Determination of Tertiary Chlorine Structures in Polyvinylchloride

E. C. Buruiană, A. Airinei, G. Robilă and A. Caraculacu

"Petru Poni" Institute of Macromolecular Chemistry, 6600 Jassy, Romania

SUMMARY

A chemical method to determine the tertiary chlorine content in PVC based on the reaction of brominated PVC samples with phenol was established. A good agreement between the long branches content and the tertiary chlorine content was found. The thermal stability of the brominated PVC increased.

INTRODUCTION

As it is well known the thermal instability of PVC is mainly due to some structural defects as branching and unsaturated groups.

RIGO et al. (1972), ABBAS et al. (1975), BOVEY et al. (1975) have found in a lithium aluminium hydride (LiAlH₄) reduced polymer ca. 5/1,000 monomer units (m.u.) short chloromethyl type branches, \(-\text{CH}-, \text{CH}_2\text{Cl}\)
besides a much less content, 0.5/1,000 m.u., of long branches (CARRENGA 1977).

STARES et al. (1979 a) indicated that LiAlH₄ is a poor reducing agent, as the polymer is incompletely reduced and double bonds could appear. Using a polymer obtained from deuterated vinyl chloride, STARES et al. (1979 b) confirmed RIGO's mechanism about the appearance of short chloromethyl branches.

The macroradical terminated in a head-to-head sequence is stabilized by the migration of a chlorine atom, as follows:
The NMR $^{13}$C analysis of the polymer reduced by means of LiAlH$_4$ sustains the above mechanism.

The long branches could appear either through a transfer to polymer (ENOMOTO 1970) or by copolymerization with unsaturated end groups in PVC (CARACULACU et al. 1978).

In a previous paper (ROBILA et al. 1977) there was described a chemical method to determine the total content of labile chlorine, without specifying the amounts of tertiary chlorine (Cl$_T$) and allylic chlorine (Cl$_A$).

The present work was undertaken in order to establish a chemical method for the determination of tertiary chlorine containing structures in PVC and to find out how these structures influence the thermal stability of the polymer.

**EXPERIMENTAL**

The PVC samples, delivered by the IUPAC Working Party on the PVC Structure, were brominated according to BOISSEL's method (1977). The samples were purified to remove bromine excess. The phenolysis of PVC samples and of brominated PVC samples was performed at 60° for 98 hrs (ROBILA et al. 1977). The determination of tertiary chlorine of brominated samples were carried out in 1% tetrahydrofuran solutions. The ultraviolet absorption spectra were recorded on a UNICAM SP 800 spectrophotometer using 10 mm cells. The thermal stability was determined conductometrically (CARACULACU et al. 1979).

**RESULTS AND DISCUSSION**

The NMR $^{13}$C spectroscopy has made possible a more detailed analysis of the structure of branches