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Analysis of pyrolysis products of poly(vinylidene fluoride-*co*-hexafluoropropylene) by pyrolysis-gas chromatography/mass spectrometry

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Poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VDF-*co*-HFP)) was pyrolyzed and the pyrolysis products were analyzed using gas chromatography/mass spectrometry (GC/MS). Major pyrolysis products were propene, butene, benzene, and cyclohexene derivatives besides VDF and HFP. 2,3,3,3-Tetrafluoropropene (2,3,3,3-TFP) can be formed from the VDF–HFP heterosequence as well as from the VDF head-to-head sequence, while 1,1,3,3-tetrafluoropropene (1,1,3,3-TFP) can be formed from the VDF head-to-tail sequence. 1,3,3,5,5-Pentafluorocyclohexene (PFCH) and benzene derivatives such as 1,3,5-trifluorobenzene (1,3,5-TFB), 1,4-difluorobenzene (DFB), and 1,2,4-trifluorobenzene (1,2,4-TFB) were formed from the VDF homosequences. 1,1,2,3,4,4,4-Heptafluorobutene (HFB) and 3-trifluoromethyl-3,4,4,6,6-pentafluorocyclohexene (FMPFCH) can be formed from the VDF–HFP heterosequences. It is possible to distinguish P(VDF-*co*-HFP) from other fluorinated polymers using the pyrolysis products formed from the VDF–HFP heterosequences.

1. Introduction

One of application fields of fluorinated polymers is polymer electrolyte membrane (PEM) because fluorinated polymers have good chemical and thermal stabilities [1–9]. Poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VDF-*co*-HFP)) has been also used for PEM [6–8]. P(VDF-*co*-HFP) can have various microstructures depending on sequencing (Scheme 1) as well as the content ratios of VDF and HFP. Physical and chemical properties of polymeric materials are affected by their microstructures. Microstructures of polymeric materials including fluorinated polymers have been analyzed by nuclear magnetic resonance spectroscopy (NMR) [10–19], infrared spectroscopy (IR) [20–23], and pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) [24–34].

Py-GC/MS is a useful analytical technique for the microstructural analysis of fluorinated polymers [27–34]. In our previous works [33,34], microstructures of poly(ethylene-*co*-tetrafluoroethylene) (PETFE) and poly(vinylidene fluoride) (PVDF) were analyzed using Py-GC/MS. Major pyrolysis products formed from the ethylene–tetrafluoroethylene heterosequences of PETFE were 3,3-difluoropropene (DFP), 3,3,4,4-tetrafluoro-1-butene (TFB), 1,1,2,2,3,3-hexafluorocyclopentane (HFCP), 1,1,2,2,3,3-hexafluorocyclohexane (HFCH), 1,1,2,2,3,3,4,4-octafluorocyclohexane (OFCH), and 3-trifluoromethyl-3,4,4,5,5-pentafluorocyclohexene (3,4,4,5,5-FMPFCH) [33]. Major pyrolysis products of PVDF were vinylidene fluoride (VDF), 1,3,5-trifluorobenzene (1,3,5-TFB), 1,4-difluorobenzene (DFB), 1,2,4-trifluorobenzene (1,2,4-TFB), and 1,3,3,5,5-pentafluorocyclohexene (PFCH) [34].

Microstructure of PVDF is determined by the repeat unit (CF_2CH_2) directions of head-to-tail (H–T, $\sim CF_2–CH_2–CF_2–CH_2\sim$), head-to-head (H–H, $\sim CH_2–CF_2–CF_2–CH_2\sim$), and tail-to-tail (T–T, $\sim CF_2–CH_2–CH_2–CF_2\sim$) sequences. Pyrolysis products of polymeric materials having H-T, H-H, and T-T sequences are differentiated according to their microstructures. For PVDF pyrolysis [34], 1,3,5-TFB and PFCH are formed only from the H-T sequence, whereas DFB is formed only from the T-T sequence. Besides pyrolysis methods, one of analytical techniques to determine the microstructure of PVDF is a solid state ^{19}F-NMR [35–37]. Mladenov et al. [19] analyzed the numbers of VDF and VDF/HFP base units in the synthesized P(VDF-*co*-HFP) using ^{19}F- and ^{1}H-NMR spectroscopy. In general, pyrolysis does not require sample pretreatment for the analysis of polymeric materials. In the present work, chemical structures of principal pyrolysis products formed from P(VDF-*co*-HFP) were analyzed using GC/MS and their formation mechanisms

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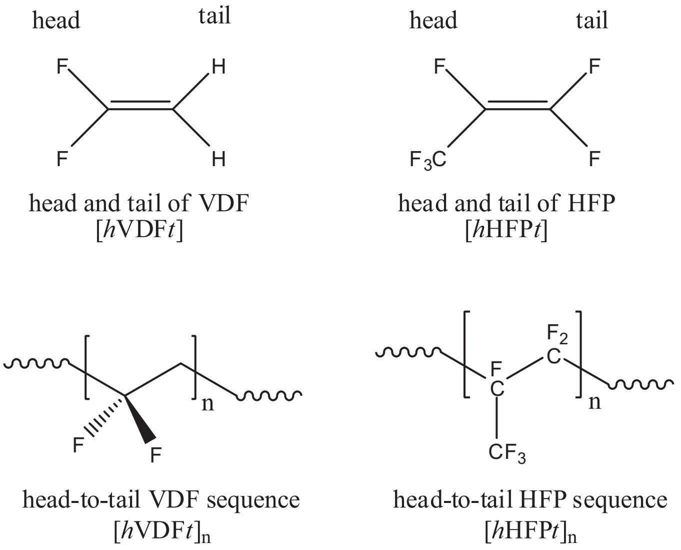

Scheme 1. Notation of P(VDF-*co*-HFP) sequences.

were suggested. Especially, the pyrolysis products formed from the VDF–HFP heterosequences were focused. Since it is not available to obtain microstructure-well defined P(VDF-*co*-HFP)s, one commercial P(VDF-*co*-HFP) was used. The candidates of major pyrolysis products formed from P(VDF-*co*-HFP) were guessed through the possible pyrolysis mechanisms and then the corresponding peaks were found in the Py-GC/MS TIC chromatograms by interpretation of the mass spectra.

2. Results and discussion

Figs. 1 and 2 show pyrolysis-GC/MS TIC chromatograms of P(VDF-*co*-HFP) which analyzed using a PLOT column. The peaks with a high matching quality were identified using a mass spectrum library, whereas those with a low matching quality were identified based on the mass spectra. The candidate pyrolysis products based on the possible mechanisms were analyzed using EIC chromatograms of the molecular ion and expected principal fragment ions. The major pyrolysis products could be divided into ethene, propene, butene, and 6-membered ring compounds. Fig. 1 shows vinylidene fluoride (VDF, 1.21 min), hexafluoropropylene (HFP, 1.74 min), 2,3,3,3-tetrafluoropropene (2,3,3,3-TFP, 2.37 min), and 1,1,3,3-tetrafluoropropene (1,1,3,3-TFP, 3.42 min). VDF and HFP are the repeat units of P(VDF-*co*-HFP). VDF is the most abundant pyrolysis product. The relative intensity of HFP was about 2% compared to that of VDF. Considering the HFP content (<15 wt%, <6.4 mol%) of P(VDF-*co*-HFP) used in this study, the HFP abundance as the pyrolysis product was very small.

Mass spectra of the 2,3,3,3-TFP and 1,1,3,3-TFP were shown in Fig. 3 and their formation mechanisms were suggested in Schemes 2 and 3, respectively. 2,3,3,3-TFP ($H_2C{=}CF{-}CF_3$) and 1,1,3,3-TFP ($F_2C{=}CH{-}CHF_2$) could be distinguished through interpretation of the mass spectra as shown in Fig. 3. The mass spectrum of 2,3,3,3-TFP (Fig. 3(a)) shows the predominant peak of m/z 69 (CF_3^+), while that of 1,1,3,3-TFP (Fig. 3(b)) shows the predominant $[M\text{-}F]^+$ peak (m/z 95, $F_2C{=}CH{-}CHF^+$) and $[M\text{-}H]^+$ peak (m/z 113, $F_2C{=}CH{-}CF_2^+$). The $F_2C{=}CH{-}CHF^+$ and $F_2C{=}CH{-}CF_2^+$ ions have their resonance structures of $F_2C{-}CH{=}CHF^+$ and $F_2C{-}CH{=}CF_2^+$ ions, respectively. 2,3,3,3-TFP can be formed from the VDF(head-to-tail)-HFP(head-to-tail) (*h*VDF*t*-*h*HFP*t*) heterosequence as well as from the VDF(tail-to-head)-VDF(head-to-tail) (*t*VDF*h*-*h*VDF*t*) homosequence as shown in Scheme 2. 1,1,3,3-TFP can be formed from the VDF(head-to-tail)-VDF(head-to-tail) (*h*VDF*t*-*h*VDF*t*) homosequence as shown in Scheme 3. Since 2,3,3,3-TFP and 1,1,3,3-TFP are formed from the VDF homosequence, they should be also formed from poly(vinylidene fluoride) (PVDF). In order to ascertain that, PVDF was pyrolyzed and the pyrolysis products were analyzed. Of the pyrolysis products of PVDF, both 2,3,3,3-TFP and 1,1,3,3-TFP were observed. The relative abundance ratios of 2,3,3,3-TFP/1,1,3,3-TFP in the TIC chromatograms of P(VDF-*co*-HFP) and PVDF were compared (Fig. 4). The relative abundance of 2,3,3,3-TFP

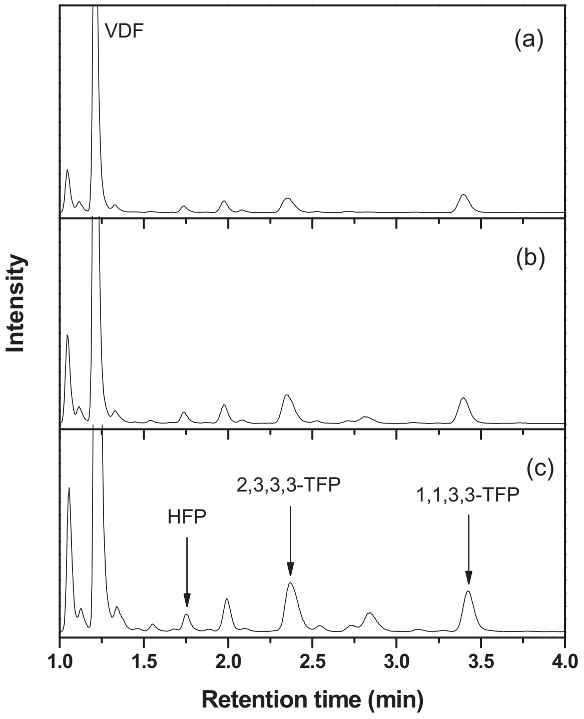

Fig. 1. Py-GC/MS TIC chromatograms (1.0–4.0 min) of P(VDF-*co*-HFP) at 700 °C (a), 800 °C (b), and 900 °C (c). Analysis was performed using a PLOT column.