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Novel fluorinated hybrid polymers from tris(α-trifluoromethyl-β,β-difluorovinyl) 1,3,5-benzenetricarboxylate by radical polyaddition with diethoxydimethylsilane

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Dedicated to Professor Teiji Tsuruta on the occasion of his 88th birthday (Beiju).

Abstract

The novel fluorinated hybrid polymer possessing alkylsilyl group was prepared by radical polyaddition of tris(α-trifluoromethyl-β,β-difluorovinyl) 1,3,5-benzenetricarboxylate [$C_6H_3(COOC(CF_3){=}CF_2)_3$)] (TFM) with diethoxydimethylsilane to afford soluble polymers though the examination of TFM with monofunctional tetrahydrofuran showed that the main product was the triaddition compound of TFM which suggested that a cross-linked polymer might be yielded by the polyaddition of TFM with difunctional ether. The polymer might perform as a functional fluorinated hybrid polymers which possess many perfluoroisopropenyl groups in side chains.

Keywords: Fluoropolymers; Hybrid polymers; Radical polymerization; Telechelics; Tris(α-trifluoromethyl-β,β-difluorovinyl) 1,3,5-benzenetricarboxylate

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1. Introduction

As has been demonstrated previously, the radical polyaddition of bis(α-trifluoromethyl-β,β-difluorovinyl) terephthalate [$CF_2{=}C(CF_3)OCOC_6H_4$-$COOC(CF_3){=}CF_2$] (BFP) with 1,4-dioxane (DOX) produces a polymer possessing about 1.0×10^4 as a molecular weight in the presence of excess amount of DOX [1,2] (Eq. (1)). The reaction has been applicable to a wide variety of organic compounds bearing carbon–hydrogen bonds [3]. Crown ether moiety is incorporated into polymer main chain by the reaction of BFP with 18-crown-6 in the presence of benzoyl peroxide (BPO) as a radical generator [4]. It is interesting to obtain such a polymer directly from a crown ether as a starting reagent because of 24 carbon–hydrogen bonds in the 18-crown-6 molecules which are likely to be attacked. One of

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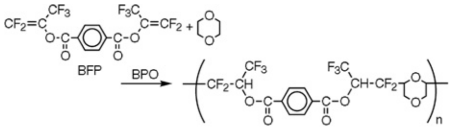
the reason why the soluble polymers are yielded from crown ether might be that the controlled intramolecular radical shift such as 1,5-shift or 1,6-shift mechanism would take place precisely during the polymerization reaction [3]. Fluorinated hybrid polymer possessing alkylsilyl groups in main chain was also prepared from BFP with diethoxydimethylsilane (DEOMS) [5].



(1)

It is then interesting to investigate a multifunctional perfluoroisopropenyl compound with difunctional ethers. This paper concerns about the radical addition reactivity of triperfluoroisopropenyl ester which might be a trifunctional compound. Tris(α-trifluoromethyl-β,β-difluorovinyl) 1,3,5-benzenetricarboxylate $[C_6H_3(COOC(CF_3){=}CF_2)_3]$ (TFM) was synthesized from 1,3,5-benzenetricarbonyl trichloride (trimesyl trichloride) with 3 eq of lithium enolate derived from 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) and butyllithium, and the radical addition and the polyaddition reactivity of TFM was examined. The polymer obtained might perform as a functional fluorinated hybrid polymers which possess many perfluoroisopropenyl groups in side chains.

2. Experimental

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

2.1. Reagents

TFM was synthesized by the reaction of trimesyl trichloride with 3 eq of lithium enolate derived from HFIP in THF [6,7]; yield 20%, bp 107 °C/0.1 kPa, purity 93% by vapor phase chromatography (GC).

TFM: ^{1}H NMR ($CDCl_3$): $\delta = 8.9$ (s, $C_6\mathbf{H}_3$); ^{13}C NMR [^{1}H{5 ppm}]: $\delta = 104$–105 ($CF_2{=}\mathbf{C}$), 117–123 ($\mathbf{C}F_3$), 129 ($\mathbf{C}_6H_3$, quaternary carbon), 138 ($\mathbf{C}_6H_3$, methine carbon), 154–159 ($\mathbf{C}F_2{=}$), 160 ($\mathbf{C}OO$); ^{19}F NMR [^{1}H{5 ppm}]: $\delta = -63$ (9F, dd, $C\mathbf{F}_3$–), −79 (F_{cis}, dq, $C\mathbf{F}_2{=}$), −88 (F_{trans}, dq, $C\mathbf{F}_2{=}$); MS (200 eV, CI, isobutane): $m/z = 601$ (M+1).

2-Benzoxypentafluoropropene $[CF_2{=}C(CF_3)O\text{-}COC_6H_5]$ (BPFP) was synthesized as reported [6,7]; HFIP (Central Glass Co.) was dried by refluxing over calcium hydride and distilled under a nitrogen atmosphere. Commercial hexane solution of butyllithium was used after determination of the concentration by acid titration. THF was purified by distillation under purified nitrogen atmosphere after being dried by refluxing with sodium benzophenone ketyl before use. DEOMS donated by courtesy of Shin-Etsu Chemical Co. was dried by calcium hydride. DOX was dried by refluxing over calcium hydride and distilled under nitrogen atmosphere. 18-Crown-6 was used as received. Benzoyl peroxide (BPO) was precipitated from chloroform and then recrystallized in methanol at 0 °C. Di-*tert*-butyl peroxide (DTBP) was used as received.

TFM with DEOMS product: ^{1}H NMR ($CDCl_3$): $\delta = 0.03$–0.3 (Si–$C\mathbf{H}_3$), 1.2–1.5 (CH–$C\mathbf{H}_3$), 4.1 (CF_2–C$\mathbf{H}$), 6.1 (CF_3–C$\mathbf{H}$), 9.0 ($C_6\mathbf{H}_3$); ^{13}C NMR [^{1}H{5 ppm}]: $\delta = -2.6$ to -1.7 (Si–$\mathbf{C}H_3$), 15–16 (CH–$\mathbf{C}H_3$), 68–69 (CF_3–$\mathbf{C}$H, CH_3–$\mathbf{C}$H), 118–123 ($\mathbf{C}F_3$–CH, $\mathbf{C}F_2$–CH), 129–130 ($\mathbf{C}_6H_3$, quaternary carbon), 136–137 ($\mathbf{C}_6H_3$, methine carbon), 161 (s, $\mathbf{C}OO$); ^{19}F NMR [^{1}H{5 ppm}]:$\delta = -65$ ($C\mathbf{F}_3$–C=), −71 to −70 ($C\mathbf{F}_3$–CH–), −81 (F_{cis}, $C\mathbf{F}_2{=}$), −90 to −89 (F_{trans}, $C\mathbf{F}_2{=}$), −124 to −116 (–$C\mathbf{F}_2$–).

2.2. Procedure

The addition reaction of TFM with THF was carried out by adding 5 eq of TFM with 40 eq of THF in the presence of 2 eq of BPO or DTBP. The radical polymerization of TFM was carried out in sealed glass ampule by adding 25–50 eq of TFM and 1 eq of BPO or DTBP. The polymerization temperature was set at 80 °C for BPO and 120 °C for DTBP. The polyadditions of TFM with DEOMS, DOX and 18-crown-6 were carried out in sealed ampoule which was carefully flame dried. After a definite time, the concentration of TFM was measured with GC with tridecane as an internal standard. The polymer was isolated by reprecipitation in 98% ethanol and dried thoroughly in vacuo. The molecular weight of the polymer was determined by size exclusion chromatography (SEC). The structure of the resulting reaction product was determined by ^{1}H, ^{13}C and ^{19}F NMR.

2.3. Measurements

GC measurement was carried out with a Hewlett–Packard 6890 equipped with flame ionization