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Radical polyaddition reaction of bis(α -trifluoromethyl- β , β -difluorovinyl) 2,3,5,6-tetrafluoroterephthalate

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Abstract

To develop the radical polyaddition of bisperfluoroisopropenyl esters to preparation of polymers bearing higher fluorine content, the polyaddition reactivity of bis(α -trifluoromethyl- β , β -difluorovinyl) 2,3,5,6-tetrafluoroterephthalate [CF₂=C(CF₃)OCOC₆F₄COOC(CF₃)=CF₂] (TFT) with 1,4-dioxane (DOX) and diethoxydimethylsilane (DEOMS) were described. The results of the model reactions of 2-pentafluorobenzoxypentafluoropropene [CF₂=C(CF₃)OCOC₆F₅] (PFBP) with THF, DOX and DEOMS showed that the reactions took place almost quantitatively and the main products were mono-addition compound for THF and di-addition compounds for DOX and DEOMS, respectively. The polyaddition of TFT with DOX or DEOMS yielded corresponding polymers of about 1×10^4 as a molecular weight bearing unimodal molecular weight distribution by the initiation of peroxides such as benzoyl peroxide and di-*tert*-butyl peroxide. TFT showed the slightly higher reactivity compared to that of non-fluorinated analogue, bis(α -trifluoromethyl- β , β -difluorovinyl) terephthalate (BFP), by the results of ternary polyaddition of TFT/BFP/DOX system. Polymers bearing TFT moiety showed the higher thermostability and contact angle. (C) 2003 Elsevier B.V. All rights reserved.

 $\label{eq:keywords:Bis} \textit{Keywords:} Bis(\alpha-trifluoromethyl-\beta,\beta-difluorovinyl) 2,3,5,6-tetrafluoroterephthalate; Fluoropolymer; Heteroatom-containing polymers; Polyaddition; Radical polymerization$

1. Introduction

As has been reported previously, the radical polyaddi tion of bis(α -trifluoromethyl- β , β -difluorovinyl) terephthalate [CF₂=C(CF₃)OCOC₆H₄COOC(CF₃)=CF₂] (BFP) with 1,4dioxane (DOX) yields polymers, as shown in Eq. (1) [1]; which suggests that a wide variety of organic compounds possessing carbon-hydrogen bonds might be incorporated into polymer main chains. The 2,5-diaddition on DOX development of radical addition reaction of perfluoroisopropenyl group ($CF_2=C(CF_3)-$) with the organic compounds possessing carbon-hydrogen bonds enables to prepare a wide variety of fluorinated polymers from the compounds which have never been supposed as starting materials for preparation of polymers. The reaction has been developed to preparation of polymers with 1,2-dimethoxyethane [3], diformylalkane [4], triethylamine [5] and dialkoxydialkylsilanes [6].

$$CF_{2}=C-O-C-C-C-C=CF_{2} + \bigcirc O \xrightarrow{BPO} \cdots \xrightarrow{CF_{3}} CF_{3} \xrightarrow{CF_{3}} O \xrightarrow{CF_{$$

was demonstrated by X-ray crystallographic analysis of the reaction product of 2-benzoxypentafluoropropene $[CF_2=C(CF_3)OCOC_6H_5]$ (BPFP) with DOX [2]. The

In this report, the preparation of polymers by radical polyaddition of $bis(\alpha$ -trifluoromethyl- β , β -difluorovinyl) 2,3,5,6-tetrafluoroterephthalate [CF₂=C(CF₃)OCOC₆F₄-COOC(CF₃)=CF₂] (TFT) with DOX and diethoxydimethyl-silane (DEOMS) is discussed in order to obtain polymers of higher fluorine content compared to those from BFP with

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Table 1	
Radical addition reaction of PFBP	

Ether	Conversion ^a (%)	Addition product ^a (%)		
		1:1	1:2	
THF	100	98	2	
DOX	81	24	76	
DEOMS	80	32	68	

PFBP: 4.9 mmol; ether: 39.0 mmol; BPO: 0.98 mmol; reaction temperature: 80 $^\circ$ C; reaction time: 3 days.

^a Conversion of PFBP measured by GC.

DOX and DEOMS since the results of detailed study on the high reactivity of DOX [1] and DEOMS [6] has previously been reported. The reactivity difference between TFT and BFP was also examined by the ternary polyaddition of TFT, BFP and DOX. Prior to the polyaddition of TFT, the radical addition of 2-pentafluorobenzoxypentafluoropropene [CF₂=C(CF₃)OCOC₆F₅] (PFBP) with THF, DOX and DEOMS was examined as model reactions in order to confirm that the addition reaction may be applicable to preparation of polymers and to find out the proper polyaddition reaction conditions. The comparison of reactivity of PFBP and non-fluorinated analogue, BPFP, was also studied.

2. Results and discussion

2.1. Addition reaction

In order to clarify the radical addition reactivity of monofunctional compound, the reactions of PFBP with THF, DOX and DEOMS in the presence of BPO were examined. The results are summarized in Table 1. The addition reactions take place almost quantitatively and the higher yields of diaddition products of DOX and DEOMS are demonstrated. The detailed analytical results of the products are described in Section 4. It turns out that THF performs as a monofunctional, and DOX and DEOMS work as bifunctional compounds. As has been reported that the addition of BPFP onto DOX takes place at 2- and 6-positions of DOX [2], the reactions are concluded to proceed by Eqs. (2)–(4):



Fig. 1. Time dependency on the yields of mono-addition (a) and diaddition products (b) of PFBP with DOX.

The information on the yields of di-addition product is essential to develop the radical addition for preparation of polymers. The reaction of PFBP with DOX was analyzed by the relative area ratios of GC peaks assigned to mono- and di-addition products. The results are shown in Fig. 1. The concentration of di-addition product increases rapidly with reaction time while the yield of mono-addition product scarcely increases. The reactivity of PFBP with DOX is concluded to be high enough to develop the reaction to polymer preparation.

The results of the comparison of the reactivity of PFBP to that of BPFP are depicted in Fig. 2, which shows that slightly higher reactivity of PFBP is pointed out.

2.2. Polyaddition reaction

The results of PFBP with DOX indicate that the radical addition is applicable to preparation of polymers by bifunctional TFT as a starting material. The results of polyaddition of TFT with DOX are shown in Table 2. The polyaddition takes place with the oxo-radical initiation as has been demonstrated in the polyaddition of BFP with DOX [1]. As expected from the results of the model reactions, oxo radicals derived from BPO and DTBP produce higher molecular weight polymers in fair yields. No high molecular weight polymer is yielded in the presence of AIBN though

$$CF_{2}=C-O-C_{6}F_{5} + O \xrightarrow{BPO} C_{6}F_{5}-C_{-}O-C_{H}-CF_{2} - O \xrightarrow{CF_{3}} O \xrightarrow{CF_{3}$$

$$CF_{3} \xrightarrow{CH_{3}} CF_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CF_{3} \xrightarrow{CH_{3}} CF_{$$

24% of TFT is consumed. The analyses of the reaction products were difficult because the products were hardly separated. The equimolar reaction of TFT with DOX produces no polymers of high molecular weights. The excess amount of DOX in feed is necessary to obtain higher conversions of TFT and higher yields of polymers of high molecular weights as has been demonstrated in the reaction system of BFP with DOX [1]. Polymer obtained was soluble in toluene, acetone, chloroform and ethyl acetate, and insoluble in methanol, ethanol and hexane.

The results of ¹H, ¹³C and ¹⁹F NMR measurements of the polymer obtained are illustrated in Fig. 3. TFT units and

3.6–4.4 ppm are assignable to protons of dioxane moiety in polymer chain. No peaks at -80.7 and -95.6 ppm assignable to CF_2 = of TFT are observed in Fig. 3(d), and the absorptions from -114 to -122 ppm assignable to fluoromethylene fluorines are observable. Other assignment of each peak is depicted in Fig. 3. The complicated splitting of the peaks might come from the presence of diastereomers of the addition products. This might be proved by the fact that the ¹³C NMR spectrum in Fig. 3(c) is similar to that of Fig. 3(b) which was measured under decoupled condition of fluorine resonance. The polyaddition, therefore, is concluded to takes place according to Eq. (5).

DOX units are observed in the characterization of the polymer. In ¹H NMR the peak around 6.2 ppm is assigned to the methine proton of the TFT moiety and the peaks at



Fig. 2. Reactivity comparison of PFBP (a) and BPFP (b) with DOX.

Table 2					
Radical	polvaddition	of	TFT	with	DOX

The results of the polyaddition of TFT with DEOMS are summarized in Table 3. The recovery of polymers was difficult since no proper solvent for reprecipitation was found out. Polymer obtained was soluble in toluene, acetone and ethyl acetate, and partially soluble in methanol, ethanol and hexane. Solubility of polymers might reflect higher contents of fluorines and alkylsilyl groups. Similar tendency of reactivity to the results of TFT with DOX is observed since polymers are produced with the initiation of oxo radicals derived from BPO and DTBP, and no high molecular weight polymers are obtained in the presence of AIBN in spite of the high conversion of TFT. At least four-fold excess amount of DEOMS in feed is necessary to obtain fairly high yields of polymers by the initiation of BPO. In the presence of DTBP eight-fold excess of DEOMS is needed for preparation of high molecular weight polymers. Longer reaction time is preferable to obtain suitable yields of polymers and molecular weights. Step-growth polymerization mechanism is

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Initiator	DOX/TFT (mol/mol)	Temperature (°C)	Conversion ^a (%)	$M_n^{b} \times 10^3$	$M_{\rm w}/M_{\rm n}^{\rm b}$	Yield ^c (%)	$M_n^d \times 10^3$	$M_{\rm w}/M_{\rm n}^{\rm d}$
BPO	1	80	31	3.4	1.3	0		
	2	80	82	2.5	1.6	44	3.0	1.5
	4	80	74	3.1	1.6	63	3.3	1.7
	8	80	95	2.8	2.3	22	4.7	1.7
DTBP	1	120	82	2.9	1.6	0		
	2	120	96	2.2	2.2	20	2.8	2.2
	4	120	100	3.6	5.8	22	8.6	3.3
	8	120	100	2.4	4.0	22	3.9	4.2
AIBN	8	60	24			0		

TFT: 4.0 mmol; initiator: 0.8 mmol; reaction time: 7 days.

^a Conversion of TFT measured by GC.

^b Before reprecipitation.

^c Reprecipitated with CH₃OH.

^d After reprecipitation.



Fig. 3. ${}^{1}H$ (a), ${}^{13}C$ { ${}^{1}H$, ${}^{19}F(-85 \text{ ppm})$ } (b), ${}^{13}C$ { ${}^{1}H$ (5 ppm)} (c) and ${}^{19}F$ NMR { ${}^{1}H$ (5 ppm)} (d) of the reaction product of TFT with DOX.

Table 3 Radical polyaddition of TFT with DEOMS

Initiator	mmol	DEOMS/TFT (mol/mol)	Temperature(°C)	Time (days)	Conversion ^a (%)	$M_{\rm n}^{\rm b} \times 10^3$	$M_{\rm w}/M_{\rm n}^{\rm b}$	Yield ^c (%)	$M_{\rm n}^{\rm d} \times 10^3$	$M_{\rm w}/M_{\rm n}^{\rm d}$
BPO	0.8	1	80	7	82	2.4	1.4	7	2.7	1.4
	0.8	4	80	7	74	3.1	1.6	63	3.3	1.7
	0.8	8	80	7	95	3.3	1.8	22	4.6	1.6
DTBP	0.8	1	120	7	100	3.0	3.3	11	7.7	2.2
	0.8	4	120	7	31	3.4	1.3	0		
	0.8	8	120	0.5	42			0		
	0.8	8	120	1	81	3.2	1.1	0		
	0.8	8	120	2	99	4.7	3.5	10	8.6	2.9
	0.8	8	120	3	98	4.2	2.7	20	7.6	2.2
	0.8	8	120	7	97	4.1	2.8	23	6.1	2.2
	0.8	8	120	14	99	4.7	2.6	23	5.6	2.2
	0.4	8	120	7	96	3.8	1.9	23	4.9	1.8
	1.6	8	120	7	97	3.8	2.8	22	6.3	2.4
AIBN	0.8	8	60	7	57			0		

TFT: 4.0 mmol.

^a Conversion of TFT measured by GC.

^b Before reprecipitation.

^c Reprecipitated with CH₃OH (5% H₂O).

^d After reprecipitation.

suggested since the molecular weights tends to increase with the reaction time.

The results of NMR measurements of the polymer obtained are illustrated in Fig. 4. In ¹H NMR (Fig. 4(a)) the peak around 6.2 ppm is assigned to the methine proton of the TFT moiety and the absorptions assignable

to the methyl protons bound to silicone atom appear at 0.1-0.3 ppm. The peaks assignable to the methine proton of ethylsilyl group in the main chain appear at 4.1-4.4 ppm. Other assignment of each peak is depicted in Fig. 4. The polyaddition, therefore, is concluded to takes place by Eq. (6):



Table 4

Ternary polyaddition	of TFT/BFP/DOX and	TFT/BFP/DEOMS
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Compound	mmol	Initiator ^a	mmol	Temperature (°C)	Yield (%)	$M_{ m n} imes 10^4$	$M_{\rm w}/M_{\rm n}$
DOX ^a	24	BPO	0.6	60	50	0.12	1.6
	24		1.2	60	91	0.43	3.2
24 24	24	DTBP	0.6	80	49	0.97	5.5
	24		1.2	80	61	1.05	3.7
DEOMS ^b	24	BPO	0.6	60	98	0.14	1.5
	12		1.2	60	46	0.21	2.7
	24		1.2	60	72	0.30	4.3
	48		1.2	60	75	0.40	3.8
	72		1.2	60	83	0.37	3.0
	24	DTBP	0.6	80	96	0.24	3.9
	24		1.2	80	107	0.74	8.5

TFT: 3.0 mmol; BFP: 3.0 mmol; time: 3 days.

^a Reprecipitated with CH₃OH.

^b Vacuum purified.

2.3. Ternary polyaddition reaction

As has been mentioned above the slightly higher reactivity of monofunctional PFBP is demonstrated compared to that of BPFP in Fig. 2. Ternary polyadditions of TFT, BFP and DOX or DEOMS would offer the information on the reactivity difference between TFT and BFP. The results are shown in Table 4. Polymers are produced under all the conditions examined here and the polymer of the highest molecular weight is about 1×10^4 . The higher yields of polymers might come from the lowered solubility of ternary polymers probably because fluorine contents are decreased.

The more detailed reactivity comparison between TFT and BFP was examined by the ternary polyaddition of TFT, BFP and DOX. The results are depicted in Fig. 5. The numbers on the abscissa indicate the mole fraction of TFT in feed, and those of ordinate show the mole fraction of TFT moiety in polymer. The reaction should be ceased under low conversions, preferably lower than 10%, since the decreases of starting materials scarcely affect kinetics of polymerization reaction. This method is often adopted in analyzing a copolymerization reactivity on the binary system of vinyl monomers. The compositions of TFT contents in polymers were calculated of the concentrations of TFT and BFP measured by GC (Fig. 5(a)) and the area ratios of NNE¹³C NMR measurement of carbonyl carbons (Fig. 5(b)) of the ternary polymers. The results show in good agreement. The slightly higher reactivity of TFT is concluded since the composition curves are above the diagonal line. The result agrees with that of the reaction between monofunctional compounds shown in Fig. 2. The monomer reactivity ratios of TFT (M_1) and BFP (M_2) are $r_1 = 1.19$,



Fig. 4. ¹H (a), ¹³C {¹H, ¹⁹F (-85 ppm)} (b), ¹³C {¹H (5 ppm)} (c) and ¹⁹F NMR {¹H (5 ppm)} (d) of the reaction product of TFT with DEOMS.



Fig. 4.. (Continued).



Fig. 5. Ternary polymer composition curves of TFT/BFP/DOX determined with GC (a) and 13 C NMR of oligomer (b) (see text).

Table 5				
Surface and	thermal	character	of	polymer

 $r_2 = 0.78$, respectively, calculated with Kelen–Tüdös method. It might then be concluded that the block-type polymer bearing slightly higher content of TFT moiety is yielded at the early stage of the ternary polymerization.

The results of surface and thermal character of polymers are summarized in Table 5. Thermogravimetric analysis of the polymers bearing TFT units shows that the 5% weightloss temperature is about 300 °C. Contact angle measurement of the polymer film prepared by spin-coating method results 100° for water and 30.5° for methanol as the highest values. These results indicate that the fluoroalkyl groups tend to be on the surface of the film of the air-side and dioxanyl or alkylsilyl groups may bind to the other side of the film since dioxanyl or alkylsilyl groups has a strong affinity for glass surface. The penetration of water droplet through the film was observed in the case of the ternary polymer of TFT/BFP/DOX. Detailed study on the surface of ternary polymers related to the phenomenon of water penetration is under way.

Polymer	Molecular weight	Film thickness (µm)	Contact angle	T_{d5}^{b} (°C)	
			H ₂ O	CH ₃ OH	
TFT/DOX	Low $M_{\rm w}$	9.9	96.0	12.0	190
TFT/DOX	High $M_{\rm w}$	12.0	96.4	10.0	300
TFT/DEOMS	Low M _w	6.7	99.6	30.5	225
TFT/DEOMS	High $M_{\rm w}$	6.5	100.0	26.0	300
TFT/BFP/DOX	High $M_{\rm w}$	12.1	90.6	22.8	302
TFT/BFP/DEOMS	High $M_{\rm w}$	14.4	92.3	28.6	294
BFP/DOX	High $M_{\rm w}$	3.3	92.0	9.6	275
BFP/DEOMS	High $M_{\rm w}$	6.8	100.0	21.6	275

^a Liquid drop method.

^b 5% weight-loss temperature.

3. Conclusion

The radical polyaddition of $bis(\alpha$ -trifluoromethyl- β , β difluorovinyl) 2,3,5,6-tetrafluoroterephthalate with 1,4dioxane and diethoxydimethylsilane produced successfully polymers of about 10⁴ as a molecular weight possessing higher fluorine contents. The slightly higher reactivity of fluorinated terephthalate is demonstrated compared to that of non-fluorinated analogue. The high thermostability and contact angle were proved.

4. Experimental

All experiments related to reaction and polymerization were carried out under a purified nitrogen atmosphere in order to preclude oxygen and moisture.

4.1. Reagent

BPFP was synthesized according to the method reported by Nakai and coworkers [7]. PFBP was synthesized by the reaction of pentafluorobenzoyl chloride with lithium enolate derived from 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) with 2 eq. of butyllithium in THF. Commercial benzoyl chloride and pentafluorobenzoyl chloride (64 °C/23 mmHg) were distilled under reduced pressure before use. Commercial butyllithium in hexane solution was used after determination of the concentration by alkalimetry. HFIP (Central Glass Co.) was dried by refluxing over calcium hydride and distilled under reduced pressure. TFT was synthesized by 2,3,5,6-tetrafluoroterephthaloyl chloride with 2 eq. of lithium enolate of HFIP according to the modified method of preparation of BFP [1] (yield: 65%, bp 75 °C/1 mmHg, mp 39–41 °C). Tetrafluoroterephthaloyl chloride (Showa Denko Co.) was used as received. TFT: ¹³C NMR [¹H {5 ppm}]: $\delta = 103.6 - 104.5$ (m, CF₂=C), 113.5 (s, C-CO), 119.3 (q, $J = 272.3 \text{ Hz} \text{ CF}_3$), 145.1 (d, $J = 266.0 \text{ Hz} \text{ C}_6\text{F}_4$), 156.0 (t, $J = 298.0 \text{ Hz CF}_2=$), 154 (s, COO). ¹⁹F NMR $[^{1}H \{5 \text{ ppm}\}]: \delta = -66.0 \text{ (3F, s, CF}_{3}), -80.7 \text{ (1F, s,}$ $CF_{2} = (cis)$, -95.6 (1F, s, $CF_{2} = (trans)$), -134.6 (4F, s, C₆**F**₄). MS (EI, m/z): 498 $[M]^+$, 479 $[M - F]^+$, 351 $[M - (CF_2 = C(CF_3)O -)]^+$, (CI, isobutane *m/z*): 499 $[M+1]^+$.

PFBP: ¹³C NMR [¹H {5 ppm}]: $\delta = 103.0-105.0$ (m, CF₂=C), 119.8 (qdd, J = 6.7, 8.6, 271.6 Hz CF₃), 155.5 (s, COO), 156.3 (qt, J = 3.0, 298.2 Hz CF₃)), 105.2 (td, J = 3.8, 14.4 Hz C₆F₅ (*i*)), 138.3 (qd, J = 12.0, 253.7 Hz C₆F₅ (*m*)), 145.1 (md, J = 264.3 Hz C₆F₅ (*o*)), 146.6 (md, J = 280.0 Hz C₆F₅ (*p*)). ¹⁹F NMR [¹H {5 ppm}]: $\delta = -66.1$ (3F, s, CF₃), -81.3 (1F, s, CF₂= (*cis*)), -90.1 (1F, s, CF₂= (*trans*)), -135.2 (2F, s, C₆F₅ (*o*)), -144.1 (1F, s, C₆F₅ (*p*)), -159.0 (2F, s, C₆F₅ (*m*)). MS (EI, *m/z*): 323 [*M* - F]⁺, 279 [CF₂=C(CF₃)O]⁺, 195 [C₆F₅CO-]⁺, (CI, isobutane *m/z*): 342 [*M*]⁺, 343 [*M* + 1]⁺. THF was purified by distillation under purified nitrogen atmosphere after being dried by refluxing with potassium benzophenone ketyl before use. DOX was dried by refluxing over calcium hydride and distilled under nitrogen atmosphere. DEOMS was donated by courtesy of Shin-Etsu Chemical Co. Benzoyl peroxide (BPO) was precipitated from chloroform and then recrystallized in methanol at 0 °C. Di-*tert*-butyl peroxide (DTBP) was used as received.

4.2. Addition reaction

The addition reaction of PFBP with ethers such as THF, DOX and DEOMS was carried out in sealed glass ampoule by adding PFBP (4.9 mmol, 1.0 ml), BPO (0.98 mmol) and ether compound (39.0 mmol) at 80 °C for 3 days. The reaction was ceased by bubbling oxygen and the concentration of PFBP was measured by vapor-phase chromatography (GC) by means of tridecane as an external standard. The reaction system was concentrated by removing lowboiling materials under reduced pressure, and the reaction products were roughly separated by the chromatography of silica gel 60 column with hexane: diethyl ether (20:1 to 5:1 v/v) as an eluent. The addition products were isolated by preparatory size exclusion chromatography (SEC). The products were analyzed by GC, mass-spectrum, and 1 H, 13 C and 19 F NMR.

Mono-addition product of PFBP with THF: ¹H NMR: $\delta = 1.93 - 2.05$ (2H, m, CH₂-CH₂-CH₂), 2.69-2.24 (2H, m, CH₂-CH₂-CH), 3.81-3.99 (2H, m, O-CH₂-CH₂), 4.18-4.34 (1H, m, O-CH-(CF₂)CH₂), 6.01-6.16 (1H, m, $CF_2 - CH - (CF_3)O$). ¹³C NMR [¹H {5 ppm}], ¹⁹F{-85 ppm}]: $\delta = 24.4$, 25.1 (s, CH₂-CH₂-CH₂), 25.5, 25.7 (s, CH₂-CH₂-CH), 67.9, 68.3 (s, CF₂-CH(CF₃)O), 69.8, 70.0 (s, O-CH₂-CH₂), 76.0 (s, O-CH-(CH₂)CF₂), 105.97, 106.06 (s, C₆F₅ (*i*)), 117.9 (s, CH-CF₂-CH), 118.85, 118.89 (s, CF₃), 137.8, 138.3 $(s, C_6F_5(m)), 144.0, 144.6 (s, C_6F_5(o)), 146.1 (s, C_6F_5(p)),$ 156.3, 157.0 (s, COO). ¹⁹F NMR [¹H {5 ppm}]: $\delta = -71.7$, -72.2 (3F, t, J = 10.0 Hz, CF₃), -118.4, -119.7, -122.8, -125.1 (2F, wq, J = 10.0, 264.9 Hz, CF₂), -136.7 (2F, s, $C_6F_5(o)$, -146.2, -146.5 (1F, t, J = 23.0 Hz, $C_6F_5(p)$), -160.1, -160.3 (2F, t, J = 3.0 Hz, $C_6 F_5(m)$). MS (EI, m/z): 395 $[M - F]^+$, 219 $[M - COC_6F_5]^+$, 195 $[C_6F_5CO]^+$, 167 $[C_6F_5]^+$, 71 $[C_4H_7O]^+$, (CI, isobutane m/z): 415 $[M+1]^+$ 195 $[C_6F_5CO]^+$.

Di-addition product of PFBP with DOX: ¹H NMR: $\delta = 3.55-3.78$, 3.80–4.04 (4H, m, O–CH₂–CH), 3.85–4.32 (2H, m, CF₂–CH–(CH₂)O), 6.16 (2H, br, CF₂–CH–(CF₃)O). ¹³C NMR [¹H {5 ppm}], ¹⁹F {–85 ppm}]: $\delta = 63.8$, 64.3 (s, O–CH₂–CH), 66.2, 66.8 (s, CF₂–CH(CF₃)O), 73.0, 74.9 (s, O–CH–(CH₂)CF₂), 105.97, 106.06 (s, C₆F₅ (*i*)), 116.6, 117.7 (m, CH–CF₂–CH), 122.0, 122.4 (m, CF₃), 1382, 138.9 (s, C₆F₅ (*m*)), 144.4, 145.1 (s, C₆F₅ (*o*)), 146.3 (s, C₆F₅ (*p*)), 156.7, 157.8, 158.2 (s, COO). ¹⁹F NMR [¹H {5 ppm}]: $\delta = -71.4to - 72.3$ (3F, m, CF₃), -115.7to - 120.2 (2F, m, CF₂), -136.1to - 136.7 (2F, m, C₆F₅ (*o*)), -145.1to - 145.5 (1F, m, C₆F₅ (*p*)), -159.4to - 159.8 (2F, m, C₆F₅ (*m*)). MS (EI, *m/z*): 769 [*M* - F]⁺, 195 [C₆F₅CO]⁺, 167 [C₆F₅]⁺.

Di-addition product of PFBP with DEOMS: ¹H NMR: $\delta = -0.01to0.31$ (6H, m, Si-CH₃), 1.11-1.29 (6H, m, CH-CH₃), 4.10-4.21 (2H, m, O-CH-(CF₂)CH₃), 4.15 (1H, br, O-CH-(CF₂)CH₂), 5.97 (1H, br, CF₂-CH-(CF₃)O). ¹³C NMR [¹H {5 ppm}], ¹⁹F {-85 ppm}]: $\delta = -2.5to0.7$ (m, Si-CH₃), 14.6-18.0 (m, CH-CH₃), 57.6 ~ 57.7 (m, CF₂-CH(CH₃)O), 66.9-69.0 (m, O-CH-(CF₃)CH₂), 105.5, 105.4 (s, C₆F₅ (*i*)), 118.0 (m, CF₃), 118.1-118.9 (m, CF₂), 138.1, (s, C₆F₅ (*m*)), 144.4, 144.6 (s, C₆F₅ (*o*)), 146.1 (s, C₆F₅ (*p*)), 156.7, 156.9 (s, COO). ¹⁹F NMR [¹H {5 ppm}]: $\delta = -72.3to - 74.0$ (3F, m, CF₃), -119.2to - 120.0, -122.2to - 123.6, -127.8to - 128.9 (2F, m, CF₂), -138.4 (2F, s, C₆F₅ (*o*)), -147.5, -147.7 (2F, t, J = 23.0 Hz, C₆F₅ (*m*)), -161.6, -161.8 (1F, t, J = 23.0 Hz, C₆F₅ (*m*)).

The polyaddition reaction was carried out by adding TFT, ether compound and BPO in sealed ampoule which was carefully flame dried. After a definite time, the reaction was ceased by bubbling oxygen and the concentration of TFT was measured with GC by means of tridecane as an external standard. The polymer was isolated by reprecipitation and then dried thoroughly in vacuo. The ternary polymerization of TFT/BFP/DOX was analyzed by the measurement of the concentrations of TFT and BFP by GC, and the area ratios of NNE ¹³C NMR measurement of carbonyl carbons [8], and ternary polymer composition curve was analyzed by Kelen–Tüdös method [9] to obtain monomer reactivity ratios. The molecular weight of the polymer was determined by SEC. The structure of the resulting reaction product was determined by ¹H, ¹³C and ¹⁹F NMR.

4.3. Measurements

¹H, ¹³C and ¹⁹F NMR spectra were recorded on a JEOL JNM-ECP500 Fourier transform NMR spectrometer at 500 MHz for ¹H {non-decoupled and [¹⁹F (irradiation offset: -85 ppm)]}, 125 MHz for ¹³C {[¹H (5 ppm)], [¹H (5 ppm)] and ¹⁹F (-85 ppm)]}, and 470 MHz for ¹⁹F [¹H (5 ppm)] NMR with deuterated chloroform as a solvent. Chemical shift of ¹⁹F NMR was determined on the basis of absolute magnetic field intensity. GC measurement was carried out with a Hewlett-Packard 6890 equipped with flame ionization detection with a DB-1, wide-bore fused silica capillary column (15 m × 0.53 mm, film thickness: 1.5 µm, J &

W). The column temperature was programmed from 100 to 300 °C at 20 °C min⁻¹. The mass spectra were measured on a JEOL JMS-SX102. Isobutane was used as a reagent gas of chemical ionization (CI) method. SEC was measured with a Tosoh HLC-802A apparatus at 40 °C with a Shodex KF802.5-KF801(\times 2) for low-molecular-weight compounds and a Shodex KF 805L (\times 2) for high-molecular-weight compounds with THF as an eluent (flow rate: 1.0 ml min^{-1}). The molecular weight measured by SEC was calculated from the calibration curve for standardized polystyrene. Preparatory SEC was carried out with an LC-908JAI (Japan Analytical Ind.) with Gel H1 & H2 column series with chloroform as an eluent at room temperature (flow rate: 3.8 ml min^{-1}). Thermogravimetric analysis was carried out with a TGA 51 thermogravimeter with a thermal analyst 2000 (TA Instruments) under nitrogen atmosphere with a heating rate of 10 °C min⁻¹. The contact angle was measured by a liquid drop method with CA-D (Kyowa Kaimen Kagaku Co.). Film thickness was measured by a Mitutoyo SURFTEST SV-600 and a Mitutoyo Auto Leveling Table SV-600.

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