Efficient fluoride recovery from poly(vinylidene fluoride), poly(vinylidene fluoride-co-hexafluoropropylene) copolymer and poly(ethylene-co-tetrafluoroethylene) copolymer using superheated water with alkaline reagent

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Efficient Mineralization of Poly(vinylidene fluoride), Poly(vinylidene fluoride-*co*-hexafluoropropylene) Copolymer and Poly(ethylene-*co*-tetrafluoroethylene) Copolymer Using Superheated Water with Alkaline Reagent

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Abstract: Mineralization of poly(vinylidene fluoride) (PVDF), poly(vinylidene fluoride-*co*-hexafluoropropylene) [poly(VDF-*co*-HFP)] copolymer, and poly(ethylene-*co*-tetrafluoroethylene) copolymer (ETFE) in superheated water in the presence of an alkaline reagent was investigated with the aim of developing a technique to recycle the fluorine element. These polymers underwent almost complete defluorination to form fluoride ions (F^-) in the reaction solution at a relatively low temperature (250 °C) under Ar atmosphere. When PVDF was reacted with aqueous KOH (1.0 M) for 6 h, the amount of which corresponds to 10 times the molar amount of fluorine content (as atoms) in PVDF, the yield of F^- released into the reaction solution reached 95%. This transformation was accompanied by the formation of carbon rich reside, which consists of amorphous carbon. When the treatment was performed with O_2 instead of Ar, significant differences were observed in the products: while F^- ions efficiently produced in the reaction solution, carbon rich residue did not form and the major species that composed the total organic carbon content in the reaction solution was oxalate. Four consecutive runs (that is, after one reaction at 250 °C under Ar was complete, new PVDF was charged to the reaction mixture and then reacted again) caused no decrease of the F^- yield. Poly(VDF-*co*-HFP) and ETFE copolymers also completely mineralized to form F^- ions with 100 and 98% yields, respectively, by aqueous KOH (1.0 M) treatment under Ar at 250 °C for 6 h. Introducing $Ca(OH)_2$ to the resulting reaction solutions of these copolymers after superheated water treatment produced pure CaF_2, i.e., artificial fluorspar.

1. INTRODUCTION

Fluoropolymers have been used in many industrial equipment because of their high stability against temperature, chemicals, ignition, UV-light irradiation, and other unique characteristics.[1−6] Among fluoropolymers, partially fluorinated polymers such as poly(vinylidene fluoride) (PVDF, $-(CF_2CH_2)_n-$) and vinylidene fluoride (VDF) copolymers have combined characteristics of the high stability of fluorochemicals with the melt processability of thermoplastic polyolefins, in contrast that poly(tetrafluoroethylene) (PTFE, $-(CF_2CF_2)_n-$), the typical perfluorinated polymer, cannot be processed by melt molding.[1,6] Therefore, PVDF has been used for chemical- and electrical processes and energy-related applications such as lithium ion battery electrode binders and seperators.[3,5,7] According to this trend, the production of PVDF reached the largest volume of fluoropolymer after PTFE.[7] Poly(ethylene-*co*-tetrafluoroethylene) copolymer (ETFE, $-(CH_2CH_2CF_2CF_2)_n-$) is also a commercially available, melt-processable fluoropolymer used in harsh conditions as piping, wire insulation, protective films, fuel tubing, and other purposes.[1,3]

While usages of the fluoropolymers have widely spread, waste treatment techniques do not catch up with their increasing demand. Incineration is an option to treat these polymer wastes.[8] However, hydrogen fluoride (HF) gas generated during the treatment seriously damages refractory bricks of incinerators. Therefore, most of the fluoropolymer wastes are disposed of in landfill, although some unfilled PTFE wastes from manufactures are reused in ram extrusion applications after cleaning and milling or they are degraded into low molecular weight PTFE by heating, and reused as micro powder, which was mixed with other materials.[4]

If fluorine atoms in fluoropolymer wastes are transformed into fluoride ions (F^-) by means of environmentally benign methodologies, the F^- ions can react with calcium hydroxide [$Ca(OH)_2$] to form calcium fluoride (CaF_2), which mineral is fluorspar. Nowadays, the mine

production of high-purity fluorspar, suitable for hydrofluoric acid (i.e., aqueous HF) production, is limited in a few countries.[9] Because hydrofluoric acid is a raw material for all fluorochemicals (C–F bond is built by halogen exchange using HF),[10] the development of an efficient decomposition technique of fluoropolymers to F^- ions would contribute toward closing the loop of fluorine element.[11]

Superheated water (it is also mentioned as 'subcritical water' or 'pressurized hot water') is liquid water under high pressure at temperatures ranged from 100 °C to 374 °C, i.e., critical temperature. This water is recognized as environmentally benign in waste management because it enables to transform hazardous chemicals into harmless or to generate value-added compounds.[12–17] As a matter of fact, in the recycling of nonmetallic component from electronic waste (E-waste), the superheated water reaction is analyzed to have a smaller environmental impact than that of pyrolysis.[18] Of course, lowering the reaction temperature is desirable in view of saving energy.

We previously reported that PVDF[19] and VDF-based copolymers[19, 20] efficiently mineralized in superheated water at a relatively low temperature (250 °C) by use of potassium permanganate as an oxidizing agent, and this methodology was extended to treat ETFE.[21] In these systems, the fluorine content of the polymer was decomposed into F^- ions in the reaction solution, and the carbon content was decomposed to CO_2 in the gas phase and HCO_3^- in the reaction solution. For industrial processes, a technique that can achieve under simpler conditions is preferable. Regarding carbon content, conversion to carbon rich solid (e.g., amorphous carbon) instead of CO_2 would be also an option.

Herein we report an effective method for complete defluorination of PVDF, poly(vinylidene fluoride-*co*-hexafluoropropylene) copolymer, poly(VDF-*co*-HFP), $-[(CH_2CF_2)_m(CF_2CFCF_3)]_p-$, and ETFE to F^- ions, by means of superheated water in the presence of an alkali reagent (KOH or NaOH) at relatively low concentration (up to 1.0 M).

Effect of coexisting gas on the reactivity of the polymers and the formation of 'artificial fluorspar' upon addition of $Ca(OH)_2$ to the resulting reaction solution are also described.

So far, several studies on the alkaline-reagent induced degradation of PVDF[22–31] and a VDF-based copolymer[32] were reported. However, these previous studies aimed at the surface modification of the polymer, for example, to increase the adhesion of polymer surface.[23] The level of degradation that changes bonding nature of PVDF surface is substantially lower than that required for waste treatment, because the latter requires whole degradation of the PVDF bulk. The present study is the first report on the decomposition of PVDF and related copolymers in superheated water combined with an alkaline reagent.

EXPERIMENTAL SECTION

2.1. Materials and reagents. Ar (99.99%), O_2 (99.999%), and a standard gas mixture CO_2 (1.00%)/N_2 were purchased from Nissan Tanaka (Saitama, Japan). PVDF powder was from SynQuest Laboratories (Alachua, FL). Size exclusion chromatography (SEC) showed that the weight-average molecular weight (M_w) was 6.5×10^5 and the polydispersity (M_w/M_n) was 2.5, relative to polystyrene standard. Poly(VDF-*co*-HFP) copolymer was the same as that used in our previous report:[33] the VDF/HFP molar ratio was 95.3/4.7 and the M_w determined by SEC in dimethylformamide was 4.5×10^5, relative to poly(methyl methacrylate), with the M_w/M_n of 3.2. Combustion ion chromatography demonstrated that the percentages of fluorine in PVDF and poly(VDF-*co*-HFP) copolymer were 60.7 and 59.4 wt%, respectively. The F^- yields of the reactions were calculated according to these analytical values of the fluorine contents in the polymers. Granulated ETFE was obtained from Millipore Sigma (St. Louis, MO, USA). ETFE is essentially an alternating copolymer.[1] Consistently, the percentage of fluorine in the ETFE was determined to be 58.6 wt% by combustion ion chromatography, which value was only slightly lower the value for complete alternating copolymer (59.3 wt %).

As well as PVDF and poly(VDF-*co*-HFP) copolymer, the F^- yields of the reactions for ETFE were calculated based on this analytical value. 1,3,5-Trifluorobenzene ($C_6H_3F_3$, >98%) and other reagents were supplied from Fujifilm Wako Pure Chemical Industries (Osaka, Japan).

2.2 Superheated water treatment. An autoclave, in which the internal volume was 31 mL, was mainly used. Some reactions for ETFE were also performed in a bigger autoclave (96 mL) attached with an impeller that can stir the reaction mixture. Each autoclave was fitted with a gold vessel to prevent contamination from the autoclave material (stainless steel, Japanese Industrial Standards SUS 316). In a typical run using 31 mL autoclave, to the gold vessel in the autoclave was added the polymer powder (30 mg), followed by an aqueous solution of KOH or NaOH (10 mL, 0.25–1.00 M). Then, the autoclave was pressurized up to 0.60 MPa with Ar and sealed. Next, the autoclave was placed in an electric furnace and heated to the desired reaction temperature with a rate of ca. 10 °C min^{-1}. After holding a specified time, the autoclave was quickly cooled to 25 °C by an electric fan. The gas in the autoclave headspace was recovered into a sampling bag and subjected to gas chromatography–mass spectrometry (GC/MS). After sampling the gas, the cap of the autoclave was opened in air. The liquid-solid mixture in the vessel was transferred into a polypropylene tube, which was subjected to centrifugation. The collected liquid phase was characterized by ion chromatography, total organic carbon (TOC) measurement, and attenuated total reflection infrared (ATR-IR) spectrometry. The solid residue was dried under vacuum and subjected to Raman spectroscopy, combustion-ion chromatography, and carbon analysis.

Control reactions using O_2 instead of Ar were also performed. Consecutive runs, that is, repeating the procedure that an additional PVDF amount was charged to the resulting reaction mixture after a charge of PVDF had been reacted in superheated water, then the mixture was reacted in superheated water again, were also carried out.

2.3. Synthesis of artificial fluorspar. Formation of CaF_2 from the reaction solution generated from the superheated water treatment by adding $Ca(OH)_2$ was investigated. After PVDF (30 mg) was treated with 1.0 M of [KOH] under Ar at 250 °C for 6 h, the resulting reaction mixture was centrifugated. The collected liquid was diluted to 25 mL with pure (Milli-Q) water. To the solution was added $Ca(OH)_2$, which molar amount was the same as that of the F^- molar amount contained in the solution. Shaking this mixture generated a white powder. The powder was collected and washed with 1.0 M of [HCl], followed by pure water. The purified powder was dried under vacuum for overnight, and then subjected to X-ray diffractometry (XRD).

2.4. Instrumental analysis. The fluorine weight percentages in the initial polymers and the solid residues formed from the reactions were determined by combustion ion chromatography at Nissan Arc (Yokosuka, Japan). The instrument consisted of a combustion unit (AQF-100, Nittoseiko Analytech, Yamato, Japan; matrix combustion temperature, 1100 °C) and an ion chromatograph (Dionex ICS-3000, Thermo Fisher Scientific, Waltham, MA). The F^- concentrations in the reaction solutions were determined by an ion-chromatograph (IC-2001, Tosoh, Tokyo, Japan) attached with an analytical column (TSKgel Super IC-Anion, Tosoh). The mobile phase was an aqueous solution consisting of 6 mM sodium tetraborate, 15 mM boric acid, and 0.2 mM sodium hydrogen carbonate, and the flow rate was 0.8 mL min^{-1}. Another ion-chromatograph with an analytical column (TSKgel Super IC-AP) was also used to quantify organic acid anions in the reaction solutions. The mobile phase was an aqueous solution consisting of 1.7 mM sodium hydrogen carbonate, 1.8 mM sodium carbonate, and acetonitrile (23 vol %).

The total organic carbon (TOC) concentrations in the reaction solutions were determined by a TOC instrument (N/C 3100 BU, Analytik Jena, Jena, Germany). In this instrument, a halogen removal column was employed to avoid corrosion of the non-dispersive IR detector.

Raman spectra of solid residues and PVDF before the treatment were measured at 532 nm excitation using a Raman imaging microscope (WITec α 300, Oxford Instruments, Harpenden, UK). A FTIR spectrometer (Spectrum 100, Perkin Elmer, Waltham, MA, USA) attached with a diamond ATR cell was used for observing ATR-IR spectra of the reaction solutions. The sample droplets were placed into the ATR cell, evaporated to dryness with a stream of N_2 gas, and the IR spectra were recorded.

Carbon contents in the residues were determined by a carbon/sulfur analyzer (EMIA-Expert, Horiba, Kyoto, Japan) or a total carbon analyzer (N/C 3100 BU with HT 1300, Analytik Jena, Jena, Germany).

The collected gas after the superheated water reactions was analyzed by means of a GC/MS instrument (QP2010 SE, Shimazu, Kyoto, Japan) attached with a fused-silica capillary column (Rt-Q-BOND, Restek, Bellefonte, PA). The carrier gas was helium, and the sample injection temperature was maintained at 120 °C. The sample gas was injected into the GC/MS system in split mode (20/1 ratio), and the analyses were conducted in full-scan mode (*m*/*z* 2.0–200). The column oven temperature program was as follows: keeping at 30 °C for 5 min, raising to 200 °C at 20 °C min^{-1} rate, and maintaining at that temperature for 20 min. XRD patterns of the artificial fluorspar were recorded by using an X-ray diffractometer with copper Kα radiation (MultiFlex; Rigaku, Tokyo, Japan).

In the present study, the F^- yield, the remaining TOC ratio, and the CO_2 yield were determined by the following eqs 1– 3, respectively.

F^- yield = [(F^- moles in the reaction solution) / (fluorine atom moles in the initial polymer)] (1)

TOC ratio = [(TOC moles in the reaction solution) / (carbon atom moles in the initial polymer)]

(2)

CO_2 yield = [(CO_2 moles in the gas phase) / (carbon atom moles in the initial polymer)]

(3)

RESULTS AND DISCUSSION

3.1 Decomposition of PVDF.

3.1.1. Effect of OH^-. First, effect of KOH concentration on the PVDF reactivity was examined. Figures 1A, 1B, and 1C display KOH concentration dependences of F^- amount in the reaction solution, TOC amount in the reaction solution, and CO_2 amount in the gas phase, respectively, obtained from reactions of PVDF at 250 °C for 6 h. When the treatment was performed without KOH, almost no reaction occurred. The F^- amount in the resulting reaction solution was trace (1.4 μmol; yield ~0%) (Table 1, entry 1). Likewise, the TOC amount (3.7 μmol) in the reaction solution and the CO_2 amount (2.1 μmol) in the gas phase were negligible (both yields were ~0%). These data indicate that PVDF is stable in pure superheated water (i.e., under Ar) at 250 °C.

In contrast, an addition of KOH dramatically increased the PVDF reactivity in superheated water at this temperature. When 0.125 M of [KOH] was employed, the formed F^- amount jumped to 794 μmol, revealing 83% yield (Figure 1A). In addition, when the [KOH] was further increased to 1.0 M (charged amount, 10 mmol in 10 mL), the molar amount of which corresponds to a 10-fold molar excess relative to the amount of fluorine atoms (959 μmol) in the initial PVDF, the F^- amount increased to 910 μmol (Table 1, entry 2, the average value of two reactions), which corresponds to 95% yield. Therefore, the fluorine content in the initial PVDF led to an almost complete mineralization. The KOH-induced F^- formation was

accompanied by increasing TOC amount in the reaction solution. The TOC amount gradually increased with increasing [KOH] up to 1.0 M (Figure 1B). This observation indicates that non-fluorinated organic compounds generated with increasing [KOH], because the F^- yield was considerably high even at low [KOH] such as 0.125 M (Figure 1A, the F^- yield was 83%). When [KOH] was 1.0 M, the TOC amount reached 144 μmol (Table 1, entry 2, the average value of two reactions), which corresponds to 15% of the carbon molar amount in the initial PVDF. In the gas phase, very few CO_2 amount was detected, and the amount reduced when the reactions were performed with KOH (Figure 1C). At [KOH] of 1.0 M, the CO_2 amount was only 0.5 μmol (the yield was ~0%, the average value of two reactions, Table 1, entry 2). When [KOH] was increased from 0 to 1.0 M, the pH of the resulting reaction solution increased from 3.9 to 13.6. In such a highly basic solution, even if CO_2 formed, most of the molecules transformed into CO_3^{2-} in the reaction solution. Instead, black solid residues formed when the reactions were performed with KOH. The carbon percentage of the residue obtained from reactions with 1.0 M [KOH] was 44 wt% (the average value of two reactions). In contrast, the fluorine percentage of the residue was 0.51 wt%. These values and the weight of the residue showed that the carbon and fluorine amounts were 744 and 5.4 μmol, respectively. That is, the molar amount of carbon was 138 times higher than that of the fluorine. This carbon amount corresponds to 79% of the carbon content (937 μmol) in the initial PVDF. On the other hand, the fluorine amount corresponds to only ~1% of the fluorine content (959 μmol) in the initial PVDF, which is consistent with the fact that F^- ions produced in the reaction solution with a high yield (95%). The carbon recovery—[(total moles of carbon atoms in residue, TOC, and CO_2)/(moles of the carbon atoms in initial PVDF)] was 95% [= (744 + 144 + 0.5) / 937 × 100]. This result indicates that the carbon amount was well accounted for by the residue, TOC in the reaction solution, and CO_2 in the gas phase.

To identify this carbon rich residue, Raman spectroscopy was employed. Figures 2A and 2B display the spectra for the carbon-rich residue and PVDF before the treatment, respectively. In the spectrum of PVDF, intense peaks appeared at 2984, 1432, and 794 cm^{-1} (Figure 2B). These peaks were attributed to CH_2 groups.[27,28] In addition, several peaks appeared around 1300–870 and 606 cm^{-1}, which were attributed to CF_2 groups.[27,34] The peaks ascribed to CH_2 and CF_2 groups were not observed in the spectrum of the carbon-rich residue (Figure 2A). Instead, two intense bands appeared at 1596 and 1367 cm^{-1}. This feature was very similar to that observed for amorphous carbon,[35–37] showing two bands ascribed from stretching of C=C bonds. Furthermore, when PVDF was reacted in 1.0 M [KOH], trace amount (0.02 μmol) of $C_6H_3F_3$ was detected in the gas phase (total-ion current chromatogram in the GC/MS measurement is shown in Figure S-1 in Supporting Information).

According to these results, the PVDF degradation mechanism caused by OH^- can be explained as follows (Scheme 1).

First, OH^- favors deprotonation of methylene moiety flanked between two electron-withdrawing CF_2 groups (eq 4):

$$–CH_2CF_2–CH_2CF_2–CH_2CF_2– + OH^- \rightarrow –CH_2CF_2–CH^{(-)}CF_2–CH_2CF_2– + H_2O \quad (4)$$

The deprotonated anion is unstable to form a C=C bond in the polymer chain, accompanied by releasing F^- into the reaction solution (eq 5):

$$–CH_2CF_2–CH^{(-)}CF_2–CH_2CF_2– \rightarrow –CH_2CF_2–CH=CF–CH_2CF_2– + F^- \quad (5)$$

The initial step is also described by Ross et al.,[26] who monitored PVDF surface degradation by IR spectroscopy, using 12 M NaOH solution at 80 °C, although the IR spectra in this

report revealed that most of CH_2 and CF_2 units in bulk PVDF remained after such a treatment for 254 h.

A further deprotonation in the polymer chain results in an additional C=C bond and F^- release (eqs 6, 7).

$$–CH_2CF_2–CH=CF–CH_2CF_2– + OH^- \rightarrow –CH_2CF_2–CH=CF–CH^{(-)}CF_2– + H_2O \quad (6)$$

$$–CH_2CF_2–CH=CF–CH^{(-)}CF_2– \rightarrow –CH_2CF_2–CH=CF–CH=CF– + F^- \quad (7)$$

The sequence of these steps results in the formation of carbon rich residue. The generation of $C_6H_3F_3$ trace in the gas phase can be explained by chain scission during the defluorination processes. When the superheated water reactions were performed with KOH, the TOC amount in the reaction solution increased with increasing [KOH] (Figure 1C). This phenomenon is also consistent with the occurrence of chain scission during the defluorination processes.

As expected, not only KOH, but also NaOH induced the defluorination of PVDF to F^-. When PVDF was reacted with 1.0 M of [NaOH] at 250 °C for 6 h, the F^- amount was 858 μmol, or 89% yield (Table 1, entry 3).

Next, the effect of reaction temperature on the PVDF decomposition was examined by using 1.0 M of [KOH] at a constant reaction time of 6 h. Figures 3A, 3B, and 3C display the temperature dependences of the amounts of F^-, TOC, and CO_2, respectively. When the reaction was performed at 150 °C, very little PVDF decomposition was observed: the reaction produced 22.8 μmol of F^- (2% yield); 14.2 μmol of TOC amount (2% of the carbon content in the initial PVDF); and 0.25 μmol of CO_2 (~0% yield). Elevating temperature to 200 °C dramatically enhanced the F^- amount (846 μmol), which corresponds to 88% yield (Table 1, entry 4). Furthermore, at 300 °C, the F^- amount reached 958 μmol (100% yield) while the

TOC amount also increased to 159 μmol (17% of the carbon content of initial PVDF). The CO_2 amount in the gas phase also slightly increased to 1.2 μmol, although the yield was negligible (~0%). As described above, the F^- amount jumped at 200 °C, and kept steady at higher temperature (Figure 3A). In contrast, the TOC amount remained low up to 200 °C, then increased at 250 °C and remained the same at higher temperature (Figure 3B). This difference suggests that the defluorination proceeded at first (eqs 4–7), followed by chain scission in the remaining polymer.

Effect of the reaction time was also examined for reactions in 1.0 M of [KOH] at 250 °C (Figure 4). Almost complete mineralization of the fluorine content was observed even at a short reaction time of 2 h (Figure 4A): the F^- amount reached 903 μmol, or 94% yield. The F^- amount remained almost constant after 2 h (e.g., at 18 h, it was 933 μmol, which corresponds to 97% yield) whereas the TOC amount was 146 μmol (or 16% of the carbon content in the initial PVDF). The CO_2 amount in the gas phase was almost constant during the reaction time (Figure 4C). After 18 h, it was 0.4 μmol (yield ~0%).

3.1.2. Combination of OH^- with O_2. The reactions described above were performed under Ar. We changed the coexisting gas from Ar to O_2 that induced significant differences on the PVDF reactivity, especially on the fate of the carbon content of PVDF. Figure 5 displays the molar amounts of main products from the 6 h reactions in superheated water under O_2 using 1.0 M of [KOH], and under these conditions, the reaction temperatures varied from 150 to 300 °C. When the temperature was elevated from 150 to 200 °C, the F^- amount dramatically increased. For a reaction performed at 250 °C, this amount was 866 μmol, or 90% yield (Table 1, entry 5), which was similar to that using Ar (95%, Table 1, entry 2). The TOC ratio at this temperature (16%, Table 1, entry 5) was also similar to the value obtained from the reaction using Ar (15%, Table 1, entry 2). However, the TOC amount showed a unique temperature dependence (Figure 5B), different from that observed for the reactions under Ar

(Figure 3B). In the presence of O_2, the TOC amount increased with increasing temperature to 200 °C, then turned to decrease at higher temperature. Furthermore, the solid residue, which was observed for the reactions under Ar, almost disappeared when PVDF reacted under O_2 above 200 °C, at which the TOC amount was 186 μmol (i.e., 20% of the carbon content in the initial PVDF). Finally, at 300 °C, the amount decreased to 132 μmol, or 14% of the carbon content in the initial PVDF. This result suggests that the carbon rich moiety generated after releasing F^- (eqs 5–7) can decompose in the presence of O_2. Figure 5C shows temperature dependence of the CO_2 amount by this treatment. The amount was trace (0.4–0.6 μmol) while the temperature varied from 150 to 300 °C.

To identify the organic component that generates TOC amount in the reaction solution, ATR-IR spectra of the reaction solutions were measured. When the reaction was performed at 250 °C with O_2 for 6 h, which gave 90% F^- yield and 16% of the remaining TOC ratio (Table 1, entry 5), the spectrum of the resulting reaction solution after dryness displayed two intense absorptions at 1646 and 1374 cm^{-1}, accompanied by a broad adsorption around 3200–3300 cm^{-1} (Figure S-2 in Supporting Information). This pattern was similar to that of potassium oxalate.[38] Therefore, this reaction solution was subjected to ion chromatography, which conditions were adjusted for the detection of organic acid anions. Consistently, the measurement detected 41.0 μmol of oxalate anion [$(COO^-)_2$]. This value indicates that the amount of carbon atoms was 82.0 μmol (= 41.0 × 2), which accounts for 55% of the TOC amount (149 μmol) in the reaction solution. Therefore, majority of the TOC amount was accounted for by oxalate anion.

3.1.3. Consecutive runs. Because PVDF (30 mg) was almost completely defluorinated to form F^- by superheated water treatment with 1.0 M of [KOH] at 250 °C for 6 h, we examined consecutive runs. That is, after one reaction using PVDF with 1.0 M of [KOH] under Ar at 250 °C for 6 h was complete, new PVDF (30 mg) was charged to the resulting reaction

mixture, and then the second reaction was performed under Ar at 250 °C for 6 h. Four consecutive runs were performed, where the yield of F^- ions accumulated from the first to n^{th} run ($n \leq 4$) was defined by eq 8.

F^- yield until n^{th} run = [(F^- moles detected after n th run) /

(moles of F atoms in PVDF charged from 1st to n^{th} run)] (8)

The F^- amount and the yield are displayed in Figure 6. The F^- amount increased linearly with the number of consecutive runs, whereas the F^- yields were similar (93–98%): no decrease was observed, indicating that at least four consecutive runs were possible under the present reaction conditions.

3.2 Decomposition of poly(VDF-*co*-HFP) copolymer. Because PVDF was efficiently mineralized in superheated water in the presence of an alkaline reagent, this methodology was applied to decompose poly(VDF-*co*-HFP) copolymer. The microstructure of this copolymer contains VDF-HFP-VDF units. In such a case, F^- is expected to generate not only from the VDF units, but also from the HFP units (eqs 8, 9).[39]

$$–CH_2CF_2–CF_2C(CF_3)F–CH_2CF_2– + OH^- \rightarrow –CH_2CF_2–CF_2C(CF_3)F–CH^{(-)}CF_2– + H_2O \quad (8)$$

$$–CH_2CF_2–CF_2C(CF_3)F–CH^{(-)}CF_2– \rightarrow –CH_2CF_2–CF_2C(CF_3)=CHCF_2– \quad (9)$$

Furthermore, if the HFP-VDF-HPF units are present, they are likely to release more F^-.[39]

Figure 7 displays the effect of temperature on the amounts of (A) F^-, (B) TOC, and (C) CO_2, respectively, generated from reactions with 1.0 M of [KOH] under Ar for 6 h. When the

reaction was performed at 150 °C, little reaction proceeded, giving 43.1 μmol of F^- (i.e., 5% yield); 26.6 μmol of TOC amount (3% of the carbon content in the initial copolymer), and 0.11 μmol of CO_2 (~0% yield). Elevating reaction temperature enhanced the decomposition of this copolymer. The F^- formation greatly increased above 200 °C (Figure 7A). When the reaction was performed at 250 °C, the F^- amount reached 934 μmol, which corresponds to 100% yield (Table 1, entry 6). That is, the fluorine content in initial poly(VDF-*co*-HFP) copolymer was completely mineralized. The TOC amount also increased with increasing temperature (Figure 7B). At 250 °C, it reached 188 μmol, which corresponds to 21% of the carbon content in initial poly(VDF-*co*-HFP) (Table 1, entry 6). Small amount of CO_2 (0.1–0.2 μmol) was also detected at each temperature (Figure 7C), although the yield was ~0%.

Figure 8 displays results of (A) F^-, (B) TOC, and (C) CO_2 formations from this copolymer, where the reactions were performed in the presence of O_2 for 6 h. The temperature dependence of the amount of each product was almost identical with that performed under Ar. The reaction at 250 °C generated 951 μmol of F^- (101% yield), 200 μmol of TOC (22% of the remaining ratio), and 0.3 μmol of CO_2 (0% yield) (Table 1, entry 7).

3.3 Decomposition of ETFE. First, decomposition of ETFE was examined by use of a 31 mL-autoclave, which was used for reactions of PVDF and poly(VDF-*co*-HFP) copolymer as described above. When the reaction was performed with 1.0 M of [KOH] at 250 °C for 6 h, the F^- amount was 903 μmol, or 98% yield and the TOC amount was 243 μmol, corresponding to 26% of the carbon content in the initial ETFE (Table 1, entry 8). This means that the fluorine content in initial ETFE was completely mineralized, similar to PVDF and poly(VDF-*co*-HFP) copolymer. Significant differences in the reactivity between ETFE and PVDF were observed at lower temperature. For a reaction performed at 200 °C, very small F^- amount (1.1 μmol, 0% yield) was detected (Table 1, entry 9). In contrast, PVDF produced F^-

with a much higher yield (88%) (Table 1, entry 4). This difference suggests that OH^- can abstract H^+ from the methylene moiety of PVDF easier than that from ETFE. In PVDF, each $–CH_2–$ unit from normal head to head addition is bounded to two $–CF_2–$ units, which are strongly electron withdrawing. The alternation of $–CH_2–$ and $–CF_2–$ units may facilitate the abstraction of H^+ and subsequent C=C bond formation and F^- release (eqs 4–7). In contrast, ETFE consists of alternation of $–CH_2CH_2–$ and $–CF_2CF_2–$ units; the $–CH_2–$ unit is bound to a $–CF_2–$ unit and a $–CH_2–$ unit. This microstructure may suppress the H^+ abstraction. That is, the difference in the environment around the $–CH_2–$ group results in different reactivity of both polymers at such a low temperature (200 °C).

Next, temperature dependence of the reactivity of ETFE was investigated by use of a bigger autoclave (96 mL) with 1.0 M of [KOH] or [NaOH]. The two alkaline reagents caused no significant difference in the amounts of F^-, TOC, and CO_2 (Figures 9A, 9B, and 9C, respectively). While the F^- and TOC amounts were low below 230 °C, they increased at higher temperatures. For a reaction performed with 1.0 M of [KOH] at 260 °C for 6 h, the F^- amount reached 874 μmol, or 94% yield (Entry 1, Table S-1 in Supporting Information). Likewise, when the reaction was performed with NaOH under the same conditions, the F^- amount reached 925 μmol, or 100% yield (the average value of two reactions, entry 2, Table S-1 in Supporting Information). Reactions under O_2 atmosphere were also performed (Figure 10). At 260 °C, the F^- amount reached 893 μmol, or 97% yield (the average value of two reactions, Entry 3, Table S-1 in Supporting Information). It should be noted that when the reaction was performed at 320 °C in the presence of O_2, the TOC amount decreased to 64 μmol, that is, 7% of the carbon content in the initial ETFE. In contrast, when the reaction was performed under Ar at 320 °C, the TOC value (321 μmol, or 34% of the carbon content in the initial ETFE) did not decrease from the value at 260 °C (see Figure 9, NaOH plots).

This result suggests that non-fluorinated organic component in the water was oxidatively mineralized by O_2.

3.4 Synthesis of artificial fluorspar. Finally, we examined the transformation of F^- ions obtained from superheated water treatment into CaF_2 to close the loop on the fluorine element. After PVDF was treated with 1.0 M of [KOH] under Ar at 250 °C for 6 h, the F^- ions in the reaction solution were reacted with $Ca(OH)_2$. The powder formed was washed with aqueous HCl, followed by pure water. The XRD pattern of the dried powder showed peaks only assigned to CaF_2 (Figure 11A). The weight of the collected pure CaF_2 indicated that 77% of the fluorine atoms in the initial PVDF were recovered into CaF_2. The same treatment was performed for the solutions obtained from the reaction of poly(VDF-*co*-HFP) copolymer with 1.0 M of [KOH] at 250 °C for 6 h and from the reaction of ETFE with 1.0 M of [NaOH] at 260 °C for 6 h under Ar. Both reaction solutions generated pure CaF_2 (Figures 11B and 11C) with 84% and 73 % yields (based on the fluorine content in the initial polymer) for poly(VDF-*co*-HFP) copolymer and ETFE, respectively.

4. CONCLUSIONS

Mineralization of PVDF, poly(VDF-*co*-HFP) copolymer, and ETFE in superheated water in the presence of an alkaline reagent was investigated. These polymers caused quasi-complete defluorination, releasing F^- ions into the reaction solution at a relatively low temperature (250 °C) under Ar atmosphere. When PVDF was reacted in the presence of 1.0 M of [KOH] at 250 °C for 6 h, which amount corresponds to 10 times the molar amount of fluorine content (as atoms) in PVDF, the F^- yield released into the reaction solution reached 95%. This transformation was accompanied by formation of carbon rich residue consisting of amorphous carbon. When the PVDF reaction was performed with O_2 instead of Ar,

significant differences were observed in the products: while F^- ions efficiently produced (93% yield), carbon rich residue did not form. In such conditions, a major species that composed the total organic carbon content in the reaction solution was oxalate. Four consecutive runs (that is, after one reaction of PVDF with 1.0 M [KOH] at 250 °C under Ar for 6 h was complete, new PVDF was charged to the reaction mixture and reacted again) were performed, and no decrease of the F^- yield was observed.

The fluorine atoms in poly(VDF-*co*-HFP) copolymer and ETFE also completely mineralized to form F^- ions in the reaction solutions with 100 and 98% yields, respectively, after treatment with 1.0 M of [KOH] for 6 h under Ar. Addition of $Ca(OH)_2$ to the reaction solutions from superheated water treatment for these polymers and subsequent washing procedures with 1.0 M of [HCl] and pure water gave pure CaF_2, i.e., artificial fluorspar, with 74, 84 and 73% yields for PVDF, poly(VDF-*co*-HFP) copolymer and ETFE, respectively. Further efforts using similar approaches for recycling other fluoropolymers are under progress in our laboratories.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/.

Total ion current chromatogram of the resulting gas phase at the GC/MS measurement; ATR-IR spectrum of the resulting reaction solution; results from superheated water treatment for ETFE at 260 °C using a bigger (96 mL) autoclave.

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Notes

The authors declare no competing financial interest.

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Table 1. Products from Superheated Water Treatment of PVDF and Copolymers [a]

Entry	Polymer [b]	Alkaline reagent [Conc.(M)]	Coexisting gas	*T* (°C)	*P* (MPa)	F^- (μmol) [yield (%)]	TOC (μmol) [ratio (%)]	CO_2 (μmol) [yield (%)]
1	PVDF	none	Ar	250	4.4	1.4 [0]	3.7 [0]	2.1 [0]
2	PVDF	KOH [1.0]	Ar	250	4.4	910±4 [c] [95±1]	144±25 [c] [15±3]	0.5±0.0 [c] [0]
3	PVDF	NaOH [1.0]	Ar	250	4.4	858 [89]	225 [24]	0.4 [0]
4	PVDF	KOH [1.0]	Ar	200	2.3	846 [88]	32 [3]	0.2 [0]
5	PVDF	KOH [1.0]	O_2	250	4.1	866 [90]	149 [16]	0.4 [0]
6	Poly(VDF-*co*-HFP)	KOH [1.0]	Ar	250	4.4	934 [100]	188 [21]	0.2 [0]
7	Poly(VDF-*co*-HFP)	KOH [1.0]	O_2	250	4.2	951 [101]	200 [22]	0.3 [0]
8	ETFE	KOH [1.0]	Ar	250	5.2	903 [98]	243 [26]	0.1 [0]
9	ETFE	KOH [1.0]	Ar	200	2.3	1.1 [0]	29 [3]	0.1 [0]

[a] Internal volume of the autoclave, 31 mL; initial solution volume, 10 mL; reaction time, 6 h.
[b] Charged weight, 30 mg.
[c] Obtained from two replicate experiments under the same reaction conditions.

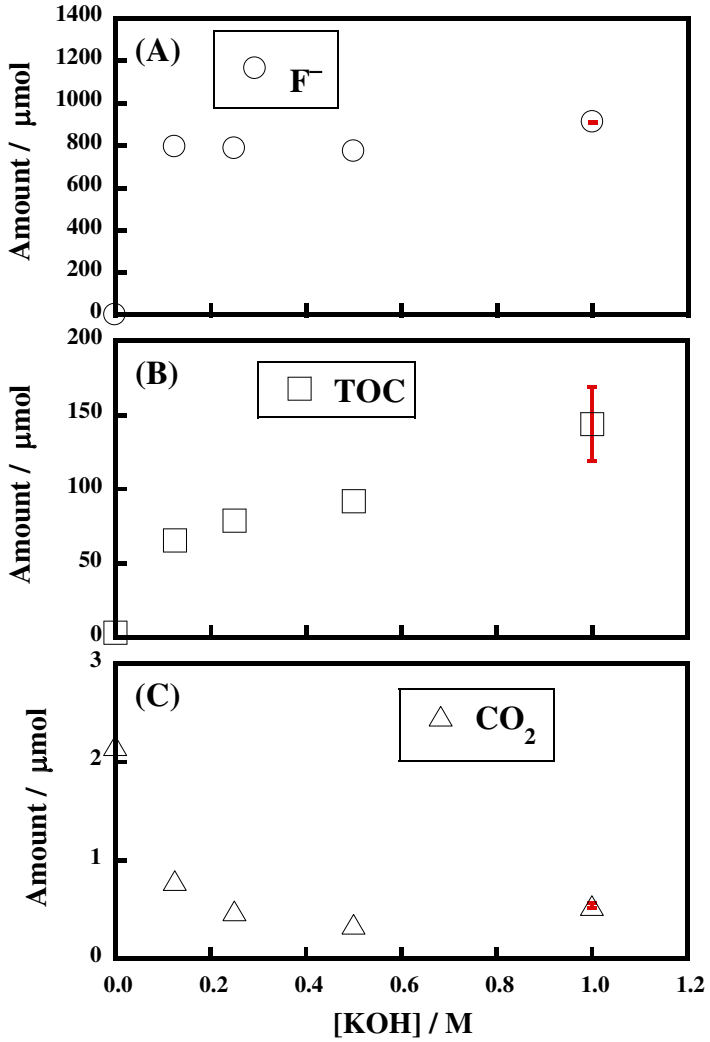


Figure 1. Initial KOH concentration dependences of (A) the F^- amount in the reaction solution, (B) the TOC amount in the reaction solution, and (C) the CO_2 amount in the gas phase. PVDF (30 mg; fluorine amount as atoms, 959 μmol; carbon content as atoms, 937 μmol) was reacted in the presence of KOH under Ar in superheated water at 250 °C for 6 h. Error bars at 1.0 M of [KOH] were obtained from two replicate experiments under the same reaction conditions.

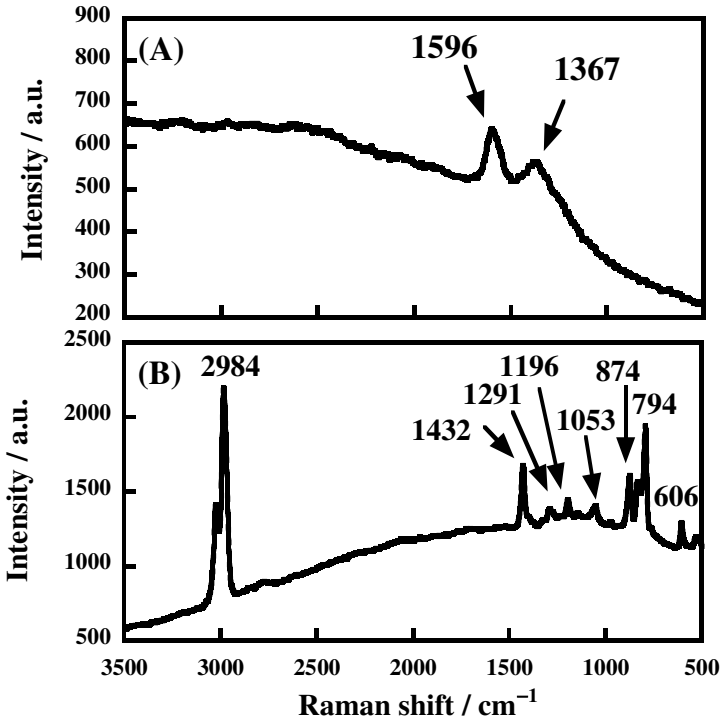
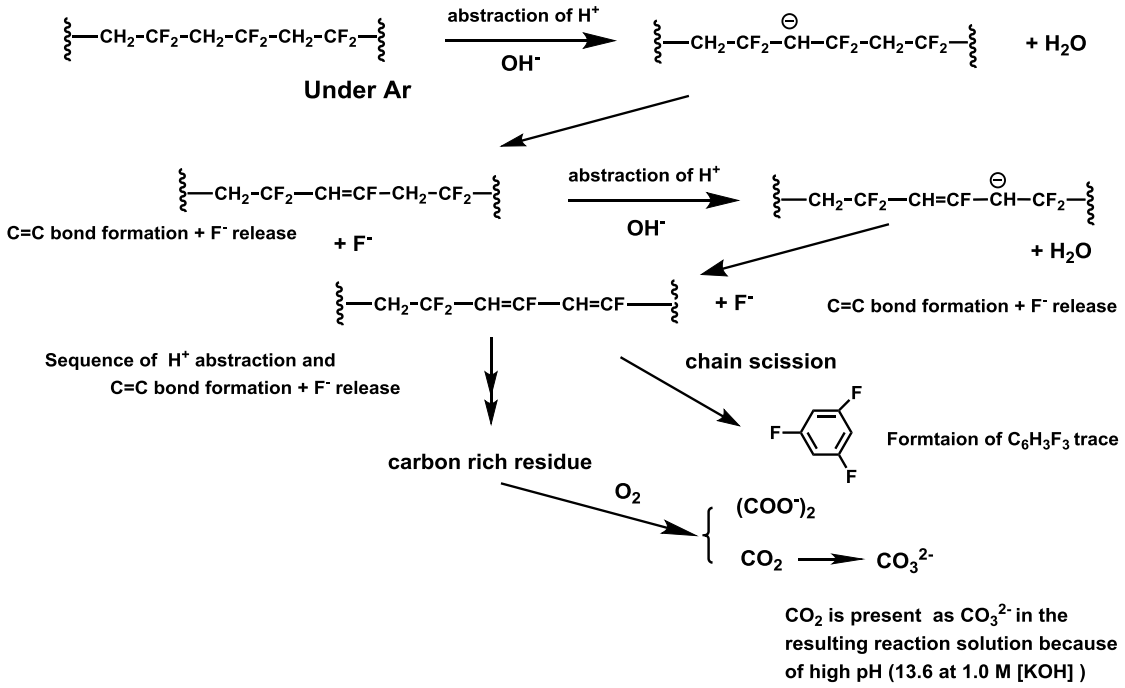


Figure 2. Raman spectra of (A) the solid residue formed from a reaction of PVDF in superheated water with 1.0 M of [KOH] under Ar and (B) PVDF before the treatment. For (A), the treatment was performed at 250 °C for 6 h.



Reaction under Ar: Efficient F^- formation + carbon rich residue

Reaction under O_2: Efficient F^- formation + no residue

Scheme 1. Proposed mechanism for PVDF decomposition induced by OH^-

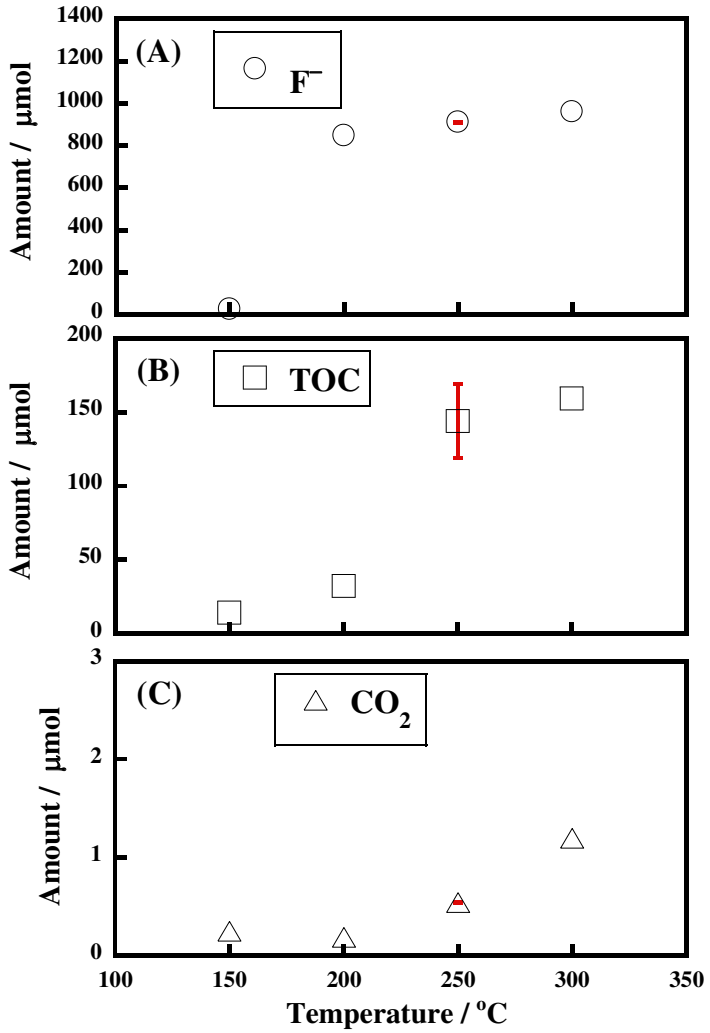


Figure 3. Effect of temperature on (A) the F^- amount in the reaction solution, (B) the TOC amount in the reaction solution, and (C) the CO_2 amount in the gas phase. PVDF (30 mg) was reacted in the presence of 1.0 M of [KOH] in superheated water under Ar for 6 h. Error bars at 250 °C were obtained from two replicate experiments under the same reaction conditions.

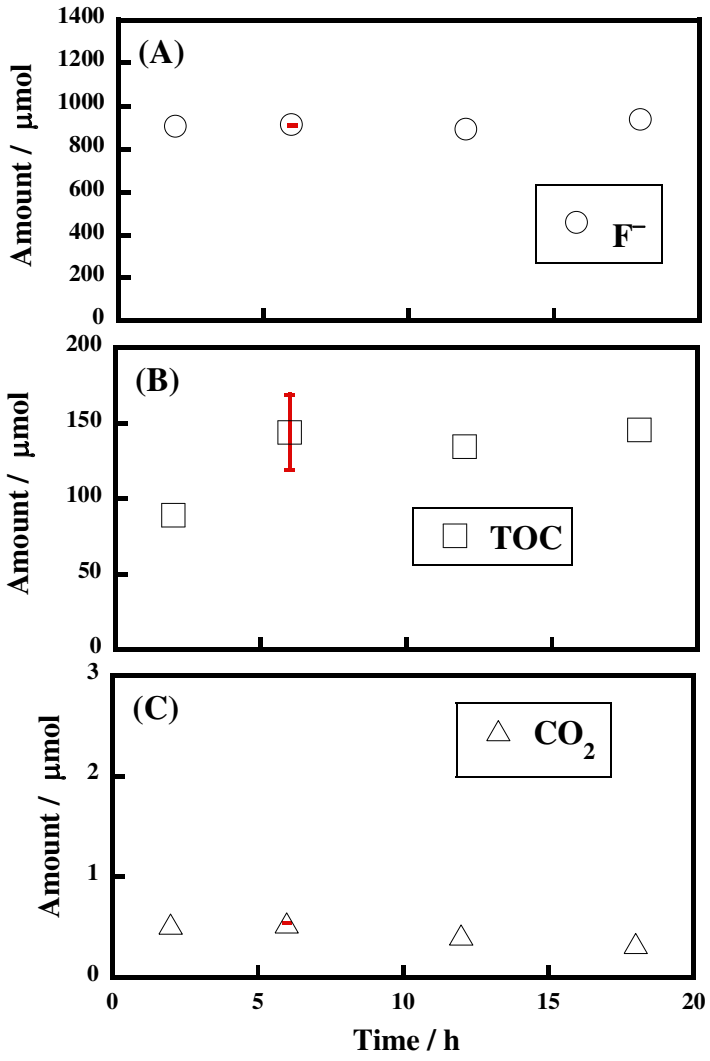


Figure 4. Effect of reaction time on (A) the F^- amount in the reaction solution, (B) the TOC amount in the reaction solution, and (C) the CO_2 amount in the gas phase. PVDF (30 mg) was reacted in the presence of 1.0 M of [KOH] under Ar in superheated water at 250 °C. Error bars at 6 h were obtained from were obtained from two replicate experiments under the same reaction conditions.

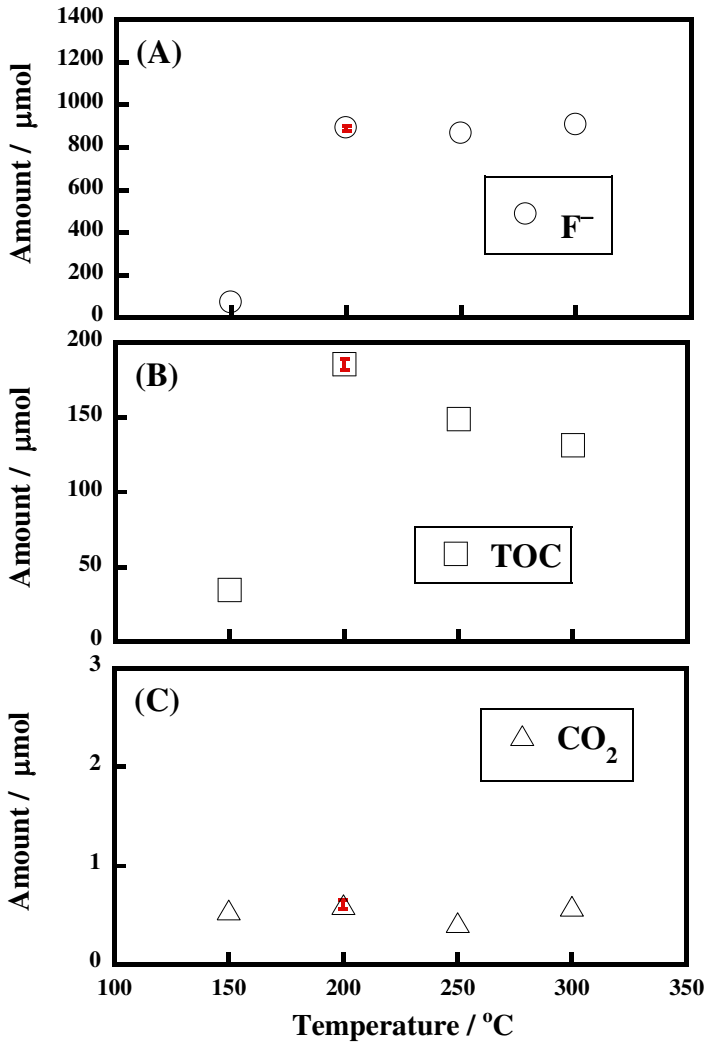


Figure 5. Temperature dependence of PVDF decomposition in the presence of O_2: (A) the F^- amount in the reaction solution, (B) the TOC amount in the reaction solution, and (C) the CO_2 amount in the gas phase. The reaction conditions were the same as those described in the caption of Figure 3, except that O_2 was used instead of Ar. Error bars at 200 °C were obtained from two replicate experiments under the same reaction conditions.

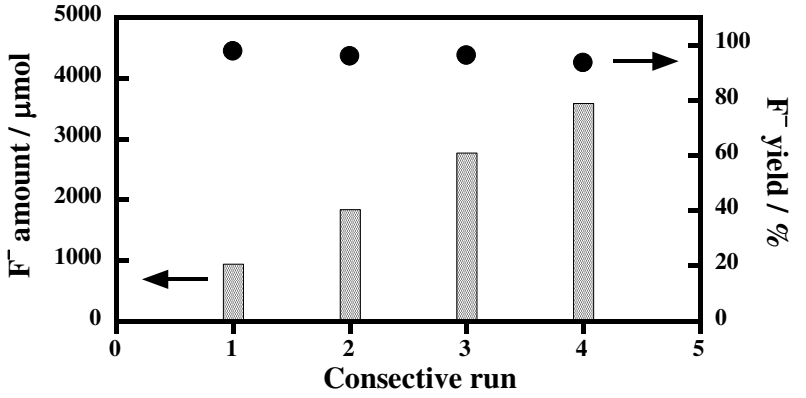


Figure 6. F^- amount and F^- yield after consecutive runs for PVDF decomposition. PVDF (30 mg) was reacted with 1.0 M of [KOH] in superheated water at 250 °C under Ar for 6 h. After the reaction, the autoclave was cooled to room temperature, and new PVDF (30 mg) was charged to the resulting reaction mixture, purged with Ar, then the mixture was further heated at 250 °C for 6 h.

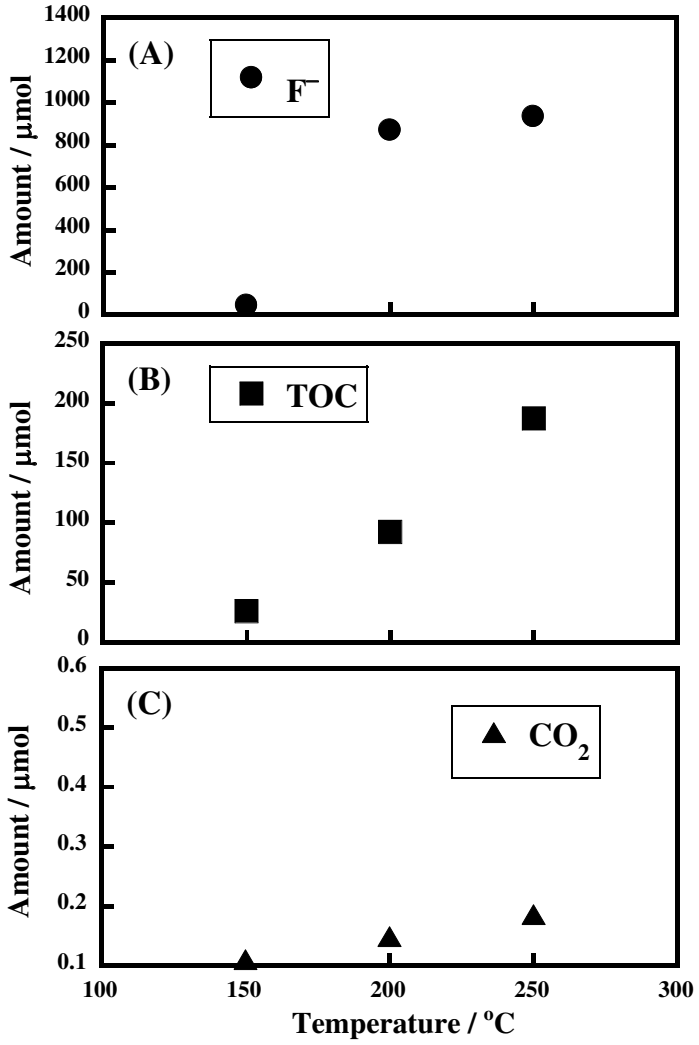


Figure 7. Effect of temperature on (A) the F^- amount in the reaction solution, (B) the TOC amount in the reaction solution, and (C) the CO_2 amount in the gas phase. Poly(VDF-*co*-HFP) copolymer (30 mg, fluorine amount as atoms; 938 μmol; carbon content as atoms, 902 μmol) was reacted in the presence of 1.0 M of [KOH] in superheated water under Ar for 6 h.

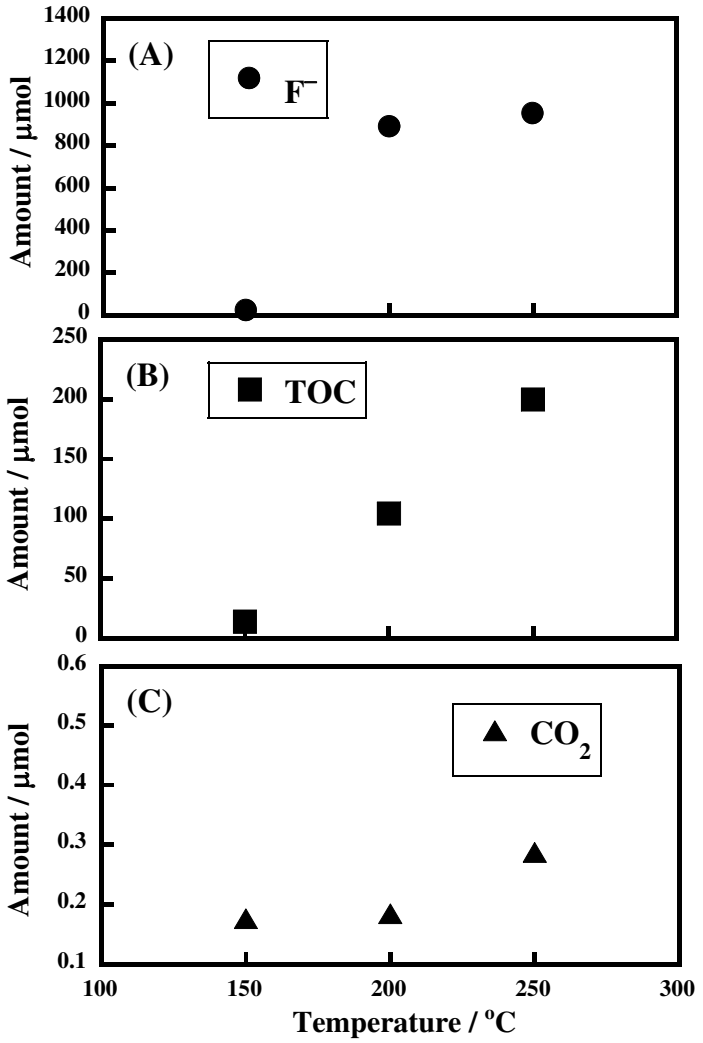


Figure 8. Temperature dependence of poly(VDF-*co*-HPF) copolymer decomposition in the presence of O_2: (A) the F^- amount in the reaction solution, (B) the TOC amount in the reaction solution, and (C) the CO_2 amount in the gas phase. The reaction conditions were the same as those described in the caption of Figure 7, except that O_2 was used instead of Ar.

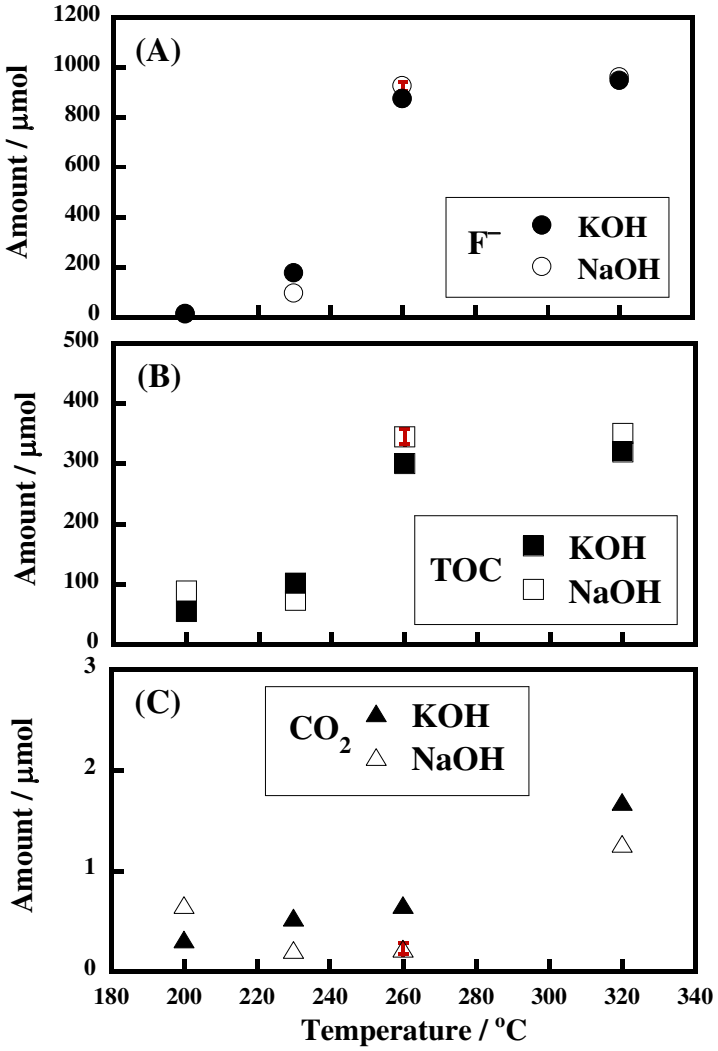


Figure 9. ETFE reactions using KOH or NaOH in a bigger autoclave (96 mL): Effect of temperature on (A) the F^- amount in the reaction solution, (B) the TOC amount in the reaction solution, and (C) the CO_2 amount in the gas phase. ETFE (30 mg) was reacted in the presence of 1.0 M of [KOH] or [NaOH] in superheated water under Ar for 6 h. Error bars for the reaction using NaOH at 260°C were obtained from two replicate experiments under the same reaction conditions.

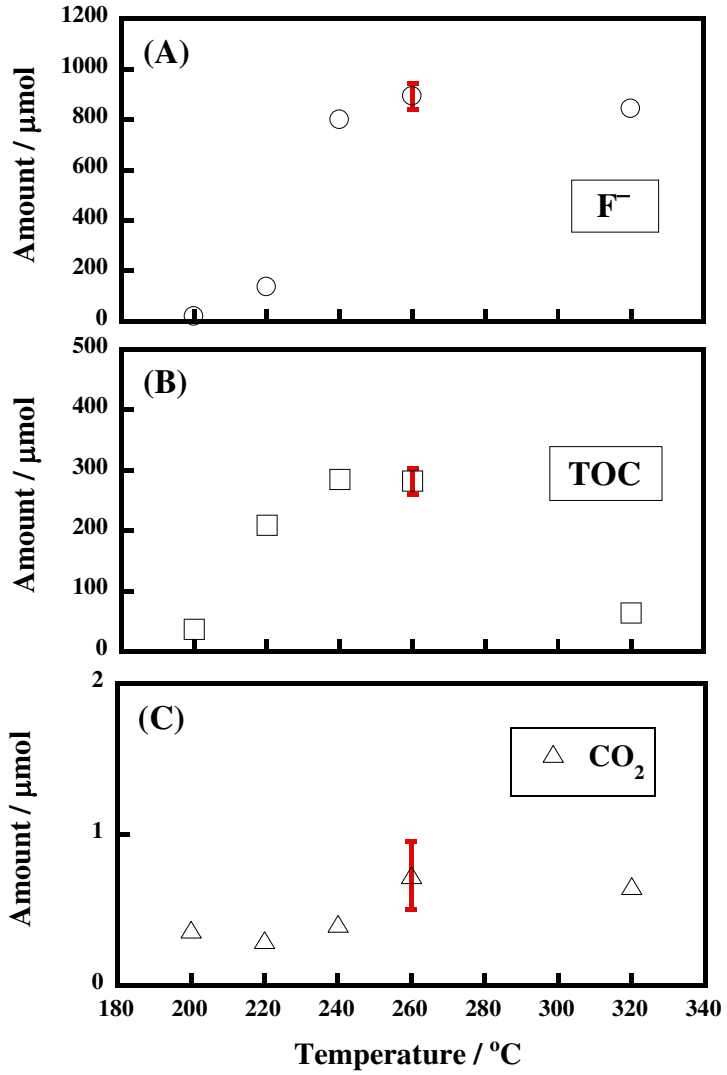


Figure 10. Temperature dependence of ETFE decomposition using NaOH in the presence of O_2: (A) the F^- amount in the reaction solution, (B) the TOC amount in the reaction solution, and (C) the CO_2 amount in the gas phase. The reaction conditions were the same as those described in the caption of Figure 9 (NaOH), except that O_2 was used instead of Ar. Error bars at 260 °C were obtained from two replicate experiments under the same reaction conditions.

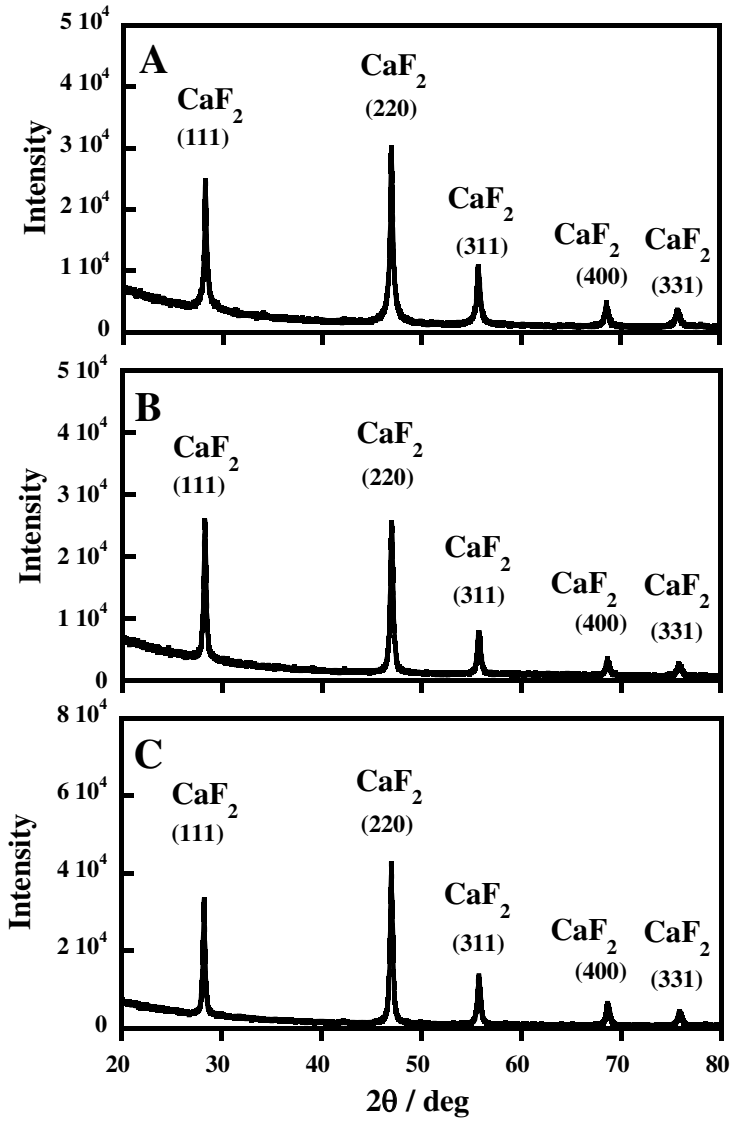
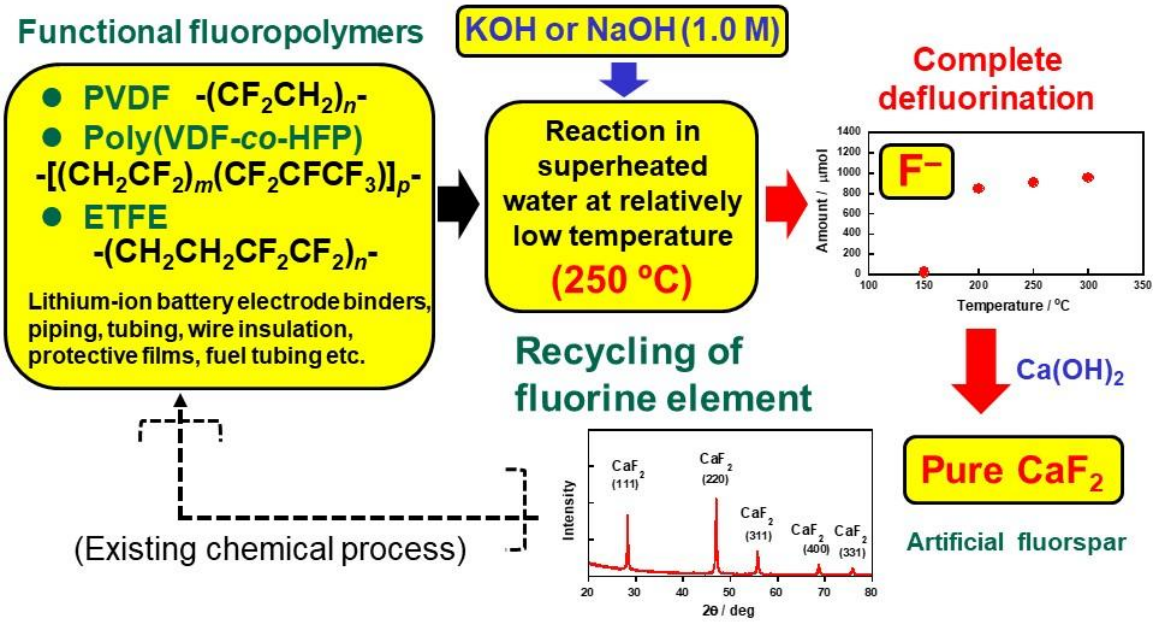


Figure 11. XRD patterns of the artificial fluorspar obtained from (A) PVDF, (B) poly(VDF-*co*-HFP) copolymer, and (C) ETFE. $Ca(OH)_2$ was added to the reaction solution from superheated water treatment, and the formed precipitate was washed with aqueous HCl and pure water, and dried.

Table of Contents (TOC)/Abstract graphic



Supporting Information

Efficient Mineralization of Poly(vinylidene fluoride), Poly (vinylidene fluoride-*co*-hexafluoropropylene) Copolymer and Poly(ethylene-*co*-tetrafluoroethylene) Copolymer Using Superheated Water with Alkaline Reagent

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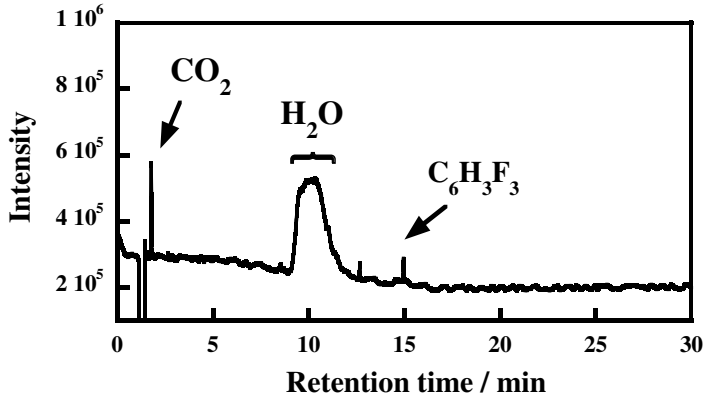

Figure S-1. Total-ion current chromatogram of the collected gas. PVDF (30 mg) was reacted in the presence of 1.0 M of [KOH] in superheated water under Ar at 250 °C for 6 h. After cooling, the gas phase was collected in a sample bag and subjected to the GC/MS measurement. A large hump around 9−12 min is ascribed from water in the gas sample.

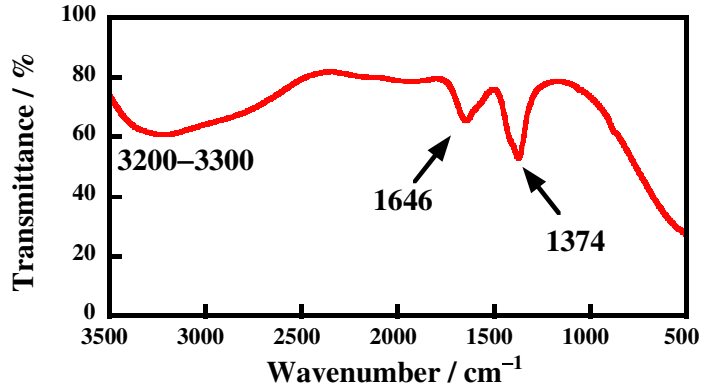

Figure S-2. ATR-IR spectrum of the resulting solution. PVDF (30 mg) was reacted in the presence of 1.0 M of [KOH] in superheated water under Ar at 250 °C for 6 h. The reaction solution was dried with nitrogen flow on the ATR cell, and then the spectrum was recorded.

Table S-1. Products from Superheated Water Treatment of ETFE at 260 °C [a]

Entry	Alkaline reagent [Conc.(M)]	Coexisting gas	*P* (MPa)	F^- (μmol) [yield (%)]	TOC (μmol) [ratio (%)]	CO_2 (μmol) [yield (%)]
1	KOH	Ar	5.7	874 [94]	301 [32]	0.7 [0]
2	NaOH	Ar	5.1	925±19 [b] [100±2]	345±13 [b] [36±1]	0.2±0.1 [b] [0]
3	NaOH	O_2	5.3	893±50 [b] [97±5]	282±22 [b] [30±2]	0.7±0.2 [b] [0]

[a] Internal volume of the autoclave, 96 mL; charged ETFE weight, 30 mg; solution volume, 30 mL; reaction time, 6 h.
[b] Obtained from two replicate experiments under the same reaction conditions.