

- 3 The Hydrogen bridge is the typical situation, see del Conde, G. and Novaro, O. *Theor. Chim. Acta (Berlin)* 1979, **51**, 79
- 4 Higuchi, J. and To, R. I. *Theor. Chim. Acta (Berlin)* 1971, **22**, 61
- 5 Wurm, H., Regel, W. and Hallensleben, L. *Makromol. Chem.* 1979, **180**, 1581
- 6 These calculations were done before knowing of the article by WRH and comprises a portion of a more extensive work in this field.
- 7 Armstrong, D. R., Perkins, P. G. and Stewart, J. J. P. *J. Chem. Soc. (A)* 1971, 3674
- 8 Armstrong, D. R., Novaro, O., Ruiz-Vizcaya, M. E. and Linarte, R. J. *J. Catal.* 1977, **48**, 8
- 9 Distances are taken for Py from 'Intermolecular Distances', The Chemical Society, London (1958) and for MAH from Herndon, W. C. and Hall, L. H. *Theor. Chim. Acta (Berlin)* 1967, **7**, 4
- 10 Mo, O., Yañez, M. and Fernandez-Alonso, J. I. *J. Phys. Chem.* 1975, **79**, 2137

Mechanism of thermal decomposition of poly(vinylidene chloride)

Alberto Ballistreri, Salvatore Foti, Pietro Maravigna, Giorgio Montaudo and Emilio Scamporrino

Istituto Dipartimentale di Chimica Industriale dell' Università di Catania, Viale A. Doria, 6
95125 Catania, Italy

(Received 25 February 1980; revised 22 April 1980)

The thermal decomposition of poly(vinyl chloride) (PVC) and poly(vinylidene chloride) (PVdC) proceed through an endothermic dehydrochlorination reaction¹, but little information exists in the literature on the mechanism of thermal decomposition of PVdC, which is assumed to be similar to that of PVC²⁻⁴.

We have previously found⁵ that direct pyrolysis in the ion source of a mass spectrometer (m.s.) can provide useful information on the volatile species evolved during the thermal decomposition of polymeric materials and so give an insight into the thermal decomposition mechanism. We have used this technique in order to detect the volatile decomposition products formed by heating PVdC. Pyrolyses were carried out in quartz probes using the direct insertion inlet of an electron impact mass spectrometer LKB-9000S following the technique described elsewhere⁵.

The experimental conditions were as follows: electron energy, 18 eV; ion source temperature, 250°C; accelerating voltage, 3.5 kV; heating rate 10°C min⁻¹.

Figure 1 shows the mass spectrum relating to the pyrolysate of PVdC at 190°C. Fragments at $m/e = 36$ (HCl), 96 (C₂H₂Cl₂), 180 (C₆H₃Cl₃), 264 (C₁₀H₄Cl₄), are the most abundant. These species are highly informative in accounting for the decomposition mechanism of PVdC.

Following the general trend of 1,1-disubstituted vinyl-polymers, PVdC tends to unzip to form monomer when heated, but the unzipping rate is greatly reduced by the concomitant dehydro-chlorination reaction, leading to the formation of linear chlorinated polyene structures (Scheme 1). The latter decompose and rearrange intramolecularly to produce aromatic compounds such as trichlorobenzene and tetrachloronaphthalene. This process occurs in parallel with an extensive crosslinking reaction which yields char⁶.

Further support to this reaction scheme comes from the effect of ZnO on the thermal decomposition of PVdC.

Figure 2 shows the volatilization rate profiles (absolute ion intensity vs. temperature) of the thermal degradation products of pure PVdC (Figure 2a) and PVdC/ZnO (10 wt %) mixtures (Figure 2b).

As a result of the presence of ZnO, the thermal decomposition of PVdC occurs at a considerably lower temperature, whereas ZnCl₂ appears among the volatile pyrolysis products.

Evidently, ZnCl₂ is produced in the early stages of the thermal decomposition by reaction of ZnO with the HCl

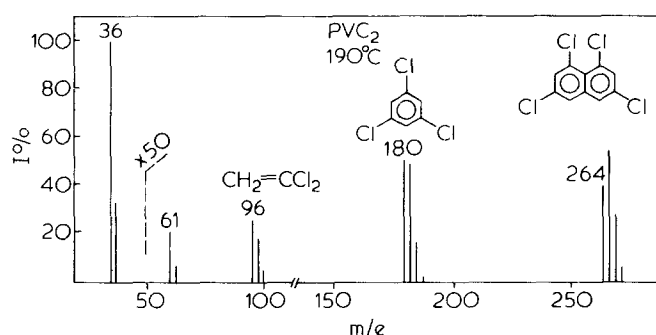


Figure 1 Mass spectrum (18 eV) of the products of thermal degradation for PVdC at 190°C

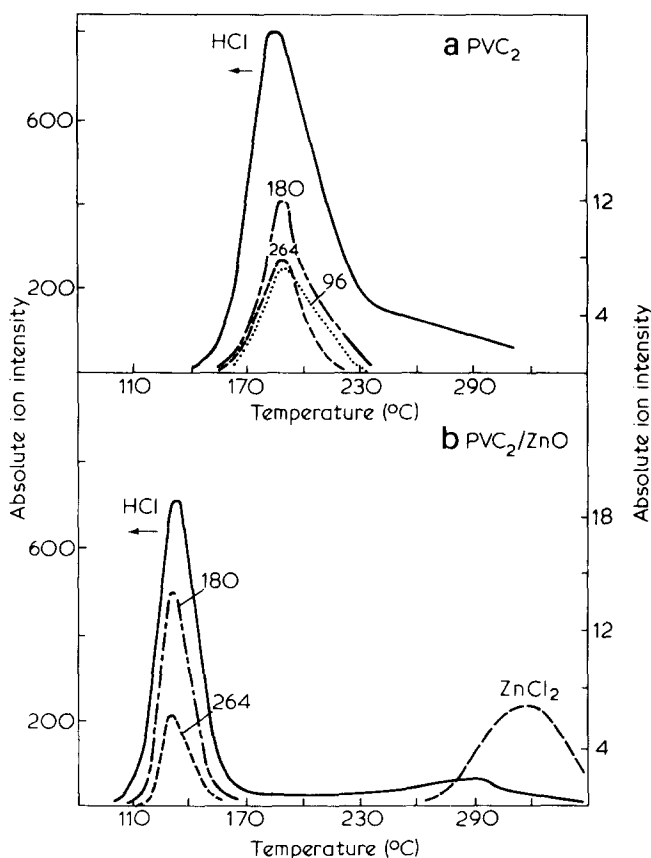
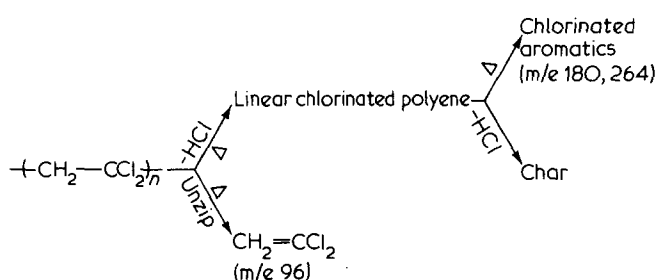


Figure 2 Absolute ion intensity of relevant mass peaks ($m/e = 96$, vinylidene chloride; $m/e = 180$, trichlorobenzene; $m/e = 264$, tetrachloronaphthalene) as a function of the temperature for: (a) PVdC; (b) PVdC/ZnO (10 wt %) mixture

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

Financial support from the Consiglio Nazionale delle Ricerche, Rome, is gratefully acknowledged.

REFERENCES

- 1 Grassie, N. 'Chemistry of High Polymer Degradation Processes' Butterworths, London 1956, p 5
- 2 David, C. 'Thermal Decomposition of Polymers' in 'Chemical Kinetics' (Eds. C. H. Bamford and C. H. F. Tipper), Elsevier, Amsterdam 1975, p 78
- 3 Conley, R. T. and Malloy, R. 'Vinyl and Vinylidene Polymers' in 'Thermal stability of Polymers' (Ed. R. T. Conley), Marcel Dekker, New York 1970, p 229
- 4 Zeman, A. *Thermal Analysis* 1971, **3**, 219
- 5 Luderwald, I., Montaudo, G., Przybylski, M. and Ringsdorf, H. *Makromol. Chem.* 1974, **175**, 2423, 2441; 1975, **176**, 1753, 1763
- 6 Murayama, N. and Amagi, Y. *J. Polymer Sci. (B)* 1966, **4**, 115
- 7 Frye, A. H. and Horst, R. H. *J. Polymer Sci.* 1960, **45**, 1

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

Somsak Vivatpanachart, Hiroyasu Nomura*, Yutaka Miyahara

Department of Chemical Engineering, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, 464, Japan

Hisatsugu Kashiwabara

Nagoya Institute of Technology, Showa-ku, Nagoya, 466, Japan

and Masato Sakaguchi

Ichimura College, Inuyama, 484, Japan

(Received 25 April 1980)

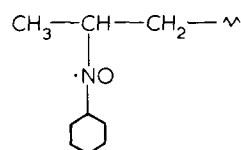
INTRODUCTION

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 $130 \text{ cycles min}^{-1}$ at liquid nitrogen

* To whom correspondence should be addressed