



Microstructural analysis of poly(vinylidene fluoride) using benzene derivative pyrolysis products

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ABSTRACT

Poly(vinylidene fluoride) (PVDF) was pyrolyzed, and the pyrolysis products were analyzed using gas chromatography/mass spectrometry (GC/MS) to develop a method for identification of the microstructures of head-to-tail (H-T), tail-to-tail (T-T), and head-to-head-to-tail-to-tail (H-H-T-T) sequences. Key pyrolysis products to determine the relative degrees of the microstructures were benzene derivatives. 1,4-Difluorobenzene, 1,2,4-trifluorobenzene, and 1,3,5-trifluorobenzene were major pyrolysis products as benzene derivatives. 1,3,5-Trifluorobenzene and 1,2,4-trifluorobenzene were formed from two HF-eliminated PVDF by 1,6-HF elimination and 1,6-rearrangement, while 1,4-difluorobenzene was generated from two HF-eliminated PVDF by 1,6-H₂ elimination and 1,6-rearrangement. 1,3,5-Trifluorobenzene was generated from the H-T sequence, whereas 1,4-difluorobenzene was formed from the T-T one. 1,2,4-Trifluorobenzene can be formed from the H-H-T-T sequence. Relative component ratios of the H-T, T-T, and H-H-T-T sequences of PVDFs can be estimated by comparing relative abundances of the benzene derivative pyrolysis products.

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1. Introduction

Fluorinated polymers have been widely used for polymer electrolyte membrane (PEM) due to their good chemical and thermal stabilities [1–4]. Poly(vinylidene fluoride) (PVDF) is widely used for PEM of fuel cells [1–3]. PVDF has semi-crystalline and thermoplastic properties. Pyrolysis-gas chromatography/mass spectrometry (pyrolysis-GC/MS) has been extensively used for a method to characterize structural information of various macromolecules [5–13], and it has suitable performance in case of synthetic polymers [7–13]. Studies on thermal degradation and pyrolysis of PVDF have been reported by several groups [14–18]. O'Shea et al. [14] studied pyrolysis of PVDF and reported that increasing the pyrolysis temperature resulted in a complex degradation process and a pyrolytic residue made up of largely aliphatic and fluoro-aromatic structures. Zulfiqar et al. [15] reported that major degraded products of PVDF were HF, vinylidene fluoride (VDF), and C₄H₃F₃. Dehydrofluorination is a typical degradation process of PVDF [14,15].

Microstructure of PVDF is determined by the repeat unit (CF₂CH₂) directions of head-to-tail (H-T, –CF₂–CH₂–CF₂–CH₂–), head-to-head (H-H, –CH₂–CF₂–CF₂–CH₂–), and tail-to-tail (T-T, –CF₂–CH₂–CH₂–CF₂–) sequences. Pyrolysis products of polymeric

materials having H-T, H-H, and T-T sequences are differentiated according to their microstructures. For natural rubber (NR, polyisoprene rubber), pyrolysis products of the isoprene dimers are differentiated according to its microstructure [19–21]. NR has H-T, H-H, and T-T sequences. Major pyrolysis dimer products of NR are 1,4-dimethyl-4-vinylcyclohexene and 1-methyl-4-(1-methylethenyl)-cyclohexene formed from the H-H and H-T sequences, respectively. Besides pyrolysis methods, one of the analytical techniques to determine the microstructure of PVDF is a solid-state ¹⁹F-NMR [22–24].

In the present work, PVDF was pyrolyzed and the pyrolysis products were analyzed using GC/MS. Based on formation mechanisms of the major pyrolysis products, their sources were divided according to the corresponding microstructures. Especially, the benzene derivative pyrolysis products were focused. Comparing relative abundances of the benzene derivative pyrolysis products, an analytical method to determine the relative degrees of microstructures can be developed. Since it is not available to obtain microstructure-well defined PVDFs, one commercial PVDF was used.

2. Experimental

PVDF was purchased from Sigma Aldrich Co. Pyrolysis-GC/MS was carried out using a pyroprobe 2000 system with a CDS 1500 interface (Chemical Data System, Oxford, USA) coupled to an Agilent 6890 gas chromatograph equipped with a 5973 mass spectrometer of Agilent Technology Inc. (USA). An HP-PLOT/Q capillary

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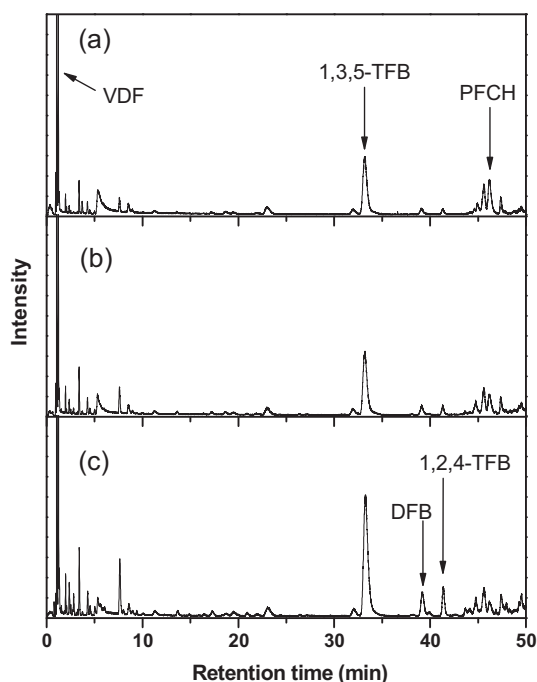


Fig. 1. Pyrolysis-GC/MS TIC chromatograms of PVDF at 700 °C (a), 800 °C (b), and 900 °C (c).

column (0.32 mm × 15 m, 20 μm film thickness) was used to separate the pyrolysis products.

PVDF (about 0.3 mg) was preheated at 250 °C for 15 s and pyrolyzed at 700, 750, 800, 850, and 900 °C for 5 s under Helium atmosphere. The temperatures of the interface and injector were 250 °C. The GC injector temperature was 250 °C and the split ratio was 1: 20. Helium was used as the carrier gas and its flow rate was 1.5 mL/min. GC oven temperature program was as follow: 100 °C (held for 2 min) to 130 °C (held for 5 min) at 1 °C/min and raised up again to 220 °C (held for 5 min) at 5 °C/min. The interface temperature of GC–MS was 250 °C. The electron ionization (70 eV) was used to ionize the pyrolysis products. The MS source temperature was 230 °C.

3. Results and discussion

Fig. 1 shows pyrolysis-GC/MS TIC chromatograms of PVDF. The repeat unit of PVDF, vinylidene fluoride (VDF, 1.21 min) was separated from the other pyrolysis products and some important pyrolysis products were shown in the chromatogram. The peaks at 33.29, 39.18, and 41.38 min were interpreted using a mass spectrum library. Those peaks were assigned to 1,3,5-trifluorobenzene (1,3,5-TFB), 1,4-difluorobenzene (DFB), and 1,2,4-trifluorobenzene (1,2,4-TFB), respectively. The peak at 46.25 min was not interpreted using a mass spectrum library because of lack of a high matching quality mass spectrum corresponding to the mass spectrum at 46.25 min. Fig. 2 shows the mass spectrum of the pyrolysis product at 46.25 min in Fig. 1. The peak was assigned to 1,3,3,5,5-pentafluorocyclohexene (PFCH). The m/z 172 ion is the molecular ion and some fragment ions of m/z 153, 133, 113, and 108 were also generated. The fragment ions of m/z 153, 133, 113, and 108 were $[M-F]^+$, $[M-HF-F]^+$, $[M-2HF-F]^+$, and $[M-H_2C=CF_2]^+$, respectively (Scheme 1). It was not easy to separate the pyrolysis products. Besides the PLOT column, DB-1 and DB-5 columns had been also used to separate the pyrolysis products. However, the pyrolysis products were not sufficiently separated when DB-1 and DB-5

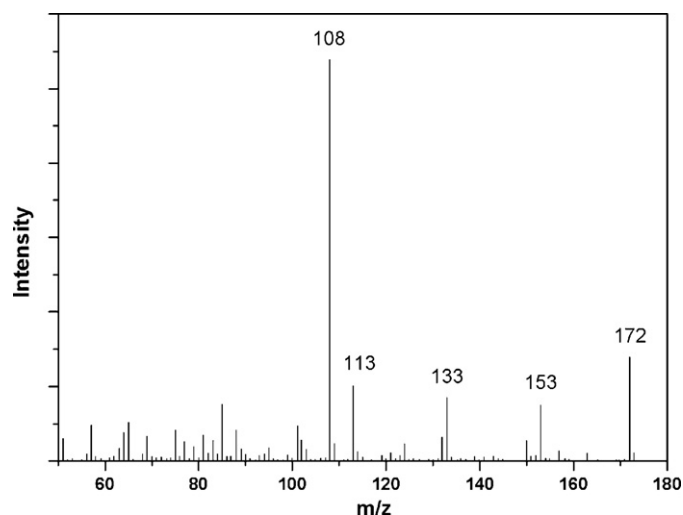


Fig. 2. Mass spectrum of the pyrolysis product at 46.25 min in the pyrolysis-GC/MS chromatogram of Fig. 1. The peak was assigned to 1,3,3,5,5-pentafluorocyclohexene.

columns were used. Hence, PLOT column is a suitable column for separation of the pyrolysis products of PVDF.

The DFB, 1,3,5-TFB, 1,2,4-TFB, and PFCH are pyrolysis products of the VDF trimer species. Hence, principal pyrolysis products of PVDF are the trimer species besides the monomer. Trifluorobenzenes such as 1,3,5-TFB and 1,2,4-TFB are formed by rearrangement including three repeat units of VDF as shown in Schemes 2–5. However, sources to generate the trifluorobenzenes were different from each other. 1,3,5-TFB is formed from the H-T sequence, whereas 1,2,4-TFB is formed from the H-H-T sequence. If precursors of the trifluorobenzenes are pre-dehydrofluorinated species such as hexafluorocyclohexane, pentafluorocyclohexene, and tetrafluorocyclohexadiene, hexafluorocyclohexane can be formed by C–C bond cleavage of the saturated backbone and rearrangement while pentafluorocyclohexene and tetrafluorocyclohexadiene can be generated by C–C bond cleavage of the unsaturated backbone and rearrangement as shown in Schemes 2 and 3. HF elimination reaction on PVDF backbone easily occurs to form $-CH=CF-$ since dehydrofluorination is a typical degradation reaction of PVDF. If the precursor is hexafluorocyclohexane, pentafluorocyclohexene, or tetrafluorocyclohexadiene, three, two, or one HF-elimination reaction from them, respectively, must occur to generate the trifluorobenzene. For 1,2,4-TFB, if its precursors are the pre-dehydrofluorinated species, it can be formed from the H-H or T-T sequence as shown in Scheme 3. The formation mechanism from tetrafluorocyclohexadiene was not described because possible structures of two HF-eliminated PVDF backbone are $-CH_2-CF_2-CH=CF-CF=CH-$ and $-CF_2-CH_2-CF=CH-CH=CF-$ for the H-H and T-T sequences, respectively. Since the C–C bond cleavage of C=C–C requires more energy than that of C–C–C, it is hard to generate tetrafluorocyclohexadiene from the $-CH_2-CF_2-CH=CF-CF=CH-$ and $-CF_2-CH_2-CF=CH-CH=CF-$.

If precursors of the trifluorobenzenes are hexafluorocyclohexane, pentafluorocyclohexene, and tetrafluorocyclohexadiene, the precursors should be detected. But hexafluorocyclohexanes (1,1,3,3,5,5-hexafluorocyclohexene and 1,1,2,2,4,4-hexafluorocyclohexene for 1,3,5-TFB and 1,2,4-TFB, respectively) with the molecular weight of 192 and tetrafluorocyclohexadiene (1,3,5,5-tetrafluorohexadiene for 1,3,5-TFB) with the molecular weight of 152 were not observed. Only 1,3,3,5,5-pentafluorocyclohexene (PFCH) with the molecular weight of 172 (for 1,3,5-TFB) was detected, whereas 1,2,2,4,4-pentafluorocyclohexene with the molecular weight of 172 (for

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