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Pyrolysis-Gas Chromatographic Analysis of Vinylchloride-Vinylacetate Copolymer

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Pyrolysis-gas chromatography was applied to rapid and precise determination of vinylchloride-vinylacetate copolymer by use of the yields of acetic acid and of benzene. The separation column was filled with packing of polymer beads (porapak Q) which are free from deterioration by hydrogen chloride evolved during the thermal degradation of copolymers. Relative yields of acetic acid, which originated from the side chains of the polymer and corresponded to vinylacetate content, and of benzene, formed mainly from successive vinylchloride units, were calculated from the relative peak area appearing on the pyrogram by making relative sensitivity correction for the flame ionization detector. By this method the composition of copolymer can be determined using 0.5—2.0 mg of sample with mean absolute deviation 0.5—0.4 wt%, with the yields of acetic acid and of benzene.

The copolymer of vinylchloride and vinylacetate (VC-VAc) shows different properties according to vinylacetate content. With the increase of vinylacetate content, solubility and adhesive affinity are imporved, and softening point is lowered. Analysis of the copolymer has mostly been carried out by means of IR, NMR and chemical determination of chlorine. A few qualitative works on the analysis of the copolymer by pyrolysis-gas chromatography (PGC), have been reported.[1–3] This is partly associated with the fact that hydrogen chloride evolved during the degradation of the polymer deteriorates the separating column, and has no sensitivity to the flame ionization detector.

Barlow *et al.*[3] reported on the analysis of the copolymer at the relatively high pyrolysis temperature of 580°C, using a hot-filament-type pyrolyzer and Katharometer detector (thermal conductivity detector). They performed the analysis with the peaks of hydrogen chloride and acetic acid on pyrogram of the copolymer with about 2% standard deviation.

In our previous works,[4,5] we characterized the microstructure of chlorine-containing polymers by PGC in which NaOH-precut column was used to adsorb hydrogen chloride evolved during the degradation of polymers.

We have worked out an analytical method for determining the composition of vinylchloride-vinylacetate copolymer with the use of PGC without NaOH-precut column.

Experimental

Materials. VC-VAc copolymers synthesized by suspension polymerization were used as samples.

The content of vinylacetate in the copolymer ranged from 0.5 to 15.7 wt% which was determined by the usual chemical analysis of chlorine.

Apparatus. A heated furnace type pyrolyzer, Hitachi KP-1, whose structure is almost the same as that used previously works[4–6] was used to decompose the polymers. It was directly attached to the inlet port of a gas chromatograph, Hitachi F6-D with flame ionization detectors.

In order to minimize the change of the pyrolysis temperature, which disturbs the reproducibility, a voltage stabilyzer was used for the pyrolyzer.

An optimum pyrolysis temperature 430°C was chosen in order to obtain characteristic, reproducible and sharp pyrograms.

A sample weighing 0.5—2.0 mg was pyrolyzed under a flow of carrier gas (N_2) at the pyrolysis temperature for 1 min. This was sufficient to achieve complete pyrolysis of the polymers.

Gas Chromatographic Conditions. Gas chromatographic analysis was carried out under the following conditions.

Column: Stainless steel tube (3 mm diam. × 0.5 m

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1) Y. Mashiko, A. Echizen and A. Nakao, *Kogyo Kagaku Zasshi*, **68**, 1206 (1965).

2) R. S. Lerhle and J. C. Robb, *Nature*, **83**, 1671 (1959).

3) A. Barlow, R. S. Lehrle and J. C. Robb, *Polymer*, **2**, 27 (1961).

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

5) S. Tsuge, T. Okumoto and T. Takeuchi, *Macromolecules*, **2**, 277 (1969).

6) S. Tsuge, T. Okumoto and T. Takeuchi, *Kogyo Kagaku Zasshi*, **71**, 1634 (1968).

7) N. Grassie, *Trans. Faraday Soc.*, **49**, 835 (1953).

length),

Packing: Polymer beads with porosity (Porapak Q; 120—150 mesh),

Temperature programing: 120—230°C, (7°C/min) isothermal after 230°C,

Carrier gas: N_2 1.0 kg/cm^2 inlet pressure (55 m*l*/min at room temperature),

Hydrogen flame: H_2 0.7 kg/cm^2, air 1.0 kg/cm^2.

Polymer beads (Porapak Q) without liquid phase and NaOH-precut column were packed in the separating column, which is not deteriorated by acidic products such as hydrogen chloride or acetic acid.

Identification of the peaks appearing on the pyrograms was carried out with the use of the retention data of various pure substances which are expected to be formed from the degradation of the polymers.

Results and Discussion

Figure 1 shows typical pyrograms of VC-VAc copolymer, PVAc (polyvinylacetate) and PVC (polyvinylchloride) at the pyrolysis temperature 430°C.

PVC yields benzene and a small amount of toluene. These degradation products are formed by dehydrochlorination reaction followed by cyclization of polymer structure.[4] On the other hand, PVAc[7] yields acetic acid and a small amount of benzene. In this case, there exist competitive thermal reactions, namely scission of the main chain followed by elimination of acetic acid and the formation of polyene structure followed by cyclization to benzene.

Although both mechanisms yield acetic acid, the former is predominant judging from the relatively small amount of benzene on pyrogram.

As might be expected from the above degradation mechanisms of PVC and PVAc, the copolymers with high content of VAc yield mainly acetic acid and a little benzene, whereas those with high content of VC yield mainly benzene.

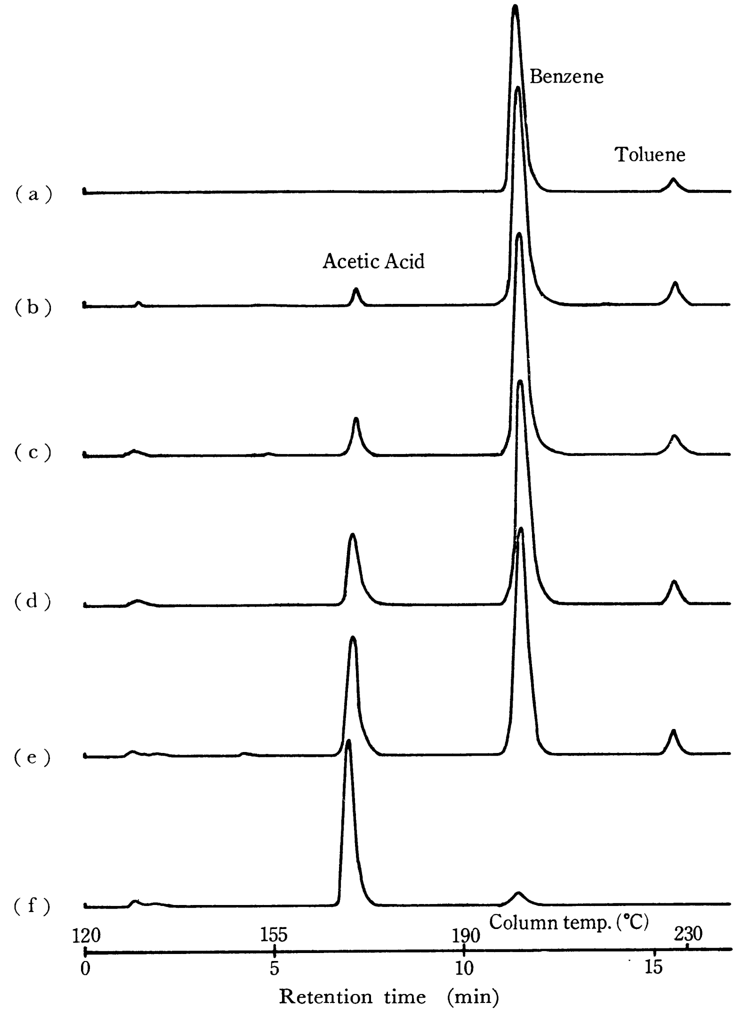

Fig. 1. Pyrogram of vinylchloride-vinylacetate copolymer at 430°C.
(a) PVC; (b)—(e) VC-VAc copolymer (VAc=2.9 (b), 5.5 (c), 11.6 (d) and 15.7 (e) wt%); (f) PVAc

For the sake of simplicity, a small amount of toluene observed with PVC and copolymers was converted into benzene in the calculation and added to the observed yield of benzene. One mole of benzene was considered to correspond to three moles of successive VC-unit, whereas one mole of acetic acid to one mole of VAc-unit.

Figure 2 shows the relation between the relative yields of acetic acid and benzene and the composition of vinylacetate (wt%). The plots (● and ▲) represent the observed values, and the solid line is obtained by the method of least squares. The linear relations can be represented as follows:

(A) Yield of acetic acid

$$Y = 2.21\,X + 5.2 \qquad (1)$$

(B) Yield of benzene

$$Y' = 2.36\,X' - 140.1 \qquad (2)$$

where X and X' are vinylacetate and vinylchloride contents in copolymer (wt%), respectively, and $X + X' = 100$. Y and Y' are the observed relative yields of acetic acid and benzene (wt%), respectively. Precision data are listed in Table 1.

With the use of Eqs. (1) and (2), the composition of vinylacetate in copolymer can be determined with mean absolute deviation 0.5 and 0.4 wt% respectively, with the yields of acetic acid and of benzene.

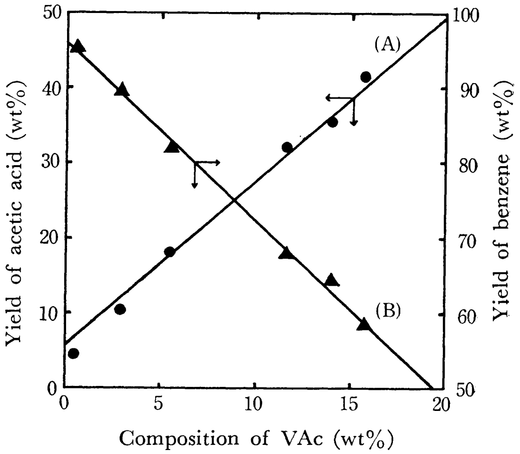

Fig. 2. Relationship between yields of acetic acid and of benzene, and composition of VAc.

(A) acetic acid; (B) benzene

Pyrolysis-gas chromatography was successfully applied to rapid and precise determination of composition of polymer evolving such acidic products as hydrogen chloride and acetic acid during its thermal decomposition without trapping the acidic substances.

TABLE 1. ACCURACY OF THE DETERMINATION OF VC-VAc COPOLYMER

(a) Results from the yield of acetic acid

Sample No.	Composition of* VAc (wt%) (A_1)	Yield of acetic acid (wt%)	Composition** of VAc (wt%) (B_1)	Deviation (B_1-A_1)
1	0.5	4.6	−0.3	−0.8
2	2.9	10.5	2.4	−0.5
3	5.5	18.2	5.9	0.4
4	11.6	32.1	12.1	0.5
5	14.0	35.7	13.8	−0.2
6	15.7	41.4	16.4	0.7

(b) Results from the yield of benzene

Sample No.	Composition of* VC (wt%) (A_2)	Yield of benzene (wt%)	Composition** of VC (wt%) (B_2)	Deviation (B_2-A_2)
1	99.5	95.4	99.8	0.3
2	97.1	89.5	97.3	0.2
3	94.5	81.8	94.0	−0.5
4	88.4	67.9	88.1	−0.3
5	86.0	64.3	86.6	0.6
6	84.3	58.6	84.2	−0.1

* Determined by the usual chemical method. **Calculated from Eq. (1) or (2).