TG–MS Analysis of Dehydrochlorination of Poly(vinylidene chloride)

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Poly(vinylidene chloride) (PVDC) was decomposed by thermal treatment to 800 °C under inert atmosphere, using thermogravimetry-mass spectrometry (TG–MS). The evolvement of hydrogen chloride was still observed at 800 °C for the degradation of PVDC. The dehydrochlorination process was divided into two stages according to difference in the formation rate of hydrogen chloride and trichlorobenzene. Dehydrochlorination was accompanied by the evolvement of trichlorobenzene during the first stage below 380 °C, but trichlorobenzene was not observed during the second stage above 380 °C.

Poly(vinylidene chloride) (PVDC) is the largest chlorine-containing waste next to poly(vinyl chloride) (PVC) in municipal waste plastics. In the dehydrochlorination process for feedstock recycling of waste plastics, chlorine components are removed from such chlorine-containing plastics in the form of hydrogen chloride, by degradation under inert gas. Studies on the dehydrochlorination mechanism of PVDC are necessary to improve this process. However thermal degradation of PVDC has not been studied from the point of a removal of chlorine. Most research in the past reported on their thermal stability at the initial stage of degradation,[1–3] or on the products of degradation under air.[4–7]

As studies under inert gas, Farr et al.[8] analyzed the weight-loss in the degradation process of head-to-tail or head-to-head PVDC samples up to a temperature of 500 °C using thermogravimetry (TG). With respect to the products of degradation under inert gas, Ballistreri et al.[9] studied the direct degradation of PVDC in the ion source of a mass spectrometer (MS) up to a temperature of 320 °C, and observed the formation of hydrogen chloride, vinylidene chloride, trichloro benzene, and tetrachlorobenzene. Moreover Pasek et al. identified mono-, di-, and trichlorobenzene, tri- and tetrachlorostyrene, and di-, tri-, and tetrachloronaphthalene as the degradation products of PVDC up to a temperature of 600 °C using gas chromatography-mass spectrometry (GC–MS).[10]

However, the degradation of PVDC is still worth studying in order to understand its dehydrochlorination behavior from the point of a removal of chlorine, since dehydrochlorination of PVDC does not end at 320 °C studied previously.[9] In this study, the dehydrochlorination behavior of PVDC was analyzed up to 800 °C in terms of both weight-loss and degradation products.

Pure PVDC in powder form was used for degradation under inert gas. The sample was homopolymer and had no additives. The degradation behavior of the sample was analyzed by the simultaneous thermogravimetry-mass spectrometry (TG–MS) described previously.[11] The sample of 10 mg was placed on a balance in the TG with a helium flow-rate of 100 ml/min. After residual air was purged by helium, the degradation of the sample was conducted up to 800 °C at 4 °C/min. The degradation products were introduced directly into the ion source of the MS. As a preliminary experiment, another reactor with solvent traps was used, in order to obtain the degree of dehydrochlorination and identify the degradation products. In this experiment, the sample of 100 mg was decomposed under nitrogen by raising the temperature to 800 °C at 10 °C/min. The degradation gas was collected by water or hexane traps at the exit of the reactor, and analyzed by ion chromatography (IC) for hydrogen chloride or GC–MS for organic compounds.

Figure 1 shows the weight-loss of the sample and the rate of the weight loss (DTG) in TG measurement at 4 °C/min. The degradation of PVDC started at 200 °C as similar to the previous study[8] of PVDC using TG under inert gas. The DTG curve, namely the rate of degradation, had a large peak at 240 °C and a small peak at 550 °C. The first large weight-loss was observed also in the previous study,[8] but second was not reported since the study did not raise a temperature to such a high temperature. The degradation of PVDC was found for the first time to continue to 800 °C, since the DTG curve did not return to baseline until 800 °C. The residue amounted to 21% at 800 °C. If all chlorine in PVDC is released as hydrogen chloride, theoretical amount of carbonaceous products of 24.7% should remain, which could not be decomposed any more. This difference was clearly caused by the emission of organochlorine compounds.

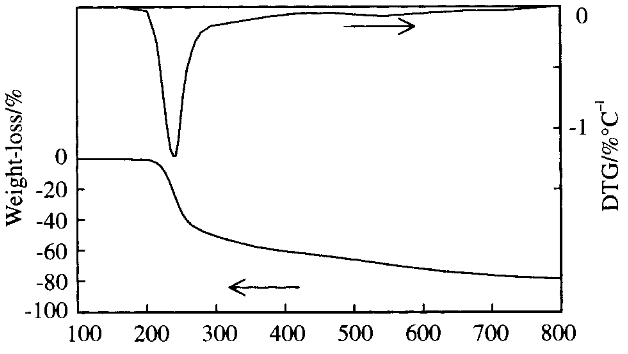

Figure 1. TG and DTG curves of the PVDC under helium at 4 °C/min.

As a result of the preliminary experiments, 89% of chlorine in the sample was converted to hydrogen chloride at 800 °C, which corresponds. as hydrogen chloride, to 67% of the sample weight. This result suggests the formation of some organochlorine compounds besides hydrogen chloride. Indeed, the formation of trichlorobenzene was observed by GC–MS analysis of the decomposition products. This is accord with the previous report.[9]

The degradation continuing up to such a high temperature of 800 °C can be accounted for by dehydrochlorination. Figure 2 shows the temperature dependence of the formation rate of hydrogen chloride and trichlorobenzene from in situ analysis of MS during the degradation of PVDC. These compounds were selected for the representations of the thermal degradation products. The formation rate means the proportion of amount of formation at each temperature to the total amount of formation of the each compound. As shown in Figure 2 (a), hydrogen chloride was found, for the first time, to be evolved even at 800 °C in the degradation of PVDC, because the curve of its formation rate did not return to baseline even at such a high temperature.

As regard to early stage of degradation, the formation of hydrogen chloride started at 190 °C and the formation rate reached maximum at 240 °C in the degradation of PVDC. These results gave excellent agreement with the results of weight-loss in TG shown above, but difference to the results in previous study of direct degradation in MS[9] as regard to reaction temperature. In the previous study,[9] the formation rate of hydrogen chloride was reported to reach maximum at 190 °C, which was 50 °C lower than the present study. This difference might be caused by difference in a measurement site. The sample temperature was measured at the bottom of sample pan in the present study, but no description on the previous study.[9]

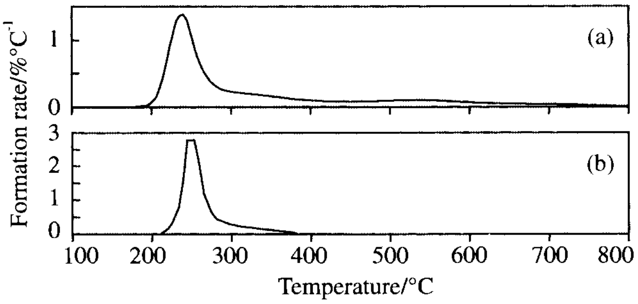

Figure 2. Mass monitoring of the molecular ion peaks of hydrogen chloride (a) and trichlorobenzne (b) during the thermal degradation of PVDC under helium at 4 °C/min.

As regard to latter stage of degradation, the formation rate had another peak at 550 °C. The dehydrochlorination process was found, for the first time, to be divided into two stages from the change in the formation rate of hydrogen chloride.

Organochlorine compound was observed in addition to hydrogen chloride. As shown in Figure 2 (b), trichlorobenzene was formed between 220 °C and 380 °C during the degradation of PVDC. The temperature range forming trichlorobenzene gave a good agreement with the range forming hydrogen chloride mainly. This agreement was also observed in the previous study.[9] As discussed previously,[9] trichlorobenzene would be formed by the cyclization of chlorine containing polyene that was dehydrochlorinated only at one side of chlorine substituents in the polymer chain.

The formation behavior of hydrogen chloride and trichlorobenzene, however, was different at the temperature range above 380 °C. Trichlorobenzene was not formed above 380 °C although hydrogen chloride was still being formed above the temperature. As discussed in the previous study,[9] the formation of linear polyene by dehydrochlorination results in the formation of trichlorobenzene as cyclic. Therefore less formation of trichlorobenzene above 380 °C means less formation of linear polyene after dehydrochlorination. Cross-linking polyene might be formed instead of linear polyene after dehydrochlorination above 380 °C.

In conclusion, it was found for the first time that dechlorination of PVDC under inert gas was not completed to high temperature of 800 °C by a simple thermal treatment. The formation of hydrogen chloride was observed to continue up to 800 °C. The progression of dehydrochlorination was accompanied by the formation of trichlorobenzene as cyclic in the first stage below 380 °C, but trichlorobenzene was not observed in the second stage above 380 °C.

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