Synthesis and Polymerization of Novel Bis(2-trifluoromethylacrylate)

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Received 23 October 2009; accepted 14 March 2010
DOI: 10.1002/pola.24037

KEYWORDS: addition polymerization; fluoropolymers; radical polymerization; 2-trifluoromethylacrylate

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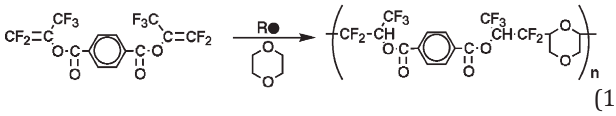
INTRODUCTION As has been reported previously, the poor polymerization reactivity of 2-trifluoromethylacrylate derivatives is demonstrated under radical polymerization conditions and high yields of 2-trifluoromethylacrylate polymers are obtained only under anionic conditions.[1] Facile radical copolymerization was demonstrated by researchers at IBM.[2,3] High radical addition reactivity of perfluoroisopropenyl group has been reported in the reaction of 2-benzoxypentafluoropropene [$CF_2{=}C(CF_3)OCOC_6H_5$] with tetrahydrofuran (THF) to produce a 1:1 addition compound.[4] The reaction has been further developed to produce fluorinated polymers from bis(α-trifluoromethyl-*β*,*β*-difluorovinyl) terephthalate [$CF_2{=}C(CF_3)OCOC_6H_4COOC(CF_3){=}CF_2$] and 1,4-dioxane (DOX) yielding a polymer of a molecular weight of 9.9×10^3 by radical polyaddition (eq 1).[4,5] High radical addition reactivity of *tert*-butyl 2-trifluoromethylacrylate, which possesses two less fluorine atoms compared with perfluoroisopropenyl group, with cyclic ethers such as THF, DOX, 1,3-dioxolane, and tetrahydropyran has been reported to afford corresponding 1:1 addition products in fairly high yields through carbon–carbon bond formation.[6] In this article, the radical reaction of ethylene bis(2-trifluoromethylacrylate) [$CH_2{=}C(CF_3)COOCH_2CH_2OCOC(CF_3){=}CH_2$] (EBFA) was investigated to afford a polymer with the molecular weights of as high as 5.6×10^4 in the presence of large amount of DOX.



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EXPERIMENTAL

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

Reagents

EBFA was synthesized by adding 0.18 mol of 2-trifluoromethylacryloyl chloride dropwise to dichloromethane solution of 0.081 mol of ethylene glycol and 0.18 mol of triethylamine at 0 °C followed by stirring at room temperature for 3 h. The reaction mixture was washed with 1 N hydrochloric acid, saturated aqueous sodium hydrogencarbonate, and then water.

EBFA was isolated by distillation; bp: 63–65 °C/0.1 kPa; yield: 40%; purity: 99% by GC. ^{1}H NMR (in $CDCl_3$): $\delta = 4.52$ (s, 4H, $-C\mathbf{H}_2C\mathbf{H}_2-$), 6.47 (q, 1H, $^4J_{HF} = 0.9$ Hz, $C\mathbf{H}_2$ cis to CF_3), 6.74 (q, 1H, $^4J_{HF} = 1.4$ Hz, $C\mathbf{H}_2$ trans to CF_3); $^{13}C\{(^1H(5$ ppm)} NMR: $\delta = 62.9$ ($-\mathbf{C}H_2\mathbf{C}H_2-$), 121.2 (q, $^1J_{CF} = 273$ Hz, $-\mathbf{C}F_3$), 131.0 (q, $^2J_{CF} = 33$ Hz, $CH_2{=}\mathbf{C}-$), 133.6 (q, $^3J_{CF} = 4.8$ Hz, $\mathbf{C}H_2{=}$), 161.0 ($\mathbf{C}{=}O$); $^{19}F\{(^1H(5$ ppm)} NMR: $\delta = -65.7$ (s, $C\mathbf{F}_3$); EIMS: $m/z = 69$ (38), 95 (23), 123 (100), 166 (6), 167 (7); CIMS: $m/z = 167$ (100), 307 (22, $M^+ + H$); HRMS (CI) Calcd. for $C_{10}H_9O_4F_6$ 307.0405, found 307.0360.

2-Trifluoromethylacryloyl chloride was synthesized[7,8] by the reaction of 2-trifluoromethylacrylic acid (1.0 mol) with phthaloyl dichloride (1.0 mol) at 120 °C for 2 h. The product was collected by fractional distillation; bp: 82 °C; yield: 68%. 2-Trifluoromethylacrylic acid supplied by Tosoh F-Tech and phthaloyl dichloride from Iharanikkei were used as received. Benzoyl peroxide (BPO) and 2,2′-azobisisobutyronitrile (AIBN) were precipitated from chloroform and then recrystallized in methanol at 0 °C. Di-*tert*-butyl peroxide (DTBP) was used as received. THF, DOX, and triethylamine were refluxed over calcium hydride and then distilled.

Procedure

Radical polymerization of EBFA in DOX was carried out under the condition depicted in Table 1. Polymer was isolated by reprecipitation in hexane. Methanol-insoluble part

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 2722–2724 (2010)

TABLE 1 Radical Reaction of EBFA in DOX

Run	DOX mmol (equiv)	Initiator[a]		Yield[b] (%)	$\overline{M}_n$ ($\times 10^4$)[c]	$\overline{M}_w/\overline{M}_n$[c]
			mmol (equiv)			
1	2.6 (40)	BPO	0.065 (1)	Gel	–	–
2	3.9 (60)		0.065 (1)	40	1.0	2.7
3	3.9 (60)		0.13 (2)	62	2.1	7.4
4	3.9 (60)		0.46 (7)	50[d]	5.6[d]	8.5[d]
5	5.2 (80)		0.065 (1)	45	0.73	2.0
6	5.2 (80)		0.13 (2)	70	0.82	4.9
7	5.2 (80)		0.33 (5)	25[d]	2.4[d]	1.7[d]
8	5.2 (80)		0.46 (7)	24[d]	2.3[d]	1.5[d]
9	7.8 (120)		0.13 (2)	43	0.27	2.0
10	10.5 (160)		0.13 (2)	49	0.32	1.4
11	2.6 (40)	DTBP	0.13 (2)	Gel	–	–
12	3.9 (60)		0.13 (2)	3	0.25	1.6
13	5.2 (80)		0.13 (2)	45	0.48	1.8
14	7.8 (120)		0.13 (2)	52	0.49	1.3
15	2.6 (40)	AIBN	0.13 (2)	Gel	–	–
16	3.9 (60)		0.13 (2)	79	0.36	3.3

EBFA: 0.33 mmol (5 equiv), reaction time: 3 days.

[a] Reaction temp. BPO and AIBN: 80 °C, DTBP: 120 °C.

[b] Hexane insoluble part.

[c] Estimated by SEC (polystyrene standards, eluent: THF).

[d] Methanol insoluble part.

was obtained by reprecipitation of THF solution of hexane-insoluble polymer in methanol.

Poly(EBFA with DOX): ^1H NMR (in $CDCl_3$, 500 MHz): δ = 1.7–2.1 (br, $-C\mathbf{H}_2-CH(CF_3)-$), 2.1–2.9 (br, $-C\mathbf{H}_2-C(CF_3)-$), 3.2–3.6 (br, $-CH_2-C\mathbf{H}-O-$, $-CH_2-C\mathbf{H}(CF_3)-$), 3.6–3.9 (br, $-C\mathbf{H}_2-C\mathbf{H}_2-O-C\mathbf{H}_2-$), 3.9–4.9 (br, $-C\mathbf{H}_2-C\mathbf{H}_2-$). $^{13}C\{^1H(5\ \text{ppm})\}$ NMR (in $CDCl_3$, 125 MHz): δ = 28.5–32.2 ($-\mathbf{C}H_2-CH(CF_3)-$), 47.4–48.0 ($-\mathbf{C}H(CF_3)-$), 56.7 and 58.8 ($-CH_2-\mathbf{C}(CF_3)-$), 61.6 and 63.8 ($-\mathbf{C}H_2-\mathbf{C}H_2-$), 66.1 and 66.3 ($-CH-O-CH_2-\mathbf{C}H_2-$), 66.7 ($>CH-O-\mathbf{C}H_2-CH_2-$), 70.4 and 70.7 ($>CH-\mathbf{C}H_2-O-CH_2-$), 71.5 and 73.1 ($>\mathbf{C}H-O-CH_2-CH_2-$), 125.0 ($-\mathbf{C}F_3$), 168.1–169.0 ($>\mathbf{C}{=}O$). $^{19}F\{^1H(5\ \text{ppm})\}$ NMR (in $CDCl_3$, 470 MHz): δ = −68.6 to −66.2 (br, $-CH_2-C(C\mathbf{F}_3)$), −68.7 (s, $-CH_2-CH(C\mathbf{F}_3)$).

Measurements

Vapor phase chromatographic (GC) measurement was carried out with a Hewlett-Packard 6890 equipped with flame ionization detector with a ZB-1, wide-bore capillary column (15 m × 0.53 mm, film thickness: 1.5 μm). The column temperature was programmed from 80 to 320 °C at 20 °C min^{-1}. Mass spectra (MS) were measured by electron ionization (EIMS) and chemical ionization methods (CIMS) on a JEOL JMS-SX102. Isobutane was used as a reagent gas of CIMS. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL JNM-ECP500 Fourier transform NMR spectrometer at 500 MHz for ^1H {nondecoupled and [^{19}F (irradiation offset: −100 ppm)]}, 125 MHz for ^{13}C {[^1H (5 ppm)], [^1H (5 ppm), and ^{19}F (−100 ppm)]}, and 470 MHz for ^{19}F [^1H (5 ppm)] NMR with deuterated chloroform as a solvent. Chemical shift of ^{19}F NMR was determined on the basis of absolute magnetic field intensity. Size exclusion chromatography (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 KF805L (2×) for high-molecular-weight compounds with THF as an eluent (flow rate: 1.0 mL min^{-1}). The molecular weight of a polymer measured by SEC was calculated from the calibration curve for polystyrene standards. Thermogravimetric analysis (TGA) was carried out with a Thermo Plus TG 8120 TG-DTA (Rigaku) under Ar atmosphere with a heating rate of 5 °C min^{-1}.

RESULTS AND DISCUSSION

EBFA was synthesized by the reactions of 2-trifluoromethylacryloyl chloride with ethylene glycol in the presence of triethylamine as a hydrogen chloride acceptor in fairy high yields. The structures were supported by MS and ^1H, ^{13}C, and ^{19}F NMR as shown in the Experimental section.

The results of radical reaction of EBFA in the presence of large excess amount of DOX are summarized in Table 1. Gel formation is observed by the addition of small amounts of DOX to the reaction (Runs 1, 11, and 15). It seems that 60 equiv or more DOX with 5 equiv of EBFA are needed to obtain soluble polymers. Polymers with molecular weight as high as 5.6 × 10^4 are produced by the addition of larger amount of initiators (Runs 4, 7, and 8). The structural analyses with NMR measurements of the polymer obtained showed no signals assigned to $CH_2{=}$ hydrogens and the

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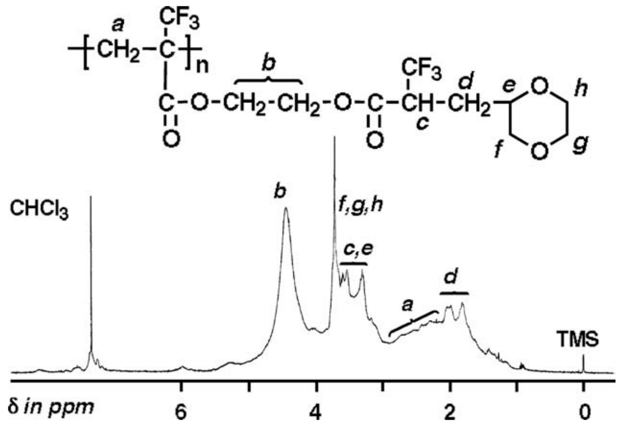
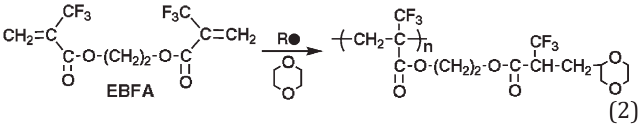


FIGURE 1 ^{1}H NMR of reaction product of EBFA in DOX.

polymer incorporates DOX moieties, as shown in Figure 1 and the Experimental section, which demonstrates that the addition polymerization of a 2-trifluoromethylacrylate takes place with radical addition of DOX at the pendant 2-trifluoromethylacrylate group quantitatively as shown by eq 2. The conclusion was supported by the results of the model reactions of ethyl 2-trifluoromethylacrylate with THF and DOX. ^{1}H NMR of the polymer obtained by the base-catalyzed hydrolysis of the polymer produced by the reaction of EBFA with DOX showed the decrease of the peaks assigned to $-CH_2-C\mathbf{H}-O-$ and $-CH_2-C\mathbf{H}(CF_3)-$ and to $-C\mathbf{H}_2-C\mathbf{H}_2-$, respectively, because of decrease of ester groups although a homopolymer of $CH_2{=}C(CF_3)COOH$ could not be isolated probably because of the incomplete hydrolysis in polymer reaction.



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It may be a new finding that the addition polymerization of 2-trifluoromethylacrylate group takes place under radical reaction conditions to afford high-molecular-weight polymers in high yields although low-molecular-weight oligomers have been previously reported. This may be ascribable to large substituents at chain ends to stabilize propagating radicals.

The 5% weight-loss temperature of the polymer was 309 °C as measured by TGA.

The authors are very much indebted to Tosoh F-Tech, Inc. for providing 2-trifluoromethylacrylic acid and Iharanikkei Co. for phthaloyl dichloride. They are grateful for the financial support in part by the "Open Research Center" Project in Saitama Institute of Technology from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, 2007–2009.

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