stabilize the radical in the solid phase. Polyethylene powder was milled together with nitrosobenzene powder, and the unstable alkyl radical produced from the chain-scission of a polyethylene chain was stabilized by the addition reaction with nitrosobenzene to

form a stable nitroxide radical which was identified as



EXPERIMENTAL

The polyethylene used was PE Hizex million supplied by Mitsui Petrochemical Industry Company Ltd. The nitrosobenzene was purified by sublimation and trapped with liquid nitrogen.

2 g polyethylene and 100 mg nitrosobenzene powder were mixed together in a specially designed ampoule with a volume of about 60 ml containing 25 glass-balls, each 0.9 cm in diameter. The sample was degassed with a diffusion pump at a pressure less than 10^{-4} mmHg for an extended period, sealed under vacuum, then milled at a milling frequency of 130 cycles min^{-1} at liquid nitrogen

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