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Radiation-Induced Radical Polyaddition of Bis(α-trifluoromethyl-β,β-difluorovinyl) Terephthalate with Excess of Various Ethers

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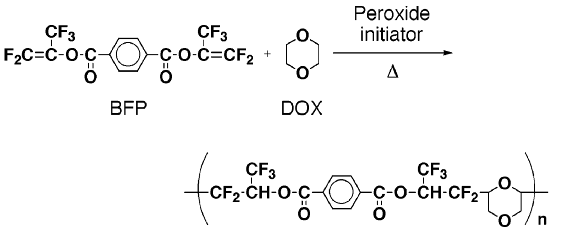
ABSTRACT: Radiation-induced radical polyaddition of bis(α-trifluoromethyl-β,β-difluorovinyl) terephthalate $[CF_2{=}C(CF_3)OCOC_6H_4COOC(CF_3){=}CF_2]$ (BFP) in the presence of an excess of cyclic and acyclic ethers in feed was examined at 0 °C using γ-ray irradiation. Irradiation of BFP with an 8-fold excess of 1,4-dioxane (DOX) and diethyl ether (EE) gave monomodal polymers consisting of the alternating unit of BFP and DOX moieties (poly(BFP-*alt*-DOX), $\bar{M}_{\mathrm{n,as-prepared}} = 5.1 \times 10^3$) and of BFP and EE (poly(BFP-*alt*-EE), $\bar{M}_{\mathrm{n,as-prepared}} = 3.9 \times 10^3$), respectively. The irradiation of BFP with an 8-fold excess of tetrahydrofuran or tetrahydropyran provided only 1:2 addition products in high yields. Monofunctional 2-benzoxypentafluoropropene $[CF_2{=}C(CF_3)OCOC_6H_5]$ (BPFP) as a model compound showed preferential formation of the 2:1 adduct to the 1:1 adduct with DOX and EE. The kinetic analysis of the model reactions revealed that the rate constants for the formation of the 2:1 adducts (k_d) of BPFP with DOX and EE were 2 orders of magnitude higher than those of the 1:1 adducts (k_m). Poly(BFP-*alt*-DOX) showed higher radiation resistance than poly(BFP-*alt*-EE) in solid state as well as in solution. It was concluded that radiation-induced step-growth polymerization under the stoichiometric imbalance of the two compounds requires a high k_d/k_m value as well as high radiation resistance for the formation of high molecular weight polymers.

1. Introduction

Fluorinated polymers exhibit high thermal stability, excellent chemical resistance, and high hydrophobicity compared to hydrocarbon analogues.[1,2] Trends in the synthesis of fluorinated vinyl polymers have recently shifted to the polymerization of fluorinated vinyl monomers bearing other functional groups[3] since functional fluorinated polymers are important for the development of fuel cell membranes[4−6] and fluorine-containing F_2 laser (157 nm) resist materials for the photolithography of semiconductor fabrication.[7−10] It is well-known that most fluorinated vinyl monomers scarcely afford corresponding homopolymers except tetrafluoroethylene and chlorotrifluoroethylene due to the electronic effect of a fluorine atom.[11−13] Polyaddition reactions proceeding in a step-growth reaction manner should be a very useful candidate for syntheses of fluorinated polymers bearing various functional groups in polymer main chains.[14] A bifunctional fluorinated vinyl compound, bis(α-trifluoromethyl-β,β-difluorovinyl) terephthalate $[CF_2{=}C(CF_3)OCOC_6H_4COO{-}C(CF_3){=}CF_2]$ (BFP), was reported to give polyaddition polymers with 1,4-dioxane (DOX) under radical condition as shown in eq 1 though BFP showed very low homopolymerization reactivity.[15,16]



(1)

The radiation-induced polyaddition of BFP with DOX at 40 °C under γ-ray irradiation was investigated where radical species would continuously be provided during a whole course of reaction.[17] The reaction provides polymers of higher molecular weights with higher thermal stability than those obtained by peroxide-induced polyaddition. The radical polyaddition with peroxide initiator might be disturbed by the decomposition products of peroxide.[18] The polymerization might be accompanied by cross-linking reaction between the obtained polymers under higher radiation doses to produce polymers of higher molecular weight distributions. This paper concerns the radiation-induced radical polyaddition of BFP with various cyclic and acyclic ethers such as DOX, diethyl ether (EE), diisopropyl ether (IPE), tetrahydrofuran (THF), and tetrahydropyran (THP) at the lower temperature to obtain monomodal fluorinated polymers without discernible side reactions since molecular motion would be suppressed

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compared to that at 40 °C. The radiation-induced reaction of monofunctional 2-benzoxypentafluoropropene [$CF_2{=}C(CF_3)OCOC_6H_5$] (BPFP) with the ethers was examined as a model reaction to elucidate the reaction mechanism of polyaddition, since the presence of excess amount of ethers was necessary for the formation of linear polymers. Kinetic analyses of the model reactions were carried out by the FACSIMILE programs which would solve ordinary differential equations, chemical reactions, and boundary conditions.[19]

2. Experimental Section

All experiments related to addition and polyaddition reactions were carried out under a purified nitrogen atmosphere in order to preclude oxygen and moisture.

Materials. Benzoyl chloride, terephthaloyl chloride, EE, IPE, and THP were purchased from Wako Pure Chemical Industries Co., Ltd., and used as received. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) supplied by Central Grass Co. was dried by refluxing over calcium hydride and distilled under a nitrogen atmosphere. THF and DOX were dried by refluxing over sodium wires with benzophenone and then distilled under a nitrogen atmosphere just before use. Butyllithium in hexane (1.6 M) was purchased from Kanto Chemical Industries Co., Ltd., and used after determination of concentration by alkalimetry. BPFP was synthesized by the reaction of benzoyl chloride with lithium enolate derived from HFIP with 2 equiv of butyllithium in THF described in the literature.[20,21] BFP was synthesized by the modified method of BPFP reported elsewhere.[15] Poly(methyl methacrylate) (PMMA) (Aldrich Chemical Industry Co., Inc.; $\bar{M}_w$ 1.5 × 10^4) and poly(carbonate) (PC) (Aldrich; $\bar{M}_w$ 6.4 × 10^4) were purified by reprecipitation from dichloromethane solution (5 wt %) to a large excess amount of methanol and then dried in vacuo.

Measurements. Gas chromatographic (GC) measurement was carried out with a Shimadzu GC-1700 AF equipped with flame ionization detector by using a DB-1 silica capillary column (30 m × 0.25 mm, film thickness: 0.25 μm, J&W Scientific). The column temperature with a heating rate 10 °C min^{-1} from 100 to 280 °C was employed. The mass spectrum (MS) was measured by the electron impact method (EIMS) and chemical ionization method (CIMS) on a Shimadzu QP-5000/GC-17A/CI-50. Methane was used as a reagent of chemical ionization. Size exclusion chromatography (SEC) was measured with a TOSOH HLC-802A apparatus at 40 °C with a Shodex KF 805L (×2) column using THF as an eluent at a flow rate of 1.0 mL min^{-1}, and the refractive index was monitored on a TOSOH RI-6 detector. The molecular weight of polymerization product was measured by SEC and calculated from the calibration curve with polystyrene standards. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL GSX270W FT-NMR spectrometer at 270 MHz for ^1H, 68 MHz for ^{13}C, and 254 MHz for ^{19}F NMR using deuterated chloroform ($CDCl_3$) as a solvent. ^{13}C and ^{19}F NMR spectra were measured under proton decoupling conditions. The infrared spectrum was obtained on JASCO FT/IR-5300. Thermal gravimetric analysis (TGA) was performed with a Rigaku Thermo Plus TG 8120 under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

General Procedure for Radiation-Induced Reactions of BFP with Ethers. γ-Ray irradiation was carried out using a ^{60}Co gamma pond facility of no. 6 cell at the Japan Atomic Energy Research Institute (JAERI, Takasaki). The radiation-induced reaction was carried out by adding BFP with ether in molar ratios of 1:4, 1:8, 1:16, and 1:32 in a glass ampule which was carefully flame-dried. The glass ampule was cooled, degassed, sealed off, and irradiated by γ-rays from a ^{60}Co source with a dose rate of 10 kGy h^{-1} at 0 °C. After a definite time the concentration of BFP was determined with GC by means of dodecane as an external standard. The obtained polymer was precipitated with a large amount of ethanol at dry ice temperature and then dried thoroughly in vacuo. The molecular weight of polymer was determined by SEC. The structure of the resulting reaction product was confirmed with mass spectrum and ^1H, ^{13}C, and ^{19}F NMR measurements.

Characterization of Irradiation Products of BFP. Poly(BFP-*alt*-EE). γ-Ray irradiation of BFP with an 8-fold excess of EE was carried out as described in the general procedure to give poly(BFP-*alt*-EE) as a white polymeric powder. The data of the obtained polymer are as follows. ^1H NMR ($CDCl_3$, 270 MHz, ppm): δ 1.02−1.35 (br, 6H, CH_3), 3.94 (br, 2H, $-CF_2CH(CH_3)O-$), 6.07 (br, 2H, $-OCH(CF_3)CF_2-$), 8.23 (br, 4H, C_6H_4). ^{13}C NMR ($CDCl_3$, 68 MHz, ppm): δ 10.2−15.1 (m, CH_3), 66.4−68.1 (m, $-OCH(CF_3)CF_2-$), 70.4−74.6 (m, $-CF_2CH(CH_3)O-$), 117.8 (t, J = 264 Hz, CF_2), 121.5 (q, J = 282 Hz, CF_3), 130.6 (s, C_6H_4), 132.7 (s, C_6H_4), 162.6 (m, $C{=}O$). ^{19}F NMR ($CDCl_3/CFCl_3$, 254 MHz, ppm): δ −71.9 to −72.6 (d, J = 85.4 Hz, 6F, $-OCH(CF_3)-$), −122 to −114 (br, 4F, $-CF_2-$). IR (KBr, cm^{-1}): 725, 872, 903, 1022, 1099, 1175, 1262, 1321, 1377, 1757, and 2986. SEC: $\bar{M}_{n,fractn} = 4.6 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.2$.

The structures of other products obtained by the irradiation of BFP with an 8-fold excess of DOX, THF, and THP were similar to those obtained by the corresponding reactions in a presence of a peroxide initiator, as previously reported.[15]

General Procedure for Radiation-Induced Reactions of BPFP with Ethers. A mixture of BPFP with a 32-fold excess of ether was introduced in a glass ampule which was carefully flame-dried. The glass ampule was cooled, degassed, sealed off, and irradiated by γ-ray irradiation from a ^{60}Co source with a dose rate of 10 kGy h^{-1} at 0 °C. After a definite time the concentrations of BPFP and reaction products were determined with GC by means of dodecane as an external standard. The structure of the resulting reaction product was confirmed with mass spectrum and ^1H, ^{13}C, and ^{19}F NMR.

The structures of other products obtained by the irradiation of BPFP with a 32-fold excess of DOX, EE, THF, and THP were the same as those obtained by the corresponding reactions in the presence of a peroxide initiator as previously reported.[15−17,22,23]

Electron-Beam Irradiation of Polymers. Poly(BFP-*alt*-DOX) ($M_{n,fractn} = 1.06 \times 10^4$) and poly(BFP-*alt*-EE) ($M_{n,fractn} = 7.9 \times 10^3$) were used along with commercial polymers such as PMMA and PC for comparison. Fine powder (ca. 100 mg) was charged into a hollow glass plate with 10 mm in diameter and 1 mm in depth. The sample which was covered with Kapton film (12 μm thickness) and placed on the water-cooled copper metal plate was irradiated with an electron beam (EB) of 1 MeV and 1 mA (0.345 kGy s^{-1}) in the atmosphere using a cascade-type electron accelerator (Dynamitron) facility of no. 2 cell at JAERI, Takasaki. M_n value and 5% weight loss temperature (T_{d5}) of irradiated polymers were evaluated by the SEC and TGA, respectively.

3. Results and Discussion

3.1. Radiation-Induced Polyaddition of BFP with DOX.

The reaction induced by γ-ray irradiation on the mixture of BFP with DOX was monitored directly by SEC to clarify the real polyaddition reaction system. SEC measurement of the system was carried out just after the reaction without any treatment. Figure 1 shows the SEC profiles of as-prepared poly(BFP-*alt*-DOX) obtained by the irradiation of BFP with an 8-fold excess of DOX at 0 °C. A low molecular weight oligomer peak is observed along with the peak assignable to BFP at the elution volume of 19.5 mL under the irradiation dose of 250 kGy. The peak assignable to BFP is decreased with increase of irradiation doses and disappears completely with a dose of 3000 kGy. The clear peak shift from oligomer to higher molecular weight regions is observed with the increase of irradiation doses implying that the polymerization takes place by stepwise reactions. No discernible shoulder at the higher molecular weight regions is observed with doses up to 3000 kGy. The radiation-induced polyaddition of BFP with DOX at 0 °C takes place to give polymers with unimodal molecular weight distribution without the

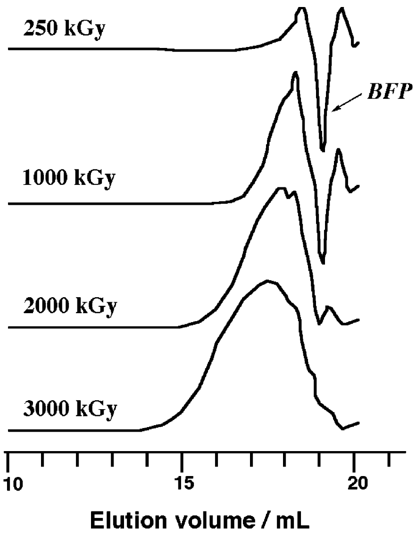


Figure 1. SEC of as-prepared polyaddition products of BFP with DOX at $[DOX]_0/[BFP]_0 = 8$ at 0 °C.

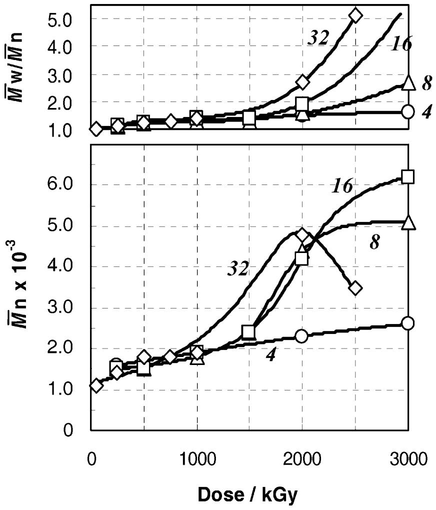


Figure 2. Irradiation dose dependence of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of as-prepared polyaddition products of BFP with DOX at $[DOX]_0/[BFP]_0 = 4$ (○), 8 (△), 16 (□), and 32 (◇).

Table 1. Radiation-Induced Polyaddition of BFP with DOX

molar ratio $[DOX]_0/[BFP]_0$	temp (°C)	dose (kGy)	conv[a] (%)	$\bar{M}_n$[b] ($\times10^3$)	$\bar{M}_w/\bar{M}_n$[b]
8	40	1500	88	2.8	1.7
16	40	1000	91	2.5	1.6
32	40	750	100	2.9	1.9
8	0	3000	92	5.1	2.7
16	0	2000	81	4.2	1.9
32	0	2000	96	4.8	2.7

[a] Conversion of BFG measured by GC. [b] The molecular weight of as-prepared poly(BFP-*alt*-DOX) was determined by SEC.

cross-linking reaction between produced polymer molecules.

$\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of polymers obtained by γ-ray irradiation of BFP with 4-, 8-, 16-, and 32-fold excess of DOX were plotted as a function of doses in Figure 2. Table 1 summarizes the highest $\bar{M}_n$ of the monomodal polymers at each molar ratio. The irradiation of BFP with an 8-fold excess of DOX at 0 °C with a dose of 3000 kGy gives monomodal polymers of $\bar{M}_n$ of 5.1×10^3 ($\bar{M}_w/\bar{M}_n = 2.7$). With further irradiation the shoulder peak at higher molecular weight region appeared in the SEC profile, and $\bar{M}_w/\bar{M}_n$ becomes more than 3.0, indicating that the cross-linking reaction of the obtained polymers took place along with the stepwise polyaddition. The irradiation of BFP with a 16- and 32-fold excess of DOX gave monomodal polymers with the highest $\bar{M}_n$ of 4.2×10^3 ($\bar{M}_w/\bar{M}_n = 1.9$) and 4.8×10^3 ($\bar{M}_w/\bar{M}_n = 2.7$) with a dose of 2000 kGy, respectively. Then, a polymer showing $\bar{M}_w/\bar{M}_n$ values lower than 3.0 might be considered to be a monomodal molecular weight distribution with no discernible shoulder peak at higher molecular weight regions in the SEC profile.

The irradiation of BFP with an 8-, 16-, and 32-fold excess of DOX at 40 °C has been reported to give poly(BFP-*alt*-DOX) with a monomodal distribution of the $\bar{M}_n$ of 2.8×10^3 ($\bar{M}_w/\bar{M}_n = 1.7$), 2.5×10^3 ($\bar{M}_w/\bar{M}_n = 1.6$), and 2.9×10^3 ($\bar{M}_w/\bar{M}_n = 1.6$), respectively, as cited in Table 1.[18] The irradiation at a lower temperature provides monomodal polymers with higher molecular weight. The high radiation resistance of poly(BFP-*alt*-DOX) enables to apply higher doses for the polyaddition system at a lower temperature. Higher irradiation doses are usually required at a lower temperature to yield higher molecular weight polymers. Most polymers are, however, suspected to be decomposed or cross-linked with doses of more than 100 kGy.[24,25]

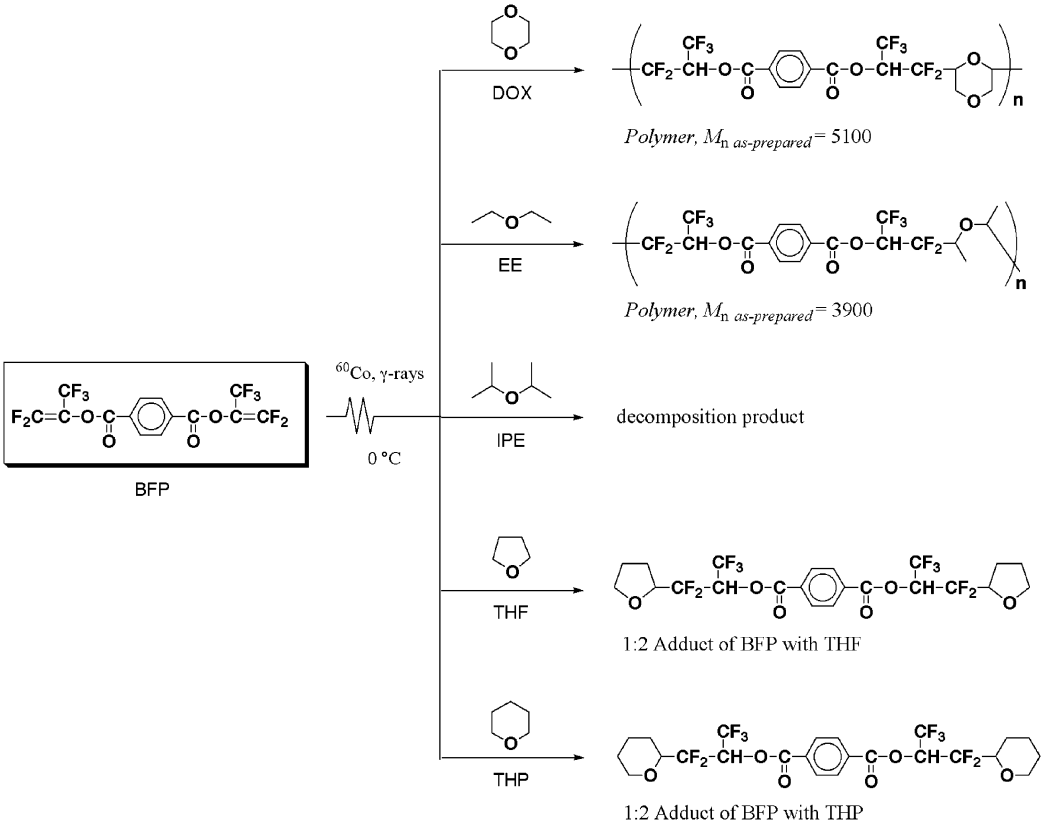
3.2. Detailed Study on Radiation-Induced Polyaddition at a Lower Temperature. The radiation-induced polyaddition of BFP with ethers was examined in the same manner as DOX (Scheme 1). Figure 3 shows the SEC profiles of as-prepared poly(BFP-*alt*-EE) obtained by the polyaddition of BFP with an 8-fold excess of EE at 0 °C. Low molecular weight oligomer peaks are observed along with the BFP peak with a dose of 250 kGy, and the oligomer peaks clearly shift to higher molecular weight regions with increase of the irradiation doses. The BFP peak completely disappears at a dose of 1000 kGy. The polymerization takes place with stepwise reactions in the same manner as the case of DOX. A shoulder peak at higher molecular weight regions which should result from the cross-linking reaction of polymers is scarcely observed with 1000 kGy and slightly appears with 1500 kGy.

$\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(BFP-*alt*-EE) obtained by the irradiation of BFP with a 4-, 8-, 16-, and 32-fold excess of EE were plotted as a function of the doses in Figure 4. As summarized in Table 2, the irradiation of BFP with a 4- and 8-fold excess of EE leads to a monomodal poly(BFP-*alt*-EE) of $\bar{M}_n = 3.7 \times 10^3$ and 3.9×10^3 with doses of 1500 and 1000 kGy, respectively. $\bar{M}_n$ of polymers decreased to 2.9×10^3 and 2.4×10^3, respectively, when the feed ratio of EE increases to 16- and 32-fold excess.

No peaks appeared in the region of oligomers in SEC when BFP was irradiated in the presence of an 8-fold excess of IPE with irradiation doses ranging from 500 to 3000 kGy. As mentioned in the latter section, neither the 1:1 nor 1:2 addition product was observed by the reaction of BPFP with IPE. It was likely that IPE was preferentially degraded with the irradiation, probably because the addition reaction of α-isopropyl radical on a β-carbon of the perfluoroisopropenyl group scarcely took place due to the steric repulsion of the bulky substituents.[26]

BFP was quantitatively consumed with a dose of 60 kGy in the reaction of THF in 32-fold excess to give only 1:2 addition product, bis[1-(2-tetrahydrofuranyl)-1,1,3,3,3-pentafluoroisopropyl] terephthalate [$(C_4H_7O){-}CF_2CH(CF_3)OCOC_6H_4COOCH(CF_3)CF_2{-}(C_4H_7O)$]. The radical

Scheme 1. Reaction Profile of BFP with Various Ethers



addition of the α-carbon of THF took place at two β-carbons of BFP. The relative concentration of the 1:1 addition product, [1,1,3,3,3-pentafluoroisopropenyl 1-(2-tetrahydrofuranyl)-1,1,3,3,3-pentafluoroisopropyl] terephthalate, reached the maximum value of 49% with 10 kGy and then converted to the 1:2 addition product in a quantitative yield with a dose of 20 kGy. The accumulation of the 1:1 adduct as an intermediate at an early stage of the reaction indicated that stepwise reactions of BFP with two THF molecules took place to give the 1:2 adduct of BFP and THF as the final product.

The irradiation of BFP in the presence of a 32-fold excess of THP with a dose of 1000 kGy provided 1:2 addition product, bis[1-(2-tetrahydropyranyl)-1,1,3,3,3-pentafluoroisopropyl] terephthalate [$(C_5H_9O){-}CF_2CH(CF_3)OCOC_6H_4COOCH(CF_3)CF_2{-}(C_5H_9O)$], produced by the radical addition of β-carbons of BFP to α-positions of two THP molecules in a 57% yield. The accumulation of 1:1 addition product, [1,1,3,3,3-pentafluoroisopropenyl

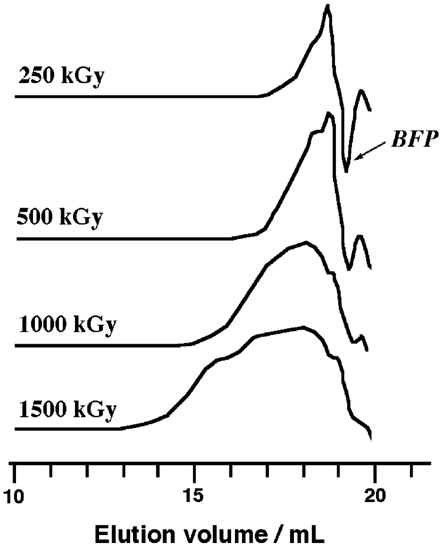


Figure 3. SEC of as-prepared polyaddition products of BFP with EE at $[EE]_0/[BFP]_0 = 8$ at 0 °C.

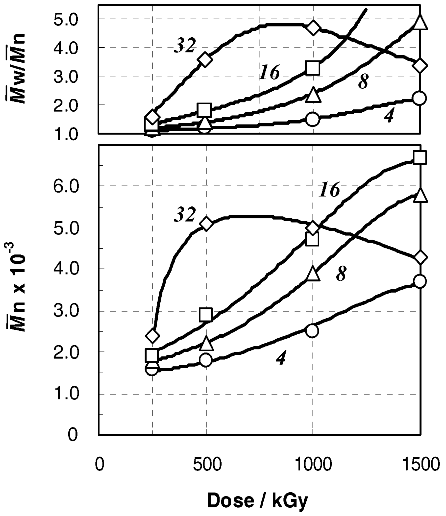


Figure 4. Irradiation dose dependence of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of as-prepared polyaddition products of BFP with EE at $[EE]_0/[BFP]_0 = 4$ (○), 8 (△), 16 (□), and 32 (◇).

Table 2. Radiation-Induced Polyaddition of BFP with EE

molar ratio $[EE]_0/[BFP]_0$	temp (°C)	dose (kGy)	conv[a] (%)	$\bar{M}_n$[b] ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$[b]
4	0	1500	100	3.7	2.2
8	0	1000	95	3.9	2.4
16	0	500	92	2.9	1.8
32	0	250	87	2.4	1.6

[a] Conversion of BFG measured by GC. [b] The molecular weight of as-prepared poly(BFP-*alt*-DOX) was determined by SEC.

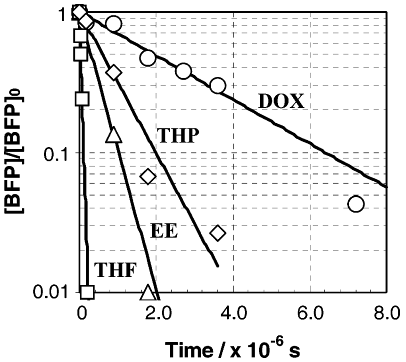


Figure 5. Relative reactivity of BFP with a 32-fold excess ethers at 0 °C.

1-(2-tetrahydropyranyl)-1,1,3,3,3-pentafluoroisopropyl] terephthalate, followed by a gradual decrease implies that the 1:2 adduct of BFP and THP was also formed by the stepwise reaction of BFP with two THP molecules. The maximum value of 47% of 1:1 adduct was obtained with a dose of 250 kGy. It is noteworthy that no polymer is obtained by the radiation-induced reactions of THP with BFP though THP possesses a similar six-membered ether ring structure to that of DOX which provides polymers with BFP under the same irradiation manner.

3.3. Reaction Kinetics for Polyaddition Reaction of BFP with Ethers. The reactivity of BFP with several ethers is found to show the great dependency on the structures of ethers. To get some information on the reaction systems of ethers, the dependency of BFP concentration on the irradiation doses was investigated to attribute to kinetic study. The results are shown in Figure 5.

The relative concentration of ethers and ether radicals which in consequence react with BFP can be assumed to be constant during the whole course of the reactions since the radiation-induced polyaddition was carried out using a 32-fold excess of ethers over BFP. The consumption of BFP proceeds under the pseudo-first-order rate law, as expressed in eq 2:

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{BFP}] = -k_i[\mathrm{BFP}] \qquad (2)$$

where k_i was the pseudo-first-order rate constant for the consumption of BFP. The integrated form of eq 2 is expressed in eq 3:

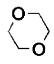
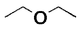
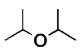
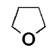
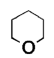
$$[\mathrm{BFP}]/[\mathrm{BFP}]_0 = 1 - \exp[-k_i(t - t_0)] \qquad (3)$$

where t_0 is the induction period. The rate constant was determined by the least-squares fitting of the experimental data for the relative concentration of BFP during the reactions using eq 3. All the rate constants for the reactions of BFP with each ether were optimized with a correlation coefficient, r^2, of larger than 98%.

The kinetic constants, k_i ($\times 10^6$ s^{-1}), of the reactions of BFP with DOX and EE which provide monomodal polymers with a higher $\bar{M}_n$ are 0.36 and 2.3, respectively, whereas k_i of the reactions of BFP with THF and THP which give only 1:2 addition products are 20 and 1.2, respectively, as shown in Table 3. It is obvious that the polymerizability of BFP with ethers is not related to the reactivity of the compounds. In the polymerizations of BFP with the excess of DOX and EE, the reactivity of EE is 6.4 times higher than that of DOX. The polymerization of BFP with the less reactive DOX gives higher molecular weight polymers though the polymerization requires higher irradiation doses. Side reactions such as cross-linking and scission are generally brought about with higher irradiation doses to reduce the molecular weights of obtained polymers at the late stage of polymerization. The radiation-induced polymerization of BFP with DOX gives, however, higher molecular weight polymers owing to the higher radiation resistance of the polymers.

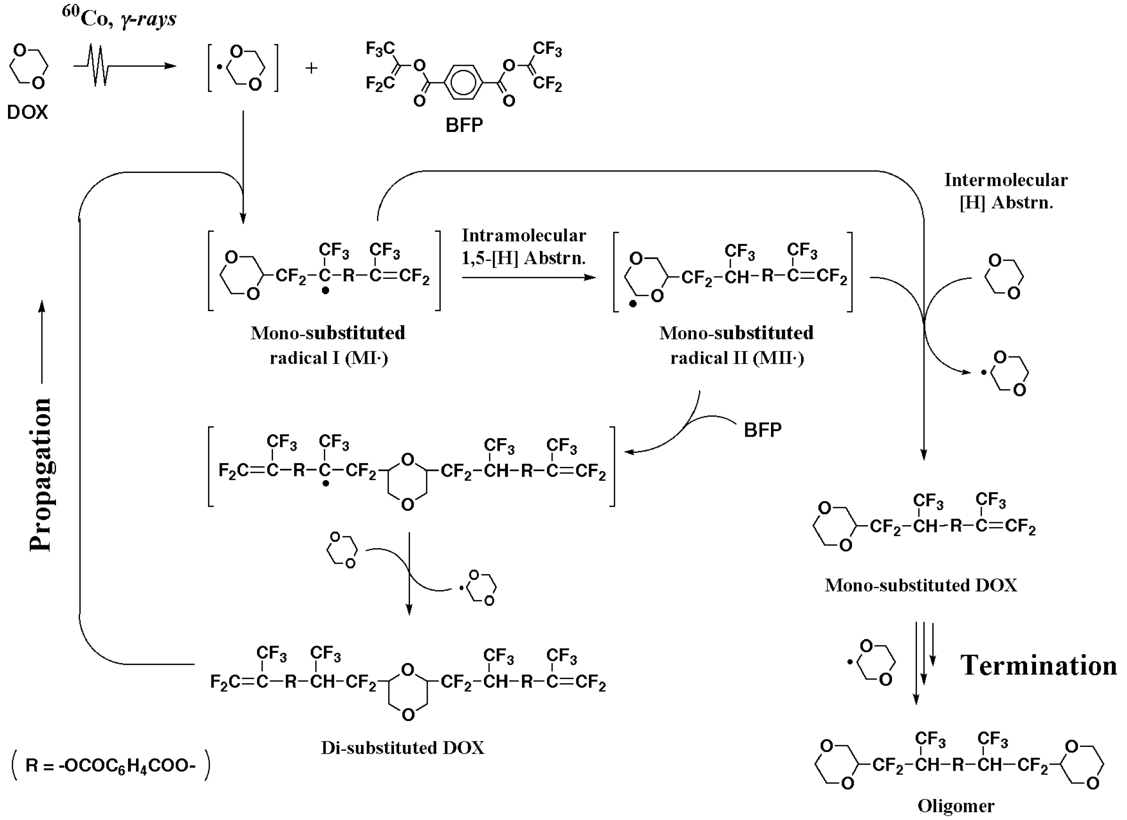
3.4. Kinetics Analysis of Model Reactions of Polymerizations. In a usual step-growth polymerization system, the stoichiometric balance of two compounds, i.e., the equivalent functional groups, is an important factor for achieving a high degree of polymerization.[27−32] The presence of excess amount of ethers such as DOX and EE is found to be needed for the formation of soluble polymers. The postulated mechanism of the radiation-induced polyaddition of BFP in the presence of excess amount of DOX is depicted in Scheme 2.[18] The key step for propagation of the polymerization is such that a monosubstituted intermediate radical II, MII$^\bullet$, produced by the first-step addition of DOX to BFP followed by intramolecular 1,5-hydrogen abstraction, reacts promptly with the second BFP

Table 3. Parameters for Radiation-Induced Polyaddition of BFP with Ethers

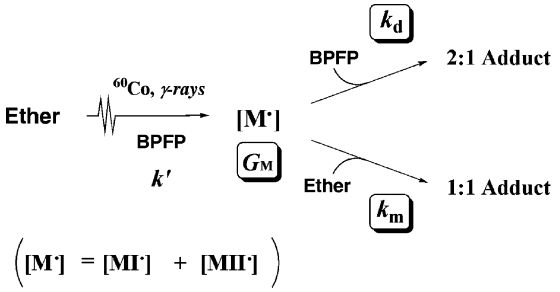
Ether	Product	Reactivity k_i of BFP (x 10^6 s^{-1})	G_M-value^a	k_m (M^{-1} s^{-1})^a	k_d (M^{-1} s^{-1})^a	Selectivity k_d/k_m
	Polymer, $\bar{M}_n = 5.1\times10^3$	0.36	1.7	2.6 x 10^7	3.1 x 10^9	120
	Polymer, $\bar{M}_n = 3.9\times10^3$	2.3	3.1	1.6 x 10^7	7.1 x 10^9	450
	decomposition	-	-	-	-	-
	1:2 Adduct	20	-	-	0	0
	1:2 Adduct	1.2	-	-	0	0

^{a} Simulated results using FACSIMILE program.

Scheme 2. Postulated Radiation-Induced Polyaddition Mechanism of BFP with DOX under Irradiation[18]



Scheme 3. Radical Reaction Flow of BPFP with Ether



molecule for the propagation. If the reaction does not take place preferentially, the excess of DOX molecules should be successively incorporated into BFP molecules to form oligomers containing monosubstituted DOX at both ends of the polymer. The kinetic constants for the first and second addition reactions may not be determined analytically because the radiation-induced polyaddition of BFP with an excess of ethers is supposed to involve many reaction paths and intermediates. The reactivity of two equivalent reaction sites at the α-carbon of ethers should, however, be evaluated with the kinetic constants for the first and second addition reactions of monofunctional BPFP since the reactivity of the β-carbon of BFP should be the same as that of BPFP. The kinetic constant ratios of the first and second addition reactions of BFP with ethers can then be estimated by the rate constant ratio of the second addition reaction (k_d) over the first one (k_m) in the radiation-induced reaction of BPFP with ethers.

Figure 6 shows the plots of the relative concentration of BPFP and the products in the reaction of BPFP with a 32-fold excess of DOX, EE, THF, and THP at 0 °C. The concentrations of ethers and ether radicals can be assumed to be constant during the whole course of the reactions, owing to the usage of a 32-fold excess of ethers over BPFP. The reaction of BPFP with DOX is found to exhibit the preferential formation of 2:1 adduct to 1:1 adduct. Similar results are obtained in the reaction of BPFP with EE. The reactions of BPFP with THF and THP which give no polymeric products by the irradiation with BFP give only 1:1 addition products. The irradiation of BPFP with IPE gave neither a mono- nor disubstituted product, and degradation products of IPE were observed in the GC/MS results. These results qualitatively show that the preferential formation of the 2:1 adduct to the 1:1 adduct in the model reactions because of larger value of k_d over k_m should be a practical measure for observing to what extent the polyaddition of BFP in the presence of an excess of ethers proceeds to give linear polymers, where a monosubstituted intermediate radical II, MII$^\bullet$, promptly reacts with the second BFP molecule.

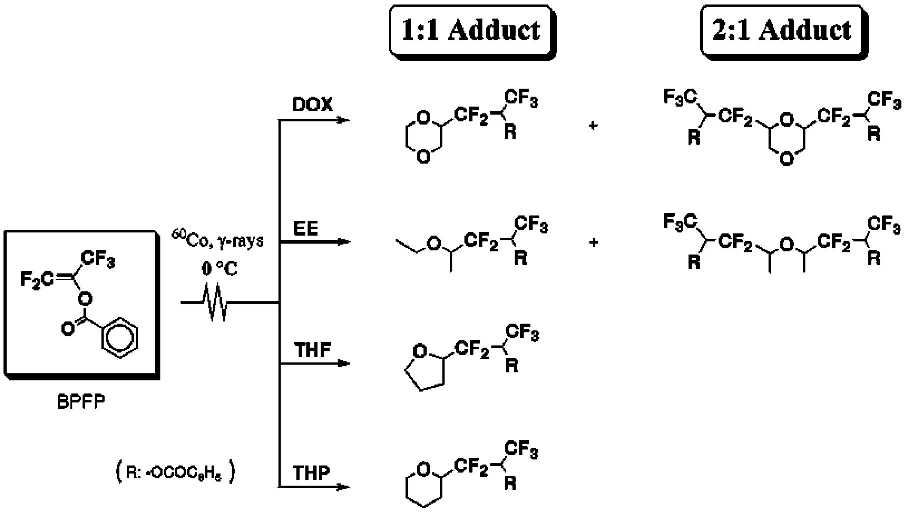
The model reaction of BPFP with ethers for the polyaddition can be simplified as shown in Scheme 3. The reaction rates of BPFP with ethers are given by the following equations:

$$\frac{d}{dt}[M^\bullet] = k'[\text{ether}][\text{BPFP}] \tag{4}$$

$$\frac{d}{dt}[\text{2:1 adduct}] = k_d[M^\bullet][\text{BPFP}] \tag{5}$$

$$\frac{d}{dt}[\text{1:1 adduct}] = k_m[M^\bullet][\text{ether}] \tag{6}$$

where $[M^\bullet]$ is the sum of the concentrations of monosubstituted ether radical I and II, $[MI^\bullet] + [MII^\bullet]$; the G_M value is defined as the number of $[M^\bullet]$ molecules formed per 100 eV absorbed;[33] k', k_d, and k_m are rate



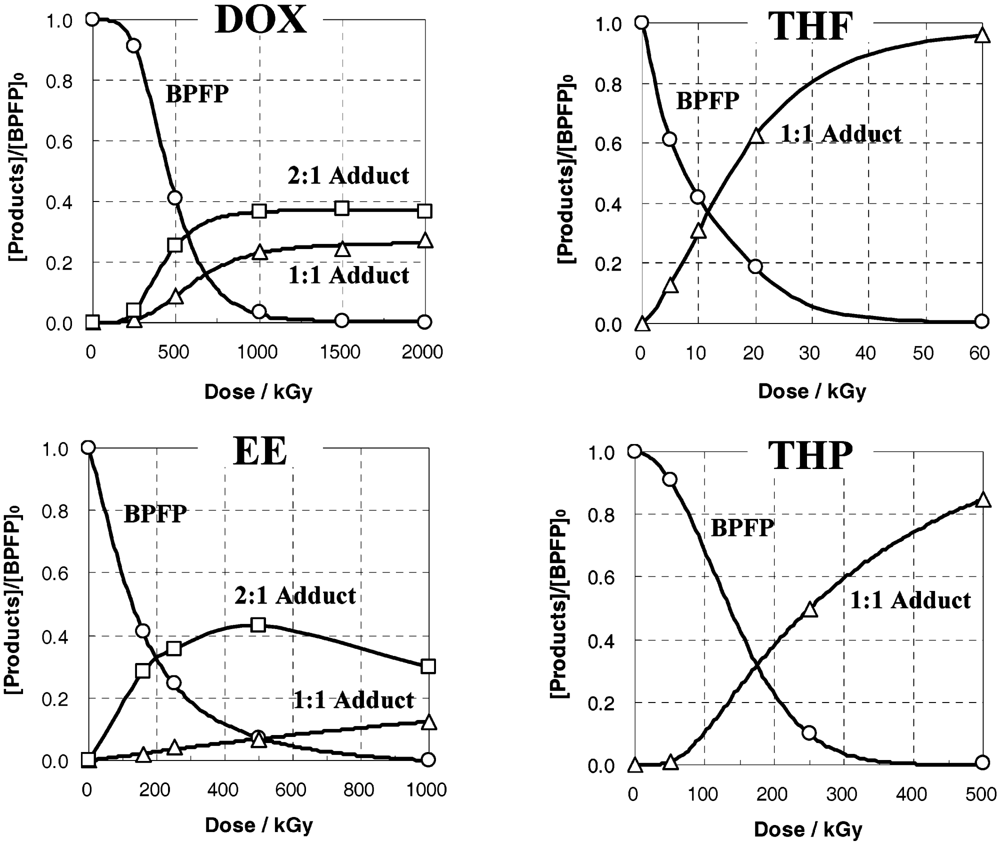


Figure 6. Relationship between dose and relative concentration in the reaction of BPFP with ethers at 0 °C: BPFP (○), 1:1 adduct (△), and 2:1 adduct (□).

constants (M^{-1} s^{-1}) for the formation of [M•], the 1:1 adduct, and 2:1 adduct, respectively. The kinetic constants k', k_d, and k_m can be estimated from the change of the relative concentrations of BPFP, 1:1 adduct, and 2:1 adduct as a function of the irradiation time with γ-rays shown in Figure 6. Equation 7 is derived from eq 4 using the G_M value and ρ as parameters:

$$\frac{d}{dt}[M^\bullet] = G_M\rho \tag{7}$$

$$\rho = \frac{2.78\ (J\cdot kg^{-1}\cdot s^{-1})}{6.02\times10^{23}\ (mol^{-1})\cdot 1.60\times10^{-19}\ (J)\cdot 100} = 2.78\times10^{-7}$$

where ρ is the conversion factor of the G_M value, 2.78 is an equivalent of the absorbed dose rate 10 kGy h^{-1} (J kg^{-1} s^{-1}), 6.02×10^{23} is Avogadro's number (mol^{-1}), and 1.60×10^{-19} is an equivalent of 1 eV (J).

The parameters of the G_M value and kinetic constants (k_d and k_m) of eqs 5−7 were optimized by fitting the experimental data of the relative concentrations of BPFP, 1:1 adduct, and 2:1 adduct vs the irradiation time using FACSIMILE programs in the reaction system with DOX.[19] As shown in Figure 7A, the change of the relative concentrations of 1:1 adduct and 2:1 adduct against the irradiation time can be reproduced by eqs 5 and 6 with G_M value = 1.7, $k_d = 3.1 \times 10^9$ M^{-1} s^{-1}, and $k_m = 2.6 \times 10^7$ M^{-1} s^{-1}, respectively. The change

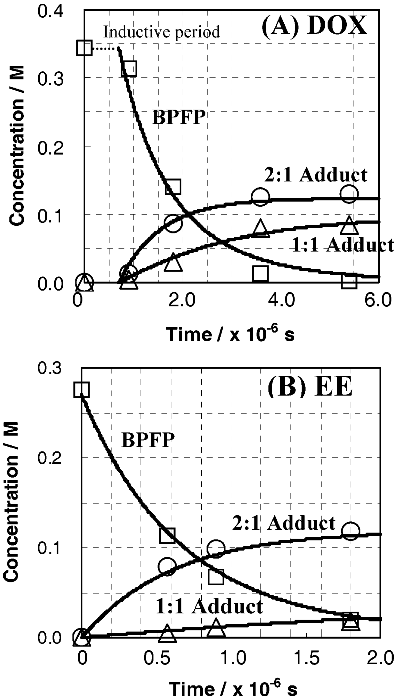
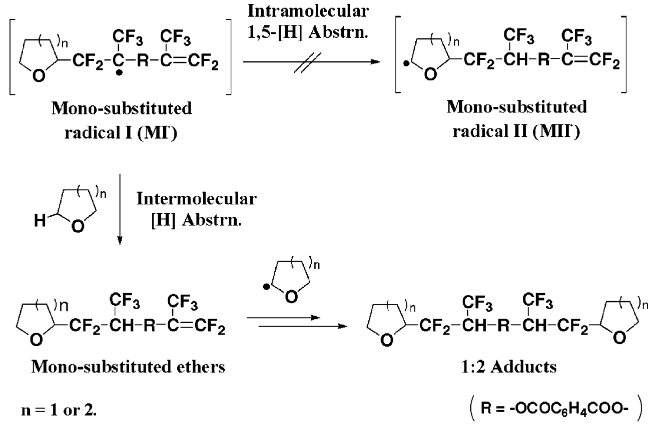


Figure 7. Concentration of the BPFP (□), 1:1 adduct (△), and 2:1 adduct (○) plotted against an irradiation time of γ-rays along with the simulation results using FACSIMILE programs.

of the relative concentrations of BPFP, 1:1 adduct, and 2:1 adduct to the irradiation time can be fitted by eqs 5 and 6 with the G_{M} value = 3.1, $k_{\mathrm{d}} = 7.1 \times 10^{9}$ M^{-1} s^{-1}, and $k_{\mathrm{m}} = 1.6 \times 10^{7}$ M^{-1} s^{-1}, respectively, in the reaction system with EE (Figure 7B).

Table 3 also shows the calculated results of the $k_{\mathrm{d}}/k_{\mathrm{m}}$ values on the reactions of BPFP with DOX and EE along with the optimized values of the parameters. The $k_{\mathrm{d}}/k_{\mathrm{m}}$ values for the reaction of BPFP with DOX and EE are 120 and 450, respectively. The 2 orders of magnitude higher rate constants are needed for the preferential formation of the 2:1 addition product and indicate the formation of a main chain bearing BFP moieties at both ends in the whole course of the reaction with DOX and EE might be demonstrated despite the usage of an excess of ethers in feed.

Scheme 4. Addition Reaction Profiles of BFP with THF and THP



The structure of the polymer main chain formed by the polyaddition of BFP with DOX was assigned to 2- and 6-disubstituted DOX, as shown in eq 1.[18,22] The molecular structure indicates that the $\mathrm{MI}^{\bullet}_{\mathrm{DOX}}$ radical at the α-position of BFP moiety which generates at the first addition of BFP to DOX abstracts the hydrogen at the other α-position of the DOX moiety by an intramolecular 1,5-hydrogen abstraction which takes place through six-membered ring transition state to yield the $\mathrm{MII}^{\bullet}_{\mathrm{DOX}}$ radical, as shown in Scheme 2.[34−38] On the other hand, the quantitative formation of 1:1 adducts of BPFP with THP and THF indicates that the free radical at the α-position of BFP moiety, $\mathrm{MI}^{\bullet}_{\mathrm{THP}}$ and $\mathrm{MI}^{\bullet}_{\mathrm{THF}}$ produced by the first additions of BFP to THP and THF, is unable to abstract the hydrogen at the other α-positions of THP and THF. This is probably because the rigid ring structures of THP and THF moieties hardly allow the conformational profit for the intramolecular 1,5-hydrogen abstraction through a six-membered ring transition state. The initially formed free radicals, $\mathrm{MI}^{\bullet}_{\mathrm{THP}}$ and $\mathrm{MI}^{\bullet}_{\mathrm{THF}}$, then, abstract the hydrogens from other THP and THF molecules via intermolecular radical transfer to give the 1:2 adducts as the final products (Scheme 4). Another possible route for generating monosubstituted radicals $\mathrm{MII}^{\bullet}_{\mathrm{THP}}$ and $\mathrm{MII}^{\bullet}_{\mathrm{THF}}$ are the hydrogen abstraction of THP and THF radicals from the 1:1 adduct. However, the probability of the reaction route must be negligible because the hydrogen abstraction of the radicals from the 1:1 adduct must be slower than the addition reactions to BPFP. At the end of the reactions, the THP and THF radicals can abstract the hydrogen radicals from the 1:1 adduct because the concentration of BPFP has decreased. However, the obtained monosubstituted ether radicals cannot react with BPFP, which has already been consumed; then, the monosubstituted ether radicals must transform reversely to the original 1:1 adduct. These considerations were supported by the fact that the relative concentration of the 1:1 adduct did not decrease with increasing irradiation doses, as shown in Figure 6.

A higher $k_{\mathrm{d}}/k_{\mathrm{m}}$ value is necessary for the propagation of the polyaddition reaction to yield high molecular weight polymers. The $k_{\mathrm{d}}/k_{\mathrm{m}}$ of the reaction of BPFP with EE is higher than that with DOX system though the polymerization of BFP with DOX gives the higher $\bar{M}_{\mathrm{n}}$ of polymers than those with EE. The discrepancy is well elucidated by the observation on the different stability of 2:1 adducts of BPFP with EE and that with DOX, as shown in Figure 6. The relative yield of 2:1 adducts of BPFP with EE shows a gradual decrease with an irradiation dose of 500 kGy and above while the relative yield of 2:1 adducts of BPFP with DOX shows almost no change in the irradiation doses in the ranges between 1000 and 2000 kGy. The different stability of the 2:1 product indicates that poly(BFP-*alt*-EE) should be less stable than poly(BFP-*alt*-DOX) against the γ-ray irradiation.

It is obvious that the radiation-induced step-growth polymerization under the stoichiometric imbalance of two compounds requires a high rate constant ratio of $k_{\mathrm{d}}/k_{\mathrm{m}}$ and high radiation resistance of the obtained polymers.

3.5. Radiation Resistance. The polyaddition of BFP and DOX proceeds without remarkable cross-linking, and the scission of the polymer main chains in the corresponding ether solution to give poly(BFP-*alt*-DOX) of $\bar{M}_{\mathrm{n,as-prepared}} = 5.1 \times 10^{3}$ with a dose of 3000 kGy though most polymers is subjected to some damage by γ-rays and electron-beam (EB) irradiation at a dose of over 100 kGy.[24,25] Evaluation of the radiation resistance of poly(BFP-*alt*-DOX) and poly(BFP-*alt*-EE) in solid

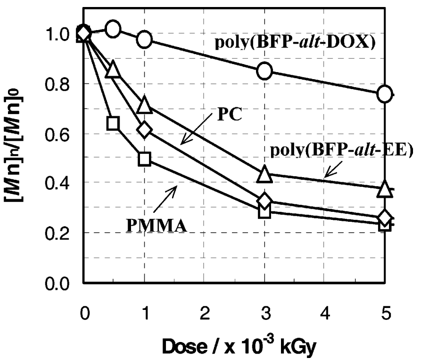


Figure 8. Normalized $\bar{M}_n$ of poly(BFP-*alt*-DOX), poly(BFP-*alt*-EE), PMMA, and PC vs exposure doses of EB at 1 MeV.

states was carried out by using EB irradiation. Radiation resistance of commercial polymers such as PMMA and PC were also evaluated by the same method for comparison. The $\bar{M}_n$ value and the temperature at which each polymer loses its weight of 5% (T_{d5}) after EB radiolysis were monitored with SEC and TGA, respectively.

Figure 8 shows the changes in the normalized $\bar{M}_n$ of the polymers which was defined as the observed $\bar{M}_n$ divided by the $\bar{M}_n$ of initial polymers, ($[\bar{M}_n]_n/[\bar{M}_n]_0$), with irradiation doses up to 5000 kGy. As was expected from the literature,[33,39] the normalized $\bar{M}_n$ of PMMA and PC which are typical degradation polymers decrease to 0.23 and 0.26 with a dose of 5000 kGy, respectively. Poly(BFP-*alt*-DOX) is, on the other hand, quite stable because of normalized $\bar{M}_n$ to be 0.76 at 5000 kGy irradiation. Poly(BFP-*alt*-EE) shows a similar normalized $\bar{M}_n$ to those of PMMA and PC to be 0.38 with a dose of 5000 kGy.

Thermal stability of the polymers after EB irradiation was also evaluated by the normalized T_{d5} value of the polymers which was defined as the observed T_{d5} divided by the T_{d5} of initial polymers. The normalized T_{d5} value of poly(BFP-*alt*-DOX) showed a higher value of 0.84 with 10 MGy than that of poly(BFP-*alt*-EE) to be 0.66, PMMA: 0.66 and PC: 0.75, respectively. Poly(BFP-*alt*-DOX) containing cyclic structures in polymer main chain could maintain better thermal stability against EB irradiation than poly(BFP-*alt*-EE) containing acyclic ether structure similar to those of PMMA and PC. It was proved that poly(BFP-*alt*-DOX) has higher radiation resistance in solid states as well as in solution than poly(BFP-*alt*-EE) and typical degradation polymers such as PMMA and PC.

4. Conclusion

Radiation-induced radical polyaddition of BFP in the presence of an excess of cyclic and acyclic ethers in feed was examined at 0 °C using γ-ray irradiation. The reaction proceeded without a remarkable side reaction to give monomodal polymers, poly(BFP-*alt*-DOX), with $\bar{M}_n$ of 5.1×10^3 when BFP was irradiated with an 8-fold excess of DOX at a dose of 3000 kGy. The irradiation of BFP with an 8-fold excess of EE at a dose of 1000 kGy gave monomodal polymers, poly(BFP-*alt*-EE), with $\bar{M}_n$ of 3.9×10^3. The irradiation of BFP with an 8-fold excess of both THF and THP provided only 1:2 adducts in quantitative yields. Monofunctional BPFP yielded preferential formation of the 2:1 adduct to the 1:1 adduct only with DOX and EE where the ratio of rate constants for the formation of the 2:1 adducts, k_d, and the 1:1 adducts, k_m, were 120 and 450, respectively, investigated as model reactions. A 2 order of magnitude higher k_d than k_m indicated that the addition reaction of ethereal radicals at the polymer chain ends produced by the addition of ethereal radicals to perfluoroisopropenyl groups followed by the intramolecular hydrogen abstraction takes place with another BFP preferentially compared to intermolecular radical transfer with excess ethers. Then the propagation reaction of the intermediate compound bearing BFP moieties at both ends of the molecule takes place even in the circumstance of the excess amount of ethers to give polymers such as poly(BFP-*alt*-DOX) and poly(BFP-*alt*-EE). The polymerization of BFP with DOX, which has lower reactivity and a lower rate constant ratio of k_d/k_m compared to those of EE, provided higher molecular weight polymers. Poly(BFP-*alt*-DOX) showed higher radiation resistance than poly(BFP-*alt*-EE) in solid states as well as in solution. It is obvious that radiation-induced step-growth polymerization requires a high rate constant ratio of k_d/k_m as well as high radiation resistance to form high molecular weight polymers.

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