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A Novel Thermally and Chemically Stable Polymer: Poly(2-difluoromethylene-1,3-dioxolane)

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Introduction. Fluorinated polymers have become of increasing interest in the development of advanced materials having superior thermal and chemical stability, excellent electrical insulating ability, and unique optical properties.[1−3] Perfluoropolymers such as Teflon AF and Cytop have been commercialized by DuPont and Asahi Glass, respectively.[2,3] These polymers have high chemical and thermal stability and are soluble in selected fluorinated solvents. However, the polymers are quite expensive due to the high manufacturing costs for their monomers.[3] Here, we report that a partially fluorinated polymer, poly(2-difluoromethylene-1,3-dioxolane) (P_1), is thermally and chemically stable and is soluble in fluorinated alcohols.

Results and Discussion. The polymer, P_1, was prepared by a free-radical polymerization of 2-difluoromethylene-1,3-dioxolane (M_1) in THF solution with AIBN at 60 °C or tri(*n*-butyl)borane−air at −78 °C as an initiator. The monomer,[4] M_1, was readily prepared through the synthetic route shown in Scheme 1. The compound $CClF_2CH(OH)_2$ was purchased from SynQuest Fluorochemicals Lab, Inc. The reaction was monitored by measuring ^{19}F NMR. The signal at −70.56 ppm ascribed to 2-chlorodifluoromethyl-1,3-dioxolane decreased and the signal at −136.75 ppm ascribed to the M_1 appeared and increased with time. The conversion was calculated on the basis of the peak areas of the two signals. After the elimination of HCl exceeded 85%, the M_1 produced was collected in a cold trap (−78 °C) with THF under reduced pressure. M_1 was found to be readily polymerized upon heating, and hence the isolation of M_1 from THF failed. However, the M_1 solution can be stored in refrigerator at −30 °C for a week without any change on the basis of an NMR analysis.

The polymer, P_1, obtained (about 80% yield) by a free-radical polymerization is not soluble in common solvents such as acetone, DMSO, toluene, THF, chloroform, and methanol but soluble in fluorinated solvents such as hexafluoro-2-propanol (HFIP) and trifluoroacetic acid (TFA). The intrinsic viscosity [η] was found to be 0.38 dL/g in a mixed solvent of $CHCl_3$/TFA (9/1, v/v) at 25 °C. The ^1H and ^{19}F NMR spectra of P_1 were recorded on a Bruker AC 300 spectrometer using $CDCl_3$/TFA (9/1, v/v) as the solvent. The TMS and $CFCl_3$ were used as the internal references for ^1H and ^{19}F NMR, respectively. As shown in Figure 1, the ^{19}F NMR spectrum indicated no vinylic fluorines. The peak at −116.00 ppm was assigned to the saturated fluorines ($-CF_2-$) on the main chain. Only one peak in the ^1H NMR spectrum at 4.26 ppm was detected and was assigned to the protons on the dioxolane ring. IR and NMR measurements indicated there was no ring-opening product, and the polymerization proceeded through vinyl addition. The hydrocarbon analogue, 2-methylene-1,3-dioxolane, has been reported to yield a partially ring-opening polymer with a radical polymerization,[5] and also we found that the six-member-ring monomer, 2-difluoromethylene-1,3-dioxane (M_2), gave a partially ring-opening product by a free-radical polymerization as described below.

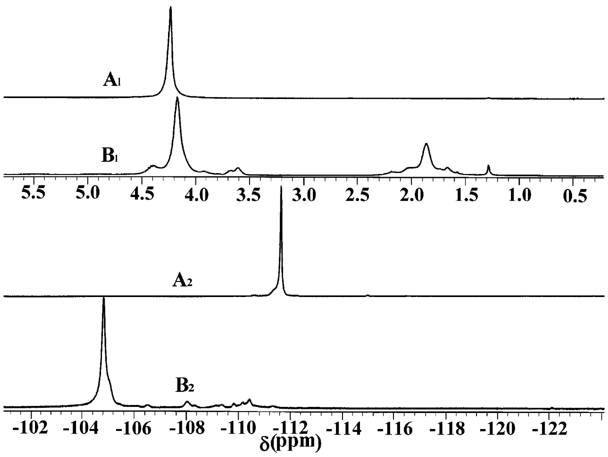
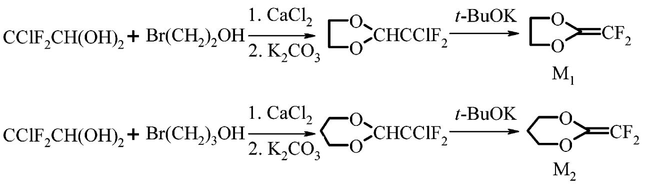
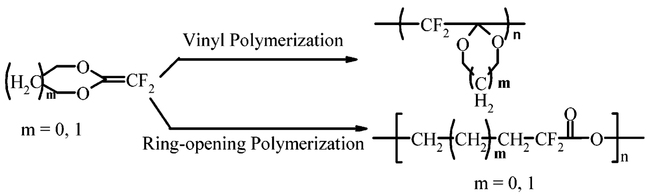


Figure 1. ^1H and ^{19}F NMR spectra of the polymers [A_1 and A_2: ^1H and ^{19}F NMR spectra of poly(2-difluoromethylene-1,3-dioxolane); B_1 and B_2: ^1H and ^{19}F NMR spectra of poly(2-difluoromethylene-1,3-dioxane), respectively].

Scheme 1. Monomer Synthesis



Scheme 2. Polymerization Mechanism



The powder X-ray diffraction pattern of P_1 indicates that it was semicrystalline. The crystallinity is about 44% as shown in Figure 2, and its melting point is 356 °C, which is higher than that of Teflon (T_m = 327 °C).[6] The glass transition of the polymer was observed at 125 °C as shown in Figure 3. The thermal gravimetric analysis of P_1 exhibited a high degree of thermal stability under nitrogen, and the onset of decomposition began at 427 °C under nitrogen. But even under an air atmosphere, the decomposition began at around 414 °C as shown in Figure 4B. A transparent thin film (~0.1

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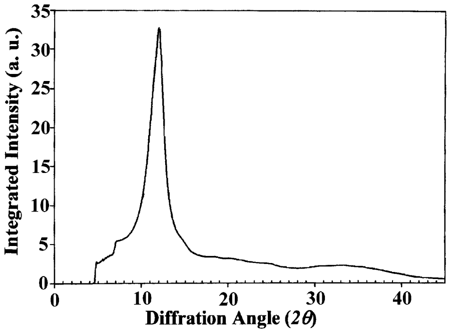

Figure 2. X-ray diffraction pattern of poly(2-difluoromethylene-1,3-dioxolane).

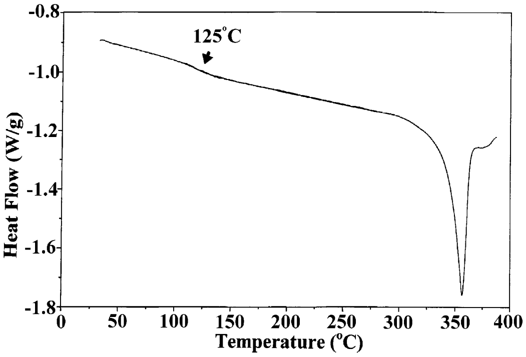

Figure 3. DSC curve of poly(2-difluoromethylene-1,3-dioxolane).

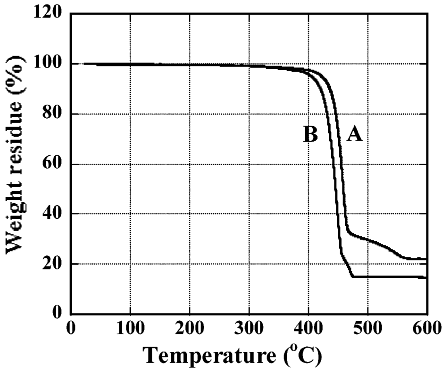

Figure 4. TGA curves of poly(2-difluoromethylene-1,3-dioxolane) in N_2 (A) and air (B).

mm) of the P_1 was obtained by casting its HFIP solution on glass or silicon. The refractive index was measured using the film on a Metricon model 2010 prism coupler. The refractive indices of the film were 1.4396 and 1.4372 at the wavelength of 632.8 and 1544 nm, respectively. The films (~0.5 mm) were dipped into 20% aqueous H_2SO_4 and 30% aqueous NaOH solutions at 60 °C over 2 days, respectively. After washing the films with water and drying, the IR spectra and weight measurements indicated that the films did not degrade in these conditions.

To compare the chemical properties of the polymers having dioxolane and dioxane rings, 2-difluoromethylene-1,3-dioxane (M_2)[7] was also synthesized (Scheme 1). M_2 was polymerized in THF with AIBN, and the polymer obtained (P_2) is soluble in common solvents such as chloroform and THF. The FTIR spectrum of the polymer showed a sharp band at 1760 cm^{-1}, corresponding to the ester absorption. The ^1H and ^{19}F NMR spectra of the polymer are shown in Figure 1. In the proton NMR, the sharp peak at 4.175 ppm was assigned to the protons of the dioxane ring (adjacent to oxygen). The peaks around 4.412 and 3.601 ppm were ascribed to the ring-opening structure. In the fluorine NMR, the sharp peak at −104.82 ppm was assigned to the saturated fluorines ($-CF_2-$) on the main chain of the segment without ring opening. The small peaks between −106 and −116 ppm were ascribed to the fluorines on the polyester part. On the basis of the NMR, the polymer contains about 22% of ring-opening structure, indicating that ring opening occurred during the radical polymerization. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) were found to be 8215 and 1.72, respectively, by size exclusion chromatography with PMMA standard in $CHCl_3$ solution. The onset of decomposition temperature of P_2 was 309 °C under a nitrogen atmosphere.

In conclusion, two cyclic difluoromethylene acetal polymers have been synthesized, of which poly(2-difluoromethylene-1,3-dioxolane) without ring-opening structure shows good solubility in fluorinated alcohols as well as high thermal and chemical stability. This polymer may have potential applications such as coating, waveguide, and photoresist materials.

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(4) During the preparation of this manuscript, the compound was reported and used in [2 + 2] cycloaddition reaction without isolation. ^{19}F NMR (ether/hexane) δ −137.9 (s). He, Y.; Junk, C. P.; Cawley, J. J.; Lemal, D. M. *J. Am. Chem. Soc.* **2003**, *125*, 5590. The monomer obtained here was also characterized by NMR: ^1H NMR ($CDCl_3$) δ (ppm): 4.36 (s, 4H). ^{19}F NMR ($CDCl_3$) δ (ppm): −136.04 (s, CF_2=).

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(7) ^{19}F NMR ($CDCl_3$) δ (ppm): −126.16 (s, CF_2=).

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