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Novel fluorinated hybrid polymer preparation from silsesquioxanes by radical polyaddition

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Abstract

Radical polyaddition of $bis(\alpha$ -trifluoromethyl- β , β -difluorovinyl) terephthalate [CF₂=C(CF₃)OCOC₆H₄COOC(CF₃)=CF₂] (BFP) with silsesquioxanes was investigated in order to produce a polymer possessing silsesquioxane moiety in polymer main chain. 1,3,5,7,9,11,13,15-octakis(dimethylsilyloxy)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.17,13]octasiloxane (T₈S) with BFP successfully afforded a polymer bearing a molecular weight of about 2.5 × 10⁵. The polymer obtained were soluble in usual organic solvent such as methanol, tetrahydrofuran and chloroform. In order to get some information on the polyaddition reaction mechanism, model reactions of 2-benzoxypentafluoropropene [CF₂=C(CF₃)O-)OCOC₆H₅] (BPFP) with dimethylphenylsilane, [(CH₃)₂SiHC₆H₅], BPFP with 1,1,3,3-tetramethyldisiloxane {[(CH₃)₂SiH]₂O}, and BFP with dimethylphenylsilane were carried out. The mechanism that the radical abstracts a hydrogen from silane compounds followed by the addition of perfluoroisopropenyl groups was proposed.

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1. Introduction

During the study on the polymerization of 2-benzoxypentafluoropropene [CF₂=C(CF₃)OCOC₆H₅] (BPFP), the radical addition reaction of BPFP with tetrahydrofuran (THF) was discovered [1]. The reaction was developed to preparation of polymers by the radical polyaddition of $bis(\alpha$ trifluoromethyl- β , β -difluorovinyl) terephthalate [CF₂=C- $(CF_3)OCOC_6H_4COOC(CF_3)=CF_2$ (BFP) with the compounds possessing carbon-hydrogen bonds such as 1,4dioxane [2], 1,2-dimethoxyethane [3], diformylalkane [4], triethylamine [5] and dialkoxydialkylsilanes [6]. Diethoxydimethylsilane has exhibited the highest polyaddition reactivity toward BFP among the dialkoxydialkylsilanes examined to afford a polymer up to 10⁶ as a number-average molecular weight. The radical polyaddition has then been proved to be a probable synthetic method for fluorinated hybrid polymers bearing alkylsilyl groups in polymer main chains.

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This report concerns the preparation of fluorinated hybrid polymers bearing silyl groups by the radical polyaddition of BFP with silsesquioxanes (T_8) to obtain polymers possessing silsesquioxane moiety in polymer main chain. The radical addition reactions of BPFP with dimethylphenylsilane and 1,1,3,3-tetramethyldisiloxane {[(CH₃)₂SiH]₂O} were also investigated as model reactions in order to get some information on the structure of the polymer obtained and the mechanism of polyaddition reaction.

2. Results and discussion

2.1. Polyaddition reaction

The silsesquioxanes examined here are illustrated in Scheme 1. The results of polyaddition reactions of BFP with silsesquioxanes such as 1,3,5,7,9,11,13,15-octakis(dimethyl-silyloxy)pentacyclo[9.5.1.1^{3,9}1^{5,15}.1^{7,13}]octasiloxane (T₈S), 1,3,5,7,9,11,13,15-octamethylpentacyclo[9.5.1.1^{3,9}1^{5,15}.1^{7,13}]octasiloxane (T₈M), and 1,3,5,7,9,11,13,15-octaisobutylpentacyclo[9.5.1.1^{3,9}1^{5,15}.1^{7,13}]octasiloxane (T8I) are

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Scheme 1. Silsesquioxanes (T8): T8S, $R = (CH_3)_2SiHO$; T8M, $R = CH_3$; T8I, $R = (CH_3)_2CHCH_2$.

summarized in Table 1. The polymers of BFP with T8S are obtained in high conversions at 120 °C in the presence of ditert-butyl peroxide (DTBP) as an initiator probably because of the highest hydrogen abstraction ability. The molecular weight of polymers tends to increase with increasing the concentrations of initiators charged in the polymerization systems. The higher molecular weight polymers are obtained in the presence of octafunctional T8S to bifunctional BFP to be from 1:1.3 to 1:2.0 in feed. The highest molecular weight of the polymer obtained is about 7.9×10^3 which is soluble in usual organic solvent such as methanol, tetrahydrofuran and chloroform. The polymers were then purified by size exclusion chromatography (SEC) to remove BFP and T8S. Typical result of SEC is shown in Fig. 1 which indicates a bimodal molecular weight distribution including high molecular weight polymers of 10^5 . The number average molecular weight of the higher molecular weight region was calculated to be 2.5×10^5 and the molecular weight distribution was 2.1, and those of the lower molecular weight region were 5.0×10^3 and 2.0, respectively.

Table 1 Radical polyaddition of BFP with silsesquioxanes



Fig. 1. SEC of polyaddition product of BFP with T8S.

The radical polyadditions of BFP with T8S initiated by benzoyl peroxide (BPO) and 2,2'-azobisisobutyronitrile (AIBN) are unsuccessful.

Any addition products and polymers were not detected by the reactions of BFP with T8M with these initiators though the conversions of BFP are between 16 and 25%. One to one addition product of T8I with BFP was, on the other hand, detected as a main product though many other products were yielded, and the clear conclusions on the structures of these products were then unable to be determined since the isolation was difficult.

2.2. Model reaction

The results of BFP with T8 indicate that the polymers are obtained by the polyaddition with T8S while methylsilyl group of T8M and isobutylsilyl group of T8I showed scarce

Т8	T8:BFP (mol:mol)	Initiator ^a	Eqivalent	Tol (eq.)	Conversion ^b (%)	$M_{\rm n}~(\times 10^3)$	$M_{\rm w}/M_{\rm n}^{\rm c}$
T8S	1:0.6	DTBP	0.4	9.5	22	<1.8	
	1:1		0.4	9.5	95	2.9	1.2
	1:1		0.4	14.3	31	<1.8	
	1:1.3		0.6	8.0	100	7.9	2.1 ^d
	1:1.6		0.6	6.0	100	6.8	4.4
	1:2		0.8	9.5	100	6.6	4.0
	1:1	BPO	0.4	9.5	62	<1.8	
	1:1	AIBN	0.4	9.5	4 ^e		
T8M	1:1	DTBP	0.4	13.7	19 ^e		
	1:2		0.4	13.7	16 ^e		
	2:1		0.4	27.5	25 ^e		
T8I	1:1	DTBP	0.4	25.9	$49^{\rm f}$		
	1:2		0.4	25.9	$8^{\rm f}$		
	2:1		0.4	40.0	36 ^f		

 a Reaction temperature: BPO, 80 °C; DTBP, 120 °C; AIBN, 60 °C.

^b Conversion of BFP measured by GC.

^c Estimated by GPC (PSt standards, eluent; THF).

^d Purified by SEC.

^e No addition product was detected.

f 1:1 addition product was obtained.

Table 2Model reaction of perfluoroisopropenyl compounds with silanes

	Eqivalent	Silane	Eqivalent	Initiator	Eqivalent	Conversion ^a (%)
BPFP	1.0	DMSH	8.0	DTBP	0.2	100
	8.0		8.0		0.2	58
	8.0		8.0		0.4	66
	8.0		8.0	BPO	0.2	>2
BPFP	1.0	TMSOH	8.0	DTBP	0.2	43
	1.0		8.0		0.4	52
	8.0		8.0		0.2	43
	1.0		8.0	BPO	0.2	13
BFP	1.0	DMSH	8.0	DTBP	0.2	100
	1.0		6.0	BPO	0.2	36

^a Conversion of BPFP or BFP measured by GC.



Fig. 2. NMR of 1:1 addition product of BPFP with DMSH: (a) 1 H (19 F decoupled), (b) 1 H, (c) 13 C (1 H decoupled), (d) 13 C (1 H and 19 F decoupled), and (e) 19 F (1 H decoupled).

reactivity. Model reactions of monofunctional BPFP with dimethylphenylsilane, $[(CH_3)_2SiHC_6H_5]$ (DMSH), BPFP with 1,1,3,3-tetramethyldisiloxane { $[(CH_3)_2SiH]_2O$ } (TMSOH), and bifunctional BFP with DMSH were carried out in order to get some information on the analyses of the polymer structures and on the polyaddition reaction mechanism. The results of the model reactions are summarized in Table 2. The tendency of increasing the conversions of BPFP and BFP by the initiation with DTBP compared to that of BPO is demonstrated. The higher conversions are obtained by the addition of increased amount of initiator in feed. These are the similar results to those of polyaddition reaction mentioned above. Eight-fold excess amount of DMSH in feed is needed to obtain enough conversions of BPFP.

area ratio is in accord with six hydrogens. The reaction is, therefore, supposed to take place by Eq. (1). The reactions of BPFP with TMSOH and BFP with DMSH take place in the similar fashion as illustrated in Eqs. (2) and (3) resulted from the measurements of MS and NMR as shown in experimental part. The ratios of 1:1 and 1:2 addition products of the reactions of monofunctional BPFP with difunctional TMSOH and difunctional BFP with monofunctional DMSH are 38:62 and 52:48, respectively.

$$CF_{2}=C_{O-C_{C}}^{CF_{3}} + H_{O-S_{1}}^{CH_{3}} \longrightarrow O_{CH_{3}}^{CF_{3}} - CF_{2}-CF_{2}-CH_{0}-C_{C} O_{C} O_{CH_{3}}^{CF_{3}} \longrightarrow O_{CH_{3}}^{CF_{3}} O_{CH_{3}}^{CF_{3}} O_{C} O_$$



The addition product of BPFP with DMSH was isolated by SEC in 38% yield and analyzed by gas chromatography (GC), mass-spectrum (MS) and ¹H, ¹³C and ¹⁹F NMR. The MS measured by electron ionization (EI) method showed the molecular ion peak at m/z = 388 which was in accord with the 1:1 addition compound of BPFP with DMSH as shown in experimental part, and fragment pattern of spectrum supported the conclusion. The results of MS measured by chemical ionization (CI) method might also support since the peaks at m/z = 387 and 389 were observed.

The NMR spectra of the product are depicted in Fig. 2. In ¹H NMR the peak at 5.7 ppm is assigned to the α -hydrogen of BPFP moiety in the product, which suggests the transfer of the hydride hydrogen bound to silane atom takes place. This is supported by the ¹³C NMR which demonstrates the peak at 69 ppm as a singlet in Fig. 2d measured under proton and fluorine decoupled condition. The doublet peak at about 0.5 ppm in Fig. 2a is assignable to methyl hydrogens whose

It may be concluded that the hydrogens of methyl groups bonded to silicone atom are scarcely reactive and the hydride bound to silicone atom shows higher reactivity in the reaction system.

2.3. Structure of the polymer

The structure of the polymer yielded from the radical polyaddition of BFP with T8S was investigated by referring to the results obtained from the model reactions. The polymer was purified by SEC and then measured by NMR. The results are shown in Fig. 3. The assignments are depicted in the figures. The hydride hydrogen bonded to silicone atom is found to transfer to the α -carbon of BFP moiety in the polymer main chain. The structure of the T8S moiety in the polymer is hardly determined since T8S possesses eight hydride hydrogens which are probable to be attacked by radical. The polyaddition might take place via Eq. (4).





Fig. 3. NMR of polyaddition product of BFP with T8S: (a) ¹H, (b) ¹³C (¹H and ¹⁹F decoupled), and (c) ¹⁹F (¹H decoupled).

The polyaddition of BFP with T8S might take place by the similar mechanism to the polyaddition of BFP with diethoxydimethylsilane [6]. The reaction might be initiated with the hydrogen abstraction of hydride bonded to silicone atom of T8S to form silyl radical which adds onto perfluoroisopropenyl group. This may be supported by the fact that the polyaddition takes place more easily by the initiation with DTBP which is well-known compound of high hydrogen abstraction ability. The fluorinated carbon radical produced at the α -carbon of BFP moiety might be destabilized by fluorine substituents and produce silyl radical again by intramolecular hydrogen abstraction of hydride hydrogen since the fluorinated carbon radical is scarcely reactive onto fluorinated vinyl group. The equimolarity of feed ratio of

BFP to T8S may then be neglected. The polymer would be yielded by the cycle. The polyaddition might be terminated by the intermolecular hydrogen abstraction.

The branched structure would be suggested since the area ratios of fluorine resonance of perfluoroisopropenyl group in Fig. 3b seem to be larger compared to those calculated from molecular weight of the polymer, probably because T8S performs as slightly more than bifunctional compound.

3. Conclusion

To develop the radical polyaddition of perfluoroisopropenyl compounds with organic compounds bearing carbonhydrogen bonds, a fluorinated hybrid polymer bearing alkylsilyl groups in polymer main chain was prepared by BFP with T8S. A polymer of 2.5×10^5 as a molecular weight was obtained though a molecular weight distribution was bimodal. The polyaddition mechanism that the hydrogen abstraction of hydride hydrogen bonded to silicone atom of T8S by radical evolved from peroxide initiators takes place followed by the addition onto perfluoroisopropenyl group and then intramolecular hydrogen abstraction was proposed.

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 by the reaction of benzoyl chloride with lithium enolate derived from 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) with 2 eq. of butyllithium in THF [7]. 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. BFP was synthesized by the similar method to that of BPFP from terephthaloyl chloride. Commercial T8M, T8S and T8I were used as received. DMSH and TMSOH were distilled under reduced pressure. THF toluene were purified by distillation under purified nitrogen atmosphere after being dried by refluxing with potassium benzophenone ketyl before use. Benzoyl peroxide was precipitated from chloroform and then recrystallized in methanol at 0 °C. DTBP was used as received.

4.2. Addition reaction

The polyaddition reaction of BFP with T8 was carried out by adding BFP (0.79 mmol, 0.22 ml), T8, initiator and toluene in sealed glass ampoule which was carefully flame dried. After a definite time, the reaction was ceased by bubbling oxygen and the concentration of BFP was measured by GC by means of tridecane as an external standard. The polymer was isolated by SEC since the polymer was soluble in usual organic solvents. 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.

The model reaction of BPFP or BFP with DMSH or TMSOH was carried out by adding silyl compound (13.05 mmol), perfluoroisopropenyl compound, peroxide initiator, and toluene in sealed glass ampoule which was carefully flame dried. After a definite time, the reaction was ceased by bubbling oxygen and the concentrations of BPFP and addition products were measured by GC by means of tridecane as an external standard. The reaction system was concentrated by removing low-boiling materials under reduced pressure, and the addition products were isolated by SEC.

Mono-addition product of BPFP with DMSH: ¹H NMR (in CDCl₃): $\delta = 0.51, 0.53$ (6H, s, Si-CH₃), 5.76 (1H, m, CF₂-C $\mathbf{\bar{H}}$ (CF₃)O), 7.21 (2H, t, J = 5 Hz, Si-C₆ $\mathbf{\bar{H}}_5(m)$), 7.26 (1H, d, J = 5 Hz, Si $-C_6 \bar{H}_5(p)$), 7.34 (2H, t, J = 5 Hz, OCO $-C_6 \bar{\mathbf{H}}_5(m)$), 7.48 (2H, d, J = 5 Hz, OCO-C₆ $\mathbf{\bar{H}}_5(o)$), 7.53 (1H, t, J = 5 Hz, OCO-C₆ $\mathbf{\bar{H}}_5(p)$), 7.77 (2H, d, J = 5 Hz, $\text{Si}-\text{C}_6\overline{\mathbf{H}}_5(o)$). ^{13}C NMR{¹H(5 ppm)}: $\delta = -6.2, -5.9$ (s, Si- $\overline{C}H_3$), 69.6 (m, $CF_2 - \bar{C}H(CF_3)O$), 122.5 (q, J = 281 Hz, $\bar{C}F_3$), 125.0 $(t, J = 270 \text{ Hz}, \overline{C}F_2), 128.3, 128.6, 130.4, 130.7, 134.2,$ 134.5 (s, $\overline{C}_{6}H_{5}$). ¹⁹F NMR {¹H (5 ppm): $\delta = -70.6$ (3F, s, $C\bar{F}_{3}$), -117.2, -122.2 (2F, d, J = 348 Hz, $C\bar{F}_{2}$). MW = 388.04: MS (EI, m/z): 375 $[M-(CH_3)]^+$, 311 [M- $C_{6}H_{5}]^{+}$, 135 $[C_{6}H_{5}Si(CH_{3})_{2}]^{+}$, 105 $[C_{6}H_{5}CO]^{+}$, 77 $[C_6H_5]^+$. (CI, m/z): 389 $[M + 1]^+$, 387 $[M - 1]^+$.

Mono-addition product of BPFP with TMSOH: MW = 386.46: MS (EI, *m/z*): 386 $[M]^+$, 371 $[M-(CH_3)]^+$, 253- $[M-(Si(CH_3)_2-O-Si(CH_3)_2H)]^+$, 133 $[Si(CH_3)_2-O-Si(CH_3)_2H]^+$, 105 $[C_6H_5CO]^+$, 77 $[C_6H_5]^+$. (CI, *m/z*): 387 $[M + 1]^+$, 386 $[M]^+$, 385 $[M - 1]^+$, 311 $[M-(O-Si(CH_3)_2H]^+$.

Di-addition product of BPFP with TMSOH: MW = 638.60: MS (EI, *m/z*): 623 $[M-(CH_3)]^+$, 533 $[M-(C_6H_5-CO)]^+$, 327 $[M-(C_6H_5-COO-CH(CF_3)CF_2-Si(CH_3)_2)]^+$, 311 $[C_6H_5-COO-CH(CF_3)CF_2-Si(CH_3)_2]^+$, 105 $[C_6H_5CO]^+$, 77 $[C_6H_5]^+$. (CI, *m/z*): 637 $[M-1]^+$.

Mono-addition product of BFP with DMSH: MW = 562.43: MS (EI, m/z): 562 $[M]^+$, 547 $[M-(CH_3)]^+$, 543 $[M-(F)]^+$, 485 $[M-(C_6H_5)]^+$, 415 $[M-(CF_2=C(CF_3)-O)]^+$, 283 $[C_6H_5-Si(CH_3)_2-CF_2-CH(CF_3)-O]^+$, 279 $[M-(C_6H_5-Si(CH_3)_2-CF_2-CH(CF_3)-O)]^+$. (CI, m/z): 637 $[M - 1]^+$, 562 $[M]^+$, 547 $[M-(CH_3)]^+$, 543 $[M-(F)]^+$, 485 $[M-(C_6H_5)]^+$, 415 $[M-(CF_2=C(CF_3)-O)]^+$.

Di-addition product of BFP with DMSH: MW = 698.70: MS (EI, m/z): 698 $[M]^+$, 683 $[M-(CH_3)]^+$, 621 $[M-(C_6H_5)]^+$, 431 $[M-(C_6H_5-Si(CH_3)_2CF_2CHCF_3)]^+$, 415 $[M-(C_6H_5-Si(CH_3)_2CF_2CHCF_3-O)]^+$, 283 $[C_6H_5-Si(CH_3)_2CF_2CHCF_3-O]^+$, 185 $[C_6H_5-Si(CH_3)_2CF_2]^+$, 135 $[C_6H_5-Si(CH_3)_2]^+$. (CI, m/z): 621 $[M-C_6H_5]^+$.

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 method. SEC was measured with a Tosoh HLC-802A apparatus at 40 °C with a Shodex KF802.5-KF801 (2×) for low-molecular-weight compounds and a Shodex KF 805L (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 and H2 column series with chloroform as an eluent at room temperature (flow rate: 3.8 mL min⁻¹).

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