

## Kinetics of Polyvinyl Chloride Degradation using TG-MS

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Degradation behavior of PVC was analyzed by means of simultaneous thermogravimetry-mass spectrometry (TG-MS). The experiments were carried out up to 650°C at eight heating rates of 0.5- 40°C/min in a helium atmosphere. Weight loss by PVC degradation was clearly divided into three stages at lower heating rate. The activation energies of these three stages were computed as 146-171, 125-223, and 217-248kJ/mol for the weight loss ranges of 0-45, 45-65 and 65-90%, respectively. Since hydrogen chloride was formed mainly in the first and second stages, it is clear that the dehydrochlorination proceeded by two stages. On the other hand, benzene was formed mainly in the first stage, but hardly formed in the second and third stages. The other aromatics, such as toluene, xylene, ethylbenzene, indene, indan and methylnaphthalene were formed mainly in the third stage.

### Introduction

Degradation behavior of polyvinyl chloride (PVC) is worth studying in order to improve the dehydrochlorination process in the feedstock recycling of waste plastics. Various studies have been reported on the degradation of PVC since the first study by Marvel et al. [1]. McNeill et al. analyzed gas, liquid and tar fraction collected during the PVC thermal degradation in air and inert atmosphere and determined its composition [2]. Knümann et al. identified the products formed in the decomposition of PVC by means of simultaneous thermogravimetry-mass spectrometry (TG-MS) for the first time, and found the formation of benzene, besides hydrogen chloride, at the dehydrochlorination stage and various aromatic hydrocarbons at the polyene decomposition stage [3]. Moreover McNeill et al. monitored the PVC thermal degradation in vacuum by mass spectrometry (MS) and confirmed the two stages of degradation from the formation of the main product [4]. In the past the degradation of PVC has been regarded as these two stage degradation: dehydrochlorination and polyene decomposition. Wu et al., however, regarded the first stage as comprising two reactions based on the weight loss in the degradation of PVC at low heating rate using thermogravimetry (TG) [5]. Although various studies have been reported, the two dehydrochlorination stages have never been confirmed from the point of the formation behavior of the products.

In the present study the degradation of PVC up to 650°C under helium was studied based on the weight loss and the formation behavior of the products measured by means of simultaneous TG-MS. Moreover the degradation behavior was discussed from both of the weight loss and the formation behavior of the products.

### Materials and Methods

The PVC powder free from any additive (Kanto Chemical, polymerization degree

1000±40, particle diameter 0.1mm) was used.

Degradation behavior of PVC was analyzed by means of simultaneous TG-MS connected directly TG (Seiko instruments TG/DTA6200) and MS (Hewlett Packard 5973 mass selective detector). The experimental apparatus is shown in Fig.1.

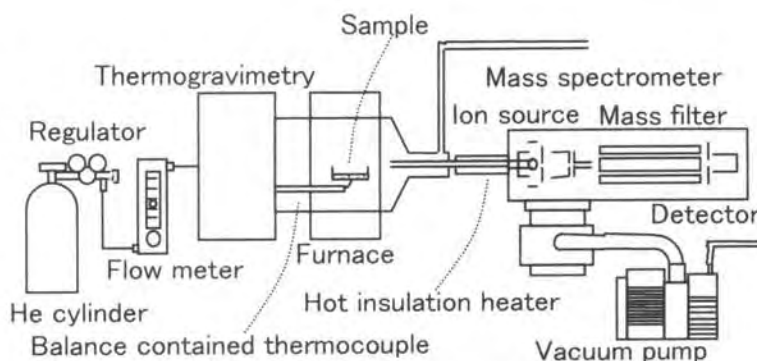


Figure 1 TG-MS Apparatus.

PVC sample of 10 mg, spread as a thin layer at the bottom of a platinum pan was put on a balance in the TG, and subjected to degradation. A flow of helium was established over the sample at a flow rate of 100 ml/min throughout these experiments. After helium purged out a residual air, the degradation of the sample was conducted up to 650°C at eight heating rates of 0.5, 1, 2, 4, 5, 10, 20, 40°C/min. The degradation products were introduced to the ion source of the MS through the inactivated stainless capillary tube heated at 250°C to prevent condensation of the evolved products.

## Results and Discussions

### Degradation behavior

TG and DTG curves in the degradation of PVC at 4.0°C/min are shown in Fig. 2. The TG curve indicates that the degradation of PVC was started at 220°C, and its rate was decreased between 300°C and 370°C and then increased from 370°C. This behavior agrees approximately with previous reports that the degradation of PVC consists of the dehydrochlorination stage up to 370°C and the polyen decomposition stage from 370°C [3,4]. In the present study, however, another peak in the DTG curve is observed during the dehydrochlorination stage. This indicates that the degradation of PVC is divided into three stages, namely first stage (weight loss ≤ 45%), second stage (weight loss ≤ 65%) and third stage (weight loss > 65%). Wu et al., also, proved the second stage by TG analysis [5]. The second stage was observed similarly at the other heating rates from 0.5 to 10°C/min. Therefore the following kinetic analysis was conducted using four degradation data of the heating rates from 0.5 to 4°C/min.

The method used for dealing with the degradation data has been developed by Ozawa. This method is primarily based on the equation

$$dx/dt = kf(x) \quad (1)$$

where  $k$  is the Arrhenius equation,  $k = A \exp(-E/RT)$ , and  $f(x)$  is a function of conversion  $x$ . Transforming the above equation diversely yields finally

$$\ln(dT/dt) = -0.4567 E/RT + const. \quad (2)$$

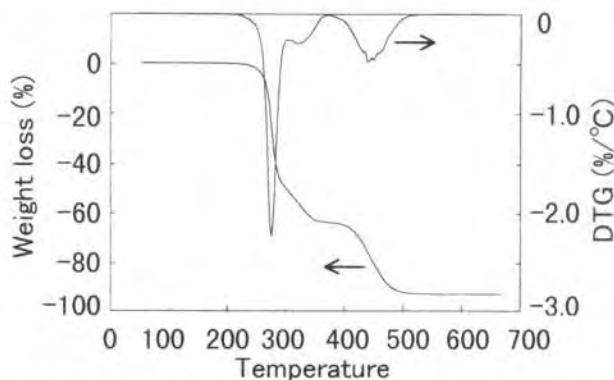


Figure 2 TG and DTG curves of PVC at heating rate of 4.0°C/min.

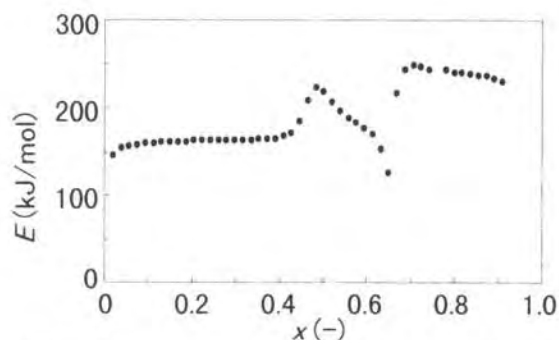


Figure 3 Computed activation energies ( $E$ ) at different degree of conversion ( $x$ ) for degradation of PVC.

At the same degree of conversion, the reaction temperatures ( $T$ ) are different under various condition of heating rates ( $dT/dt$ ). A straight line with slope  $-0.4567E/R$  is obtained by plotting  $\ln(dT/dt)$  vs.  $1/T$  for each  $x$ . The activation energy ( $E$ ) corresponding to the selected conversion would then be obtained.

The activation energies under different conversions are presented in Fig. 3. The results indicate that the values of the activation energy of PVC degradation are in the range of about 125-248kJ/mol for conversion ranging from about 0 to 0.91. These values may be divided into three groups, namely,  $E = 146-171\text{kJ/mol}$  for  $x = 0-0.45$  (first stage),  $E = 125-223\text{kJ/mol}$  for  $x = 0.45-0.65$  (second stage), and  $E = 217-248\text{kJ/mol}$  for  $x = 0.65-0.91$  (third stage). The activation energies were almost values during the first and third stage, but vary during the second stage. The changes in the activation energies on each stage indicated that the degradation must be composed of more than three reactions.

#### Formation behavior

Signals of  $m/z=36, 78, 92, 104, 106, 116, 118, 120, 128,$  and  $142$  were observed in the PVC degradation up to  $650^\circ\text{C}$  under helium. These signals correspond to the molecular ion peaks of hydrogen chloride (36), benzene (78); toluene (92), styrene (104), xylene or ethylbenzene (106), indene (116), indan (118), propylbenzene or ethylmethylbenzene (120), naphthalene (128) and methylnaphthalene (142).

The TG-MS selected ion chromatograms of the major products in the degradation of PVC at heating rate of  $4^\circ\text{C}/\text{min}$  is shown in Fig. 4. The formation of hydrogen chloride started at  $220^\circ\text{C}$  and finished nearly at  $370^\circ\text{C}$ , and had two peaks of  $280^\circ\text{C}$  and  $320^\circ\text{C}$  during the dehydrochlorination. This result supports that the dehydrochlorination proceeds by two stage reactions.

Benzene was formed during the first dehydrochlorination stage, but hardly in the second dehydrochlorination stage. It is well known that aromatic compounds such as benzene are formed due to break down of polyene chains by bimolecular addition and coiling. Therefore, it is considered that polyene decomposition occurs in the first dehydrochlorination stage.

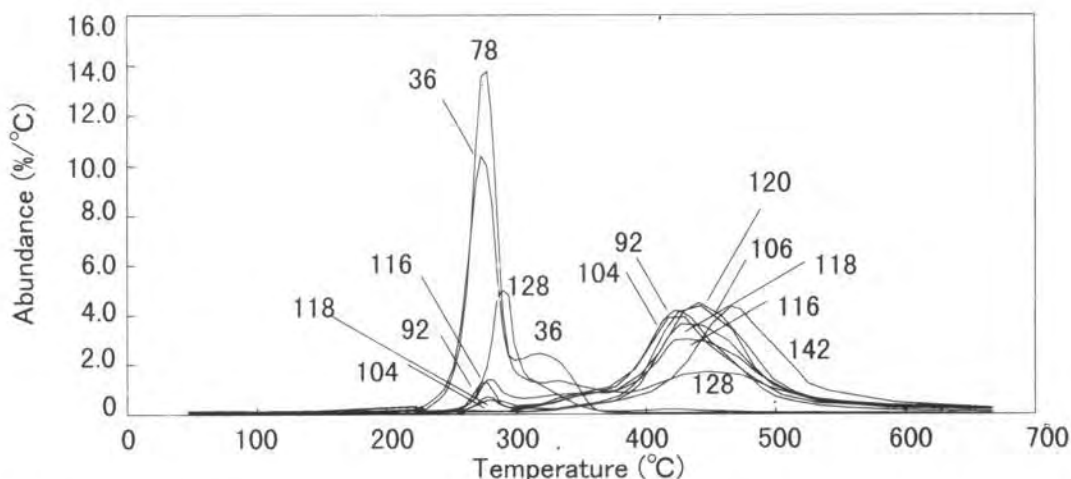


Figure 4 Selected Ion Chromatogram of the major products in the thermal degradation of PVC at heating rate of 4.0°C/min. [36:hydrogen chloride, 78:benzene, 92:toluene, 104:styrene, 106:xylene or ethylbenzene, 116:indene, 118:indan, 120:propylbenzene or ethylmethylbenzene, 128:naphthalene, 142:methylnaphthalene.]

On the other hand, naphthalene started forming at the same temperature that the second dehydrochlorination stage started, and its rate reached maximum at 290°C.

The other aromatic compounds were formed mainly after the dehydrochlorination stages over 370°C, and gave peaks between 420 and 470°C, whereas have no strong peak during the dehydrochlorination stages. This result indicates the aromatic compounds except benzene and naphthalene are produced by breakdown of polyene-aromatic network.

### Conclusions

The result of present study clearly showed that the degradation of PVC up to 650°C under helium was divided into three degradation stages, namely two dehydrochlorinations and a breakdown of polyene-aromatic network. In the first stage (first dehydrochlorination stage) benzene was formed with hydrogen chloride. In the second stage (second dehydrochlorination stage) dehydrochlorination occurred mainly. In the third stage breakdown of polyene-aromatic network occurred and various aromatic hydrocarbon expected benzene formed mainly.

### References

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