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Pyrolysis-Gas Chromatographic Determination of Chlorine in Chlorine-Containing Synthetic Polymers

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A new, simple and rapid method for determining chlorine in chlorine-containing polymers was investigated by means of pyrolysis-gas chromatography. Hydrogen chloride evolved during the thermal degradation of the polymers was eliminated by a NaOH precut column, and only the organic compounds sensitive to flame ionization detector were separated to record the pyrograms. Chlorine content of the polymers was calculated from the relative yield of the degradation products using a theoretical equation deduced from the degradation mechanisms of the polymers. This unique method permits very rapid determination of chlorine with the use of about 0.1 mg of the sample without either the use of calibration curves or weighing of the samples.

Various kinds of chlorine-containing polymers with C–C bond in the backbone chains are now available. The routine determination of chlorine in the polymers is carries out by means of either ordinary chemical method or elemental analysis. Although these methods are excellent for accuracy, they are troublesome and time-consuming.

Recently, we have presented a series of studies[1–4] on polymers by pyrolysis-gas chromatography (PGC), in which we proposed a method to obtain characteristic and reproducible pyrograms with the use of an improved pyrolyzer,[1] and successfully characterized the microstructures of such chlorine-containing polymers as vinyl chloride-vinylidene chloride copolymers[2], chlorinated polyethylene[3] and chlorinated polyvinylchlorides[4].

The present work describes a new method for the simple and rapid determination of chlorine in various kinds of chlorine-containing polymers by means of PGC.

Experimental

Materials. Four kinds of chlorine-containing polymers were prepared. Chlorinated polyethylenes (CPE) were obtained by chlorination of polyethylene with the use of CCl_4-solution method proposed by Campbell and Lyman.[5] Chlorinated polybutadienes (CPB) and chlorinated polyvinylchlorides (CPVC) were synthesized by chlorination of polybutadiene and polyvinylchloride, respectively, utilizing the $CHCl_3$-solution method.

Vinyl chloride-vinylidene chloride copolymers were prepared by suspension polymerization using azobisisobutyronitrile as a catalyst.

Apparatus. A furnace type pyrolyzer was used to decompose the polymers. Figure 1 shows a schematic diagram of the pyrolyzer. It was directly attached to the inlet port of the gas chromatograph, Yanagimoto Model GCG-550F with dual flame ionization detectors. The sample holder of the pyrolyzer was so modified as to obtain characteristic and reproducible pyrograms by reducing its heat capacity.[1] Hydrogen chloride evolved during the thermal decomposition of the polymers was eliminated by a NaOH precut column whose temperature was maintained at about 200°C. To minimize the change of the pyrolysis temperature, which influences the reproducibility of the results, a voltage-stabilizer was used for the pyrolyzer. A sample weighing about 0.1—0.3 mg was pyrolyzed under a flow of carrier gas (N_2) at fixed pyrolysis temperatures for 1 min which was sufficient for complete pyrolysis.

Gas Chromatographic Conditions. Gas chromatographic conditions and the method of identification of the peaks appearing on the pyrograms are the same as described previously.[2–4] Separation columns (3 mm i.d. ×2 m) containing 10 wt% of Carbowax 6000 coated on Diasolid L (80—100 mesh) were used. The column temperature was first programed from 50 to 210°C at a rate of 16°C/min, and then operated isothermally at 210°C. The flow rate of carrier gas (N_2) was maintained at 40 m*l*/min at 50°C. Hydrogen flame was made by means of 40 m*l*/min of H_2 and 700 m*l*/min of air. As the flame ionization detector responds nearly to the number of carbon atoms in the component, the relative yield (wt%) of the degradation products was calculated from the relative peak area on the pyrogram by making weight sensitivity corrections of each component for the flame ionization detector.

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1) S. Tsuge, T. Okumoto and T. Takeuchi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **71** 1634 (1968).

2) S. Tsuge, T. Okumoto and T. Takeuchi, *Makromol. Chem.*, **123**, 123 (1969).

3) S. Tsuge, T. Okumoto and T. Takeuchi, *Macromolecules*, **2**, 200 (1969).

4) S. Tsuge, T. Okumoto and T. Takeuchi, *ibid.*, **2**, 277 (1969).

5) T. W. Campbell and J. Lyman, *J. Polymer Sci.*, **55**, 169 (1961).

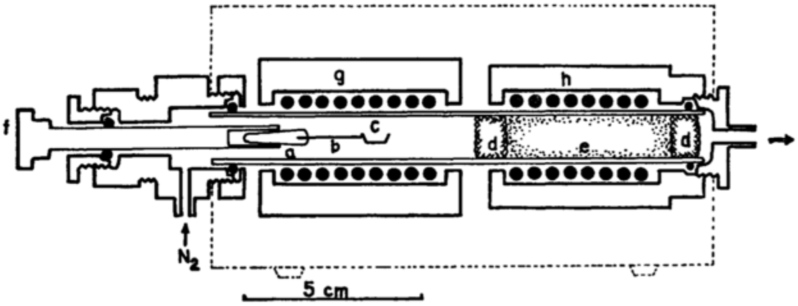


Fig. 1. Pyrolyzer: a, glass rod; b, needle; c, sample holder(Ag); d, glass wool; e, NaOH coated on Diasolid H; f, sample charging rod; g, pyrolysis heater; h, precut heater.

Results and Discussion

In order to obtain characteristic, reproducible and sharp pyrograms, the optimum pyrolysis temperatures were decided experimentally; 400°C for P(VC-VDC) and CPVC, 490°C for CPB and 660°C for CPE. The relatively high pyrolysis temperature of 660°C reflects a fairly good thermal stability of CPE.

Figure 2 shows typical pyrograms of CPE, CPB, P(VC-VDC) and CPVC. The degradation products appearing on the pyrograms can be divided into two classes. The first consists of the products formed mainly by simple thermal scissions of the polymer chains; lower hydrocarbons (C_1-C_6) and vinylidene chloride. For example:

$$\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CCl}_2\text{-} \rightarrow \text{CH}_2\text{=CH}_2 + \text{CH}_2\text{=CCl}_2$$

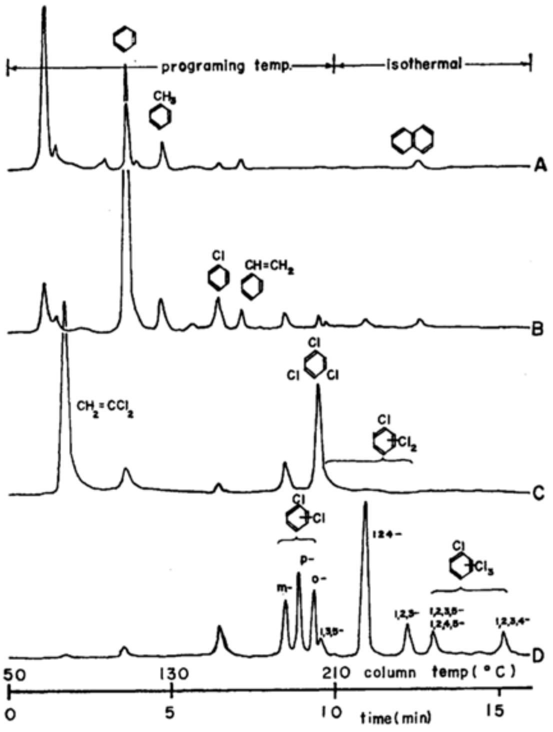


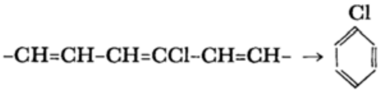
Fig. 2. Typical pyrograms of chlorine-containing polymers.
A; CPE(Cl: 28.8 wt%) at 660°C, B; CPB(Cl: 54.5 wt%) at 490°C, C; P(VC-VDC)(Cl: 68.6 wt%), D; CPVC(Cl: 73.2 wt%) at 460°C

The second consists of those formed by dehydrochlorination followed by cyclization; aromatic hydrocarbons and some chlorine-substituted benzenes. For example:

dehydrochlorination

$$\text{-CH}_2\text{-CHCl-CHCl-CHCl-CH}_2\text{-CHCl-} \rightarrow$$
$$\text{-CH=CH-CH=CCl-CH=CH-} + 3\text{HCl}$$

cyclization



In this case, it is assumed that the dehydrochlorination reaction occurs to form the conjugated polyene-structures along the chain of the polymers. Consequently, to make the latter type of degradation products correspond to the original structures of the polymer, we have to consider the products together with the eliminated 3 mol of hydrogen chloride. For the sake of simplicity, lower hydrocarbons were regarded as mono-olefines, and a small amount of toluene, styrene and naphthalene was converted into benzene in the calculation and added to the observed yield of benzene.

From these degradation mechanisms of the polymers, we obtain a calculation table (Table 1) and the following equation for the determination of chlorine in the polymers:

$$\text{Cl wt\%} = \frac{\sum_{i=2}^{7} \frac{C_i Y_i D_i}{A_i}}{\sum_{i=2}^{7} \frac{C_i Y_i}{A_i} + Y_1} \qquad (1)$$

where A is the molecular weight of the degradation product, C is the molecular weight of the original structure before dehydrochlorination, D is chlorine content (wt%) in C, Y is the observed yield (wt%) of the degradation product and the suffix i designates the component number in Table 1.

TABLE 1. CALCULATION TABLE FOR THE DETERMINATION OF CHLORINE CONTENT

No. (*i*)	Degradation product P	Molecular weight of P *A*	Eliminated HCl (mol) from C *B*	Molecular weight of the original structure $C=(A+B)$	Cl-content in C (wt%) *D*	Observed yield of P *Y*
1	Lower hydrocarbons	—	0	—	0	Y_1
2	Vinylidenechloride	97.0	0	97.0	73.2	Y_2
3	Benzene	78.0	3	187.5	56.8	Y_3
4	Chlorobenzene	112.5	3	222.0	64.0	Y_4
5	Dichlorobenzenes[a]	147.0	3	256.5	69.2	Y_5
6	Trichlorobenzenes[b]	181.5	3	291.0	73.2	Y_6
7	Tetrachlorobenzenes[c]	216.0	3	325.5	76.4	Y_7

a) Total of *o*-, *m*- and *p*-dichlorobenzene.
b) Total of 1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene.
c) Total of 1,2,3,4-, 1,2,3,5- and 1,2,4,5-tetrachlorobenzene.

TABLE 2. DATA OF REPRODUCIBILITY AND ACCURACY

Degradation product	Observed relative yield of the degradation product (wt %)											
	CPE			CPB			P(VC-VDC)			CPVC		
	Cl: 28.8 wt %[a]			Cl: 54.5 wt %[a]			Cl: 68.6 wt %[a]			Cl: 73.2 wt %[a]		
Lower hydrocarbon	73.6	74.0	73.0	18.9	19.6	16.9	—	—	—	—	—	—
Vinylidenechloride	—	—	—	—	—	—	27.1	35.6	20.4	—	—	—
Benzene	26.4	26.0	27.0	67.7	66.6	69.2	1.6	1.6	1.9	0.4	0.3	0.3
Chlorobenzene	—	—	—	8.9	8.8	8.3	13.9	11.3	15.9	3.7	4.6	3.5
Dichlorobenzenes[b]	—	—	—	3.6	3.8	4.5	43.2	37.6	45.9	30.3	29.7	29.2
Trichlorobenzenes	—	—	—	0.9	1.2	1.1	14.2	13.9	15.9	46.6	44.4	44.5
Tetrachlorobenzenes[d]	—	—	—	—	—	—	—	—	—	19.0	21.0	22.5
Cl-content (wt %)[e]	26.3	26.0	26.7	52.7	52.5	53.4	69.2	69.7	68.8	72.0	71.9	72.2
Mean (wt %)[f]	26.3			52.9			69.3			72.0		
Std. deviation	0.34			0.46			0.45			0.15		
Rel. std. dev. (%)	1.27			0.87			0.65			0.21		
Abs. dev. (f−a wt %)	−2.5			−1.6			+0.6			−1.2		

a) Determined chemically.
b, c, d) Refer to Table 1.
e) Calculated from Eq. (1).

Figure 3 shows the analytical results obtained by PGC against those by chemical analysis. The relatively good linearity of the calibration curve may support the assumptions implicit in this method. Statisticaly evaluation of the method is presented in Table 2. Three observations were made with each polymer sample. As might be expected from the small relative standard deviations, the reproducibility of the method is good, but not the accuracy data expressed as absolute deviations. This method tends to give a lower chlorine content than that obtained chemically except in the case of P(VC-VDC). This tendency is especially conspicuous with CPE. This phenomenon is related to the thermal stability and the relatively high pyrolysis temperature of the polymer. With pyrolysis temperature lower than 660°C, however, CPE did not decompose to give quantitative results. As shown in Table 2, it is possible to determine the chlorine content of CPB, P(VC-VDC) and CPVC,

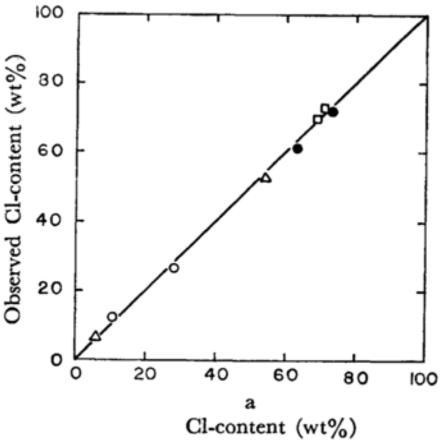


Fig. 3. Calibration curve for chlorine-containing polymers.
○, CPE; △, CPB; □, P(VC-VDC); ●, CPVC; *a*, chlorine content obtained chemically

whose optimum pyrolysis temperatures lie between 460 and 490°C, within 1% of relative standard deviation. To attain good reproducibility, the pyrolysis temperatures must be regulated by the voltage-stabilizer for the pyrolyzer.

This technique is very simple and rapid, and needs neither calibration curves nor weighing of the sample. Moreover, a very small amount of the polymer sample (0.1—0.3 mg) is sufficient.

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