Polymer Bulletin 3, 267–271 (1980)

Polymer Bulletin

Determination of Tertiary Chlorine Structures in Polyvinylchloride

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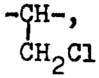
SUMMARY

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 ($LiAlH_4$) reduced polymer ca. 5/1,000 monomer units (m.u.) short chloromethyl type branches,  $-\underset{CH_2Cl}{\underset{|}{C}H}-$, besides a much less content, 0.5/1,000 m.u., of long branches (CARREGA 1977).

STARNES et al. (1979 a) indicated that $LiAlH_4$ is a poor reducing agent, as the polymer is incompletely reduced and double bonds could appear. Using a polymer obtained from deuterated vinyl chloride, STARNES 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:

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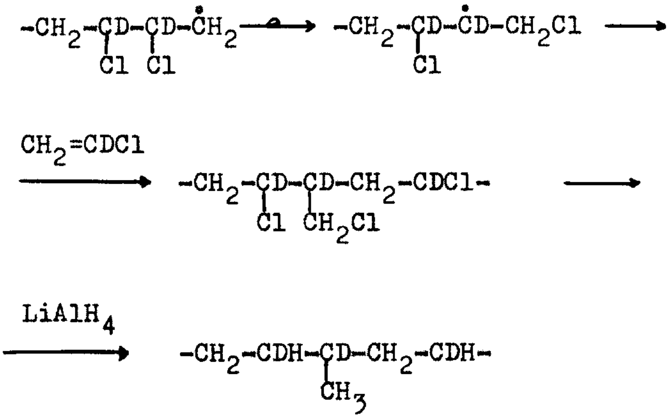


$$-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CD}}-\underset{\mathrm{Cl}}{\mathrm{CD}}-\dot{\mathrm{C}}\mathrm{H_2} \longrightarrow -\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CD}}-\dot{\mathrm{C}}\mathrm{D}-\mathrm{CH_2Cl} \longrightarrow$$

$$\xrightarrow{\mathrm{CH_2{=}CDCl}} -\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CD}}-\underset{\mathrm{CH_2Cl}}{\mathrm{CD}}-\mathrm{CH_2}-\mathrm{CDCl}- \longrightarrow$$

$$\xrightarrow{\mathrm{LiAlH_4}} -\mathrm{CH_2}-\mathrm{CDH}-\underset{\mathrm{CH_3}}{\mathrm{CD}}-\mathrm{CH_2}-\mathrm{CDH}-$$

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 determinated conductometrically (CARACULACU et al. 1979).

RESULTS AND DISCUSSION

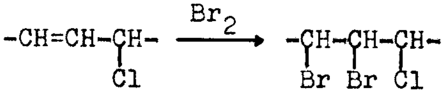
The NMR ^{13}C spectroscopy has made possible a more detailed analysis of the structure of branches in tri-n-butyltin hydride reduced PVC (STARNES et al. 1979 a). There were thus established the following types of branches in polymer (BOVEY et al. 1979; WINSLOW 1979): 4 - 5 chloromethyl branches/1,000 m.u.; .4 - 2.4 2-chloroethyl branches/1,000 m.u.; 0.4 - 1.6 2,4-dichlorobutyl branches/1,000 m.u. and 1.0 - 2.4 long branches/1,000 m.u.

According to STARNES' opinion (1979 a) these long branches would bear tertiary chlorine atoms and therefore their influence on the polymer stability would be important.

In order to determine the tertiary chlorine content we have brominated eight PVC samples according to BOISSEL's method (1977) and then phenolized them.

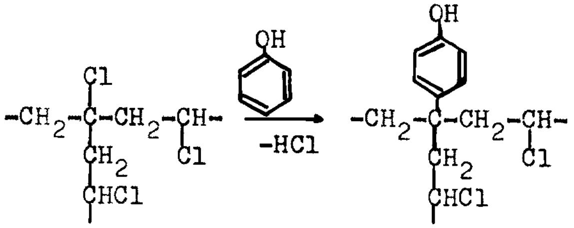
As it is known the phenol reacts quantitatively with both structures, Cl_T and Cl_A (ROBILA et al.(1977).

The bromination takes place only on the double bonds in PVC, leading to the disappearance of Cl_A structures (reaction 1). Therefore the brominated PVC samples will contain only Cl_T structures to react with phenol (reaction 2).



$$-CH=CH-\underset{Cl}{CH}- \xrightarrow{Br_2} -\underset{Br}{CH}-\underset{Br}{CH}-\underset{Cl}{CH}-$$

Reaction 1



Reaction 2

The results are summarized in Table I.

From this table, the Cl_T content is smaller than the total labile chlorine content (Cl_L). Because the total number of PVC branches is much greater than the tertiary chlorine content one can conclude that at the branching sites there is mostly hydrogen.

By comparing the content of long branches (SORVIK 1978) with the Cl_T content in PVC one can say that the long branches bear at the branching sites mainly tertiary chlorine atoms.

TABLE I

Content of structural defects in PVC to 1,000 m.u.

Sample No.	Cl_L atoms	Cl_T atoms	Long branches	Double bonds
1.	1.17	0.18	0.18	1.47
2.	2.51	1.17	1.50	3.05
3.	1.58	0.48	0.15	1.97
4.	1.64	0.28	0.94	2.05
5.	0.56	0.27	0.38	1.53
6.	0.57	0.16	0.46	1.48
7.	0.96	0.47	0.63	1.51
8.	0.76	0.18	0.17	1.80

The thermal stability of these PVC samples was determinated conductometrically before and after bromination. The starting temperature of the dehydrochlorination reaction was taken as a criterion to estimate the thermal stability, working with a linear program of increasing of temperature (CARACULACU et al. 1979). The results are given in Table II.

TABLE II

Starting dehydrochlorination temperature before and after bromination (^oC)

Sample No.	Initial sample	Sample after bromination
1.	136	154
2.	97	137
3.	138	159
4.	165	163
5.	125	169
6.	155	162
7.	153	165
8.	162	187

As one can see from the examination of Table II the thermal stability of the polymer is greatly increased by bromination. Therefore, the principal structural defects influencing the thermal stability are the double bonds.

However, a great value of the Cl_T content leads to the decrease of the thermal stability of the polymer. Thus, sample 2 (Cl_T = 1.17/1,000 m.u.) is unstable even after bromination.

As one can not find a perfect correlation between the Cl_T content and the starting temperature of dehydrochlorination, we consider also other structures as being involved in the polymer instability.

CONCLUSIONS

1. A chemical method to determine the Cl_T content in PVC was established.
2. The values of Cl_T content, determined by this method are between 0.16 - 1.17 atoms/1,000 m.u. They are smaller than those of total labile chlorine content.
3. The double bonds in PVC are removed by bromination, obtaining an increase of thermal stability. This demonstrates the contribution of these structures to the polymer instability.

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Received August 4/ Revised September 18/ Accepted September 19,198o