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On the Distribution of Chlorine-Atoms in Chlorinated Polyvinylchloride Prepared by Various Methods

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Polyvinylchloride (PVC) is often chlorinated to develop the heat stability, resistance to chemical agents and so on. The properties of the chlorinated polyvinylchloride (CPVC) may vary not only with the degree of chlorination but also with the distribution of chlorine atoms in the polymer chains. Recently we have presented the study of structure of chlorinated PVC by pyrolysis-gas chromatography with a furnace type pyrolyzer¹⁾. In this work, the distributions of substituting chlorine atoms were studied with CPVC synthesized by various methods and their differences resulting from the method were also discussed by pyrolysis-gas chromatography with a new induction heating pyrolyzer.

Three series of CPVC were prepared by the following methods of chlorination; the first one is a gas phase method, where PVC was chlorinated under the illumination of a chemical lamp in the atmosphere composed of one part of nitrogen and one part of chlorine gas, the second one is a suspension method, where the chlorination was carried out in the suspension method composed of one part of 33 % hydrochloric acid and one third of PVC, and the last one is a solution method¹⁾, where the chlorination was performed in chloroform solution of PVC. The resulting polymers by the gas phase-, the suspension- and the solution method will be abbreviated as CPVC-Gas, CPVC-Susp, and CPVC-Soln, respectively.

The degree of chlorination (A) of the polymer is defined as percentage number of monomer units containing two chlorine atoms as follows :

$$A = \frac{62.5 \cdot \text{Cl wt.-%} - 3550}{35.5 - 0.345 \cdot \text{Cl wt.-%}}$$

Pyrolysis of the polymer was carried out by a new induction heating pyrolyzer (CURIE point pyrolyzer; Japan Analytical Industry, Model JHP-2) shown in Fig. 1. Polymer sam-

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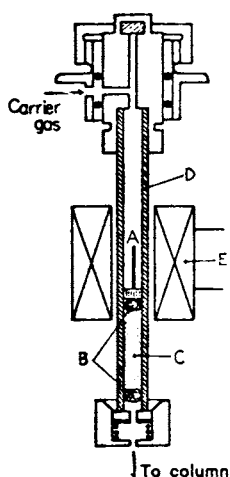


Fig. 1. Induction heating pyrolyzer. A: Sample charging foil; B: glass wool; C: NaOH coated on Diasolid H; D: quartz tube; E: induction coil

ple wrapped by a piece of foil, whose CURIE temperature lay in 423 °C, was mounted in the induction coil and decomposed instantaneously by applying current to the coil. The resulting pyrolysis products were separated by a PEG-20M-column to record pyrograms.

As shown in our previous work¹⁾, raw PVC yields benzene almost quantitatively, whereas with the rise of chlorination (A), various chlorine-substituted aromatics are observed. A typical pyrogram of CPVC-Susp (A = 56.1) is shown in Fig. 2.

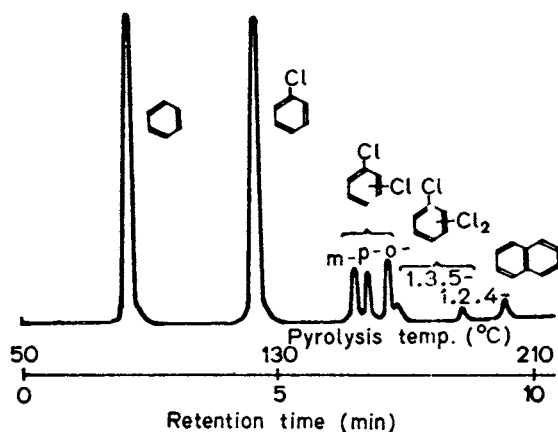


Fig. 2. Typical pyrogram of chlorinated polyvinylchloride (CPVC) prepared by suspension method. (Degree of chlorination (A) = 56.1)

Relative yields of the benzene derivatives from the various CPVC are Summarized in Table 1. Three series of CPVC differ greatly from one another especially in the yields of mono-, di-, and trichlorobenzenes, which is illustrated in Fig. 3. Although the yield of benzene decreases with the rise of chlorination, any appreciable differences are not observed between

Table 1. Relative yields of pyrolysis products (mole-%)

Degree of chlorination (A)	Benzene	Chlorobenzenes		
		mono-	di-	tri-
(CPVC-Susp)				
9.5	90.2	9.8	—	—
26.6	67.3	27.4	5.3	—
27.2	62.6	29.9	7.5	—
33.5	60.0	31.4	8.6	—
45.8	43.2	39.1	16.5	1.2
48.2	42.6	37.2	18.1	2.1
56.1	37.8	36.7	21.7	3.8
(CPVC-Gas)				
10.8	91.1	8.9	—	—
35.7	64.4	28.0	7.6	—
38.0	52.9	36.4	10.7	—
39.8	51.6	36.7	10.9	0.8
48.3	45.9	35.5	16.7	1.9
54.1	40.9	34.4	21.6	3.1
(CPVC-Soln)				
9.9	87.7	12.3	—	—
24.5	72.6	27.4	—	—
36.3	56.0	40.3	3.7	—
37.5	52.9	39.4	7.7	—
42.7	47.0	46.1	6.9	—
57.5	24.2	57.1	17.6	1.1

the three series of CPVC. On the other hand, the yields of mono-, di-, and trichlorobenzenes increase as a function of the degree of chlorination. Among them, the yield of mono chlorobenzene increases in order of CPVC-Soln, -Susp, and (or) -Gas, whereas the yields of di- and trichlorobenzenes show the contrary tendency. However, the difference between CPVC-Susp and -Gas is not so great. These results suggest that the distribution of the introduced chlorine atoms in CPVC-Soln is more homogeneous than those in CPVC-Susp and -Gas.

The distributions are reasonably considered to be dependent upon both the mobility of the polymer chains and that of chlorine atoms to be introduced. The polymer chains in solution move more freely than that in suspension or solid state. On the other hand, the mean free path of chlorine atom in gas phase is much longer than that in suspension and solution. More homogeneous distributions of chlorine atoms in CPVC-Soln

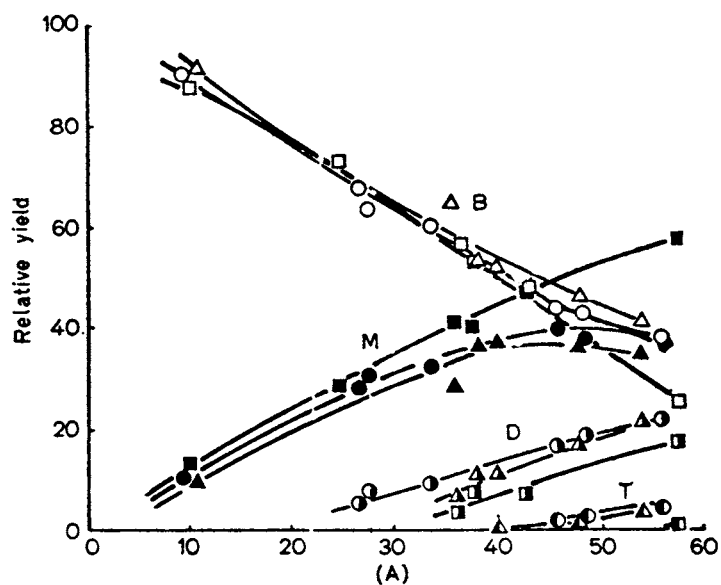


Fig. 3. Relationships between the degree of chlorination (A) and the yield of degradation products from chlorinated polyvinylchloride (CPVC). B: Benzene (containing a little amount of naphthalene); M: monochlorobenzene; D: dichlorobenzenes (*m*-, *p*-, and *o*-); T: trichlorobenzenes (1.3.5- and 1.2.4-). ○ CPVC-Susp; △ CPVC-Gas; □ CPVC-Soln.

than that in CPVC-Gas inform us that the degree of freedom of polymer chains matters more than that of chlorine atoms. In suspension, the mobility of both chlorine and the chains is small and, therefore, the distribution is most localized.