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Synthesis of Soluble Fluorinated Vinyl Ether Copolymers by Ionic Addition of Fluoroolefins to Poly(vinyl alcohol)

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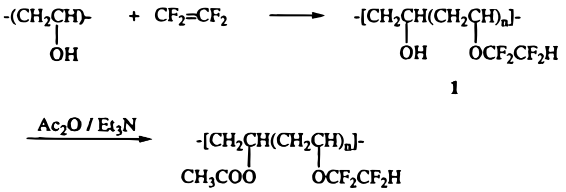
Introduction

Transparent polymers with low refractive index are of interest for optical applications such as optical fibers and waveguides.[1] Fluorinated groups are often incorporated into polymers to lower the refractive index;[2] the polymer with the lowest known refractive index is an amorphous perfluorinated ring-containing polymer (Teflon AF).[3] However, highly fluorinated polymers often require monomers that are costly or not readily available and the polymers may be difficult to process into thin films due to solubility limitations.

We now report a simple synthesis of amorphous, soluble and low-refractive index fluoropolymers by the ionic addition of available fluoroolefins to poly(vinyl alcohol). Ionic additions of alcohols and phenols to fluorinated olefins, such as tetrafluoroethylene (TFE) or perfluoropropyl vinyl ether (PPVE), are well-known[4,5] but have rarely been applied to polymeric substrates.[6]

Results

Treatment of commercial poly(vinyl alcohol) (100% hydrolyzed, MW = 125 000) in DMSO solution with varying amounts of tetrafluoroethylene and a catalytic amount of potassium *tert*-butoxide at room temperature affords polymers **1** in high yields (Table 1). The percentage of hydroxyl groups converted to ethers is determined by integration of the methine protons in the NMR spectrum and elemental analysis. It varies from a maximum of about 77% with excess TFE to approximately stoichiometric amounts with less than 1 equiv of olefin. The initially formed polymers **1** have a light tan color, which is likely formed from reaction of impurities in the poly(vinyl alcohol) with the base, but the color is readily removed by treating the polymer with hydrogen peroxide in refluxing acetone. The fluoroalkylated polymers give attractive clear films from solution or the melt. The grafted polymers are soluble in common organic solvents, such as acetone, DMSO, or THF (poly(vinyl alcohol) itself is insoluble in acetone). As expected, T_g's and refractive indices decrease as the grafting level increases, with the most highly grafted polymer having a refractive index as low as 1.385.



$$-(CH_2\underset{OH}{CH})- + CF_2{=}CF_2 \longrightarrow -[CH_2\underset{OH}{CH}(CH_2\underset{OCF_2CF_2H}{CH})_n]-$$

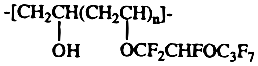
1

$$\xrightarrow{Ac_2O\,/\,Et_3N} -[CH_2\underset{CH_3COO}{CH}(CH_2\underset{OCF_2CF_2H}{CH})_n]-$$

2

A 66% grafted polymer could be acylated with acetic anhydride in the presence of triethylamine to give the corresponding poly(vinyl acetate) copolymer **2** with essentially all the remaining hydroxyl groups converted, as judged by proton NMR spectroscopy.

Poly(vinyl alcohol) (DuPont Elvanol 90−50, M_n 30 000) also reacts with perfluoropropylvinyl ether (PPVE) under similar conditions. Unlike the TFE grafts, the product **3** rapidly precipitates from the DMSO solution and is insoluble in acetone or THF. It dissolves readily in 1,1,2-trichlorotrifluoroethane (CFC-113). This polymer with about 77% of the OH groups converted to $OCF_2CFHOCF_2CF_2CF_3$ was amorphous and rubbery with a T_g of −15.6 °C.



$$-[CH_2\underset{OH}{CH}(CH_2\underset{OCF_2CHFOC_3F_7}{CH})_n]-$$

3

Discussion

The ionic grafting of TFE to commercially available poly(vinyl alcohol)s offers a simple and low cost route to novel, soluble, low refractive index polymers. The ether linkage is hydrolytically stable, and the hydrogen in the tetrafluoroethoxy side chain improves the solubility in organic solvents. In contrast, polymer **3** with the longer fluoroalkyl groups behaves more like a fluoropolymer with solubility only in the nonpolar CFC-113.

Not surprisingly, polymers **1** have a lower T_g and thermal stability and higher refractive indices than the amorphous perfluoropolymer Teflon AF (Table 1). However, the latter polymer is only soluble in costly perfluorinated solvents.[3]

In principle, polymers **1**−**3** could be produced by copolymerizations of the corresponding fluorinated vinyl ether monomers, $R_fOCH_2{=}CH_2$. The olefin $HCF_2CF_2OCH{=}CH_2$ (**4**) is a known compound,[7] but copolymers corresponding to **1** have not been reported. Synthesis of **4** requires several steps and it may be difficult to achieve a high level of incorporation of the fluorinated comonomer by standard radical copolymerization techniques.[8]

Experimental Details

Polymer Analyses. Elemental analyses were done by Schwarzkopf Microanalytical Laboratory. ^1H and ^{19}F NMR spectra were measured in the indicated solvents using TMS and CFC-11 as internal standards.

Synthesis of Poly(vinyl alcohol-*co*-vinyl 1,1,2,2-tetrafluoroethyl ether) (77% OCF_2CF_2H). A 1 gallon metal autoclave was purged with nitrogen and charged with 5.6 g (0.05 mol) of potassium *tert*-butoxide, 200 mL of DMSO, and a solution prepared by dissolving 44 g (1.75 mol of OH) of poly(vinyl alcohol) (Aldrich, MW 125 000, 100% hydrolyzed) in 2 L of DMSO. The vessel was closed, pressure tested with nitrogen, and evacuated. The vessel contents were stirred at about 25 °C and tetrafluoroethylene (TFE) was added to 200 psi. As the pressure fell, additional TFE was added, maintaining the pressure at about 150 psi and the temperature at about 25 °C until 220 g (2.2 mol) of TFE had been added. The mixture was stirred for a total of about 23 h. The reactor was vented, and the contents were mixed with 150 mL of glacial acetic acid. The viscous DMSO solution was added to excess water with stirring. The precipitated solid was cut into small pieces and chopped in a blender with water until a fine granular solid was obtained. The solid was filtered off and air-dried for 16 h giving 207.6 g. The tan solid was dissolved

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Table 1. Grafts of TFE to Poly(vinyl alcohol)

no.	[TFE]/[OH][a]	yield, %	% graft[b] H NMR	% graft[c] anal.	inh visc, dL/g	T_g, °C	T_d,[d] °C	ref index
1	0.4	95	33	46	1.02	65	255	1.4188
2	0.7	96	60	66	0.81	38	280	1.3960
3	1.25	101	78	77	1.13	24	293	1.3852
Teflon AF 1600[e]						160	>360	1.31

[a] Mole ratio of TFE fed to OH groups in polymer sample. [b] Determined by integration of peaks at δ 4.8 (H−C−OCF$_2$) vs 3.9 (H−C−OH). [c] Determined by % C analysis. [d] 10% weight loss temperature by TGA under N$_2$. [e] Data from ref 3.

in 3.5 L of acetone, and the solution was heated to reflux. Hydrogen peroxide (50 mL, 30%) was added, and the solution was refluxed for 8 h. An additional 50 mL of hydrogen peroxide was added, and refluxing was continued for 3 days, giving a colorless solution. The acetone solution was cooled, filtered, concentrated to about 1.5 L and poured slowly into 8 L of water. The precipitate was chopped several times in a blender to give a white granular solid, which was dried under vacuum for 2 days at room-temperature giving 209 g of polymer. ^{19}F NMR (acetone-d_6): δ −87.3 (2F), −137.1 (2F). Proton NMR showed peaks at δ 6.1 (assigned to CF$_2$$H$), 4.8 (assigned to H−C−OCF$_2$), and 3.9 (assigned to H−C−OH) in a ratio of 3.4:3.4:1. T_g (DSC): 23.8 °C. Refractive index: 1.3852. Inherent viscosity (acetone): 1.13 dL/g. Anal. Found: C, 35.08; H, 3.40; F, 42.37. From the % C analysis, it was calculated that 77% of the OH groups were converted to OCF$_2$CF$_2$H.

Synthesis of Poly(vinyl alcohol-*co*-vinyl 1,1,2,2-tetrafluoroethyl ether) (66% OCF$_2$CF$_2$H). The above procedure was followed, except that the total amount of TFE fed was 123 g (1.23 mol), giving 185.0 g of white polymer powder. Proton NMR showed peaks at δ 6.1 (assigned to CF$_2$$H$), 4.8 (assigned to H−C−OCF$_2$), and 3.9 (assigned to H−C−OH) in a ratio of 1.5:1.5:1. T_g (DSC): 33.7 °C. Refractive index: 1.3960. Inherent viscosity (acetone): 0.81 dL/g. Anal. Found: C, 36.25; H, 3.59; F, 43.00. From the % C analysis, it was calculated that 66% of the OH groups were converted to OCF$_2$CF$_2$H.

Synthesis of Poly(vinyl alcohol-*co*-vinyl 1,1,2,2-tetrafluoroethyl ether) (46% OCF$_2$CF$_2$H). The above procedure was followed, except that the total amount of TFE fed was 70 g (0.7 mol), giving 149.8 g of white polymer. Proton NMR showed peaks at δ 6.1 (assigned to CF$_2$$H$), 4.8 (assigned to H−C−OCF$_2$), and 3.9 (assigned to H−C−OH) in a ratio of 0.5:0.5:1. T_g (DSC): 65.2 °C. Refractive index: 1.4188. Inherent viscosity (acetone): 0.80 dL/g. Anal. Found: C, 38.98; H, 4.49; F, 35.56. From the % C analysis, it was calculated that 46% of the OH groups were converted to OCF$_2$CF$_2$H.

Synthesis of Poly(vinyl acetate-*co*-vinyl 1,1,2,2-tetrafluoroethyl ether). A 5.0 g portion of the polymer 66% grafted with TFE groups was dissolved in 80 mL of acetic anhydride. Triethylamine (5 mL) was added, and the solution was heated in a 60 °C oil bath for 22 h. The solution was cooled to room temperature and poured slowly into 1 L of water. The solution was decanted from a gummy precipitate. The precipitate was dissolved in acetone, and the solution was evaporated under reduced pressure. The solid was suspended in 450 mL of acetone, and 5 mL of 30% hydrogen peroxide was added. This solution was refluxed overnight. It was cooled to room temperature and diluted with water. The liquid phase was decanted, the solid polymer was washed with water and dried at 0.1 mm and 50 °C, giving 4.97 g of white solid. Proton NMR showed peaks at δ 6.1 (assigned to CF$_2$$H$), 5.0 (assigned to H−C−OAc), and 4.7 (assigned to H−C−OCF$_2$) in a ratio of 1:0.43:1. T_g (DSC): 18.7 °C. Refractive index: 1.3960. Inherent viscosity (acetone): 0.65 dL/g. Anal. Found: C, 38.98; H, 4.49; F, 35.56. From the % C analysis, it was calculated that the polymer contained 34% OAc and 66% OCF$_2$CF$_2$H groups.

Synthesis of Poly(vinyl alcohol-*co*-vinyl 1,1,2-trifluoro-2-heptafluoropropoxyethyl ether). Poly(vinyl alcohol) (DuPont Elvanol 90−50, M_w 56 000, M_n 30 000) (15.4 g, 0.35 mol of OH groups) was dissolved in 650 mL of DMSO in a 1 L glass round-bottom flask under nitrogen. A solution of 1.0 M potassium *tert*-butoxide in THF (35 mL, 0.035 mol) was added, and the mixture was stirred for 0.5 h. Perfluoropropyl vinyl ether (122 g, 0.47 mol) was added in one portion, resulting in an exothermic reaction and formation of a precipitate. This mixture was stirred for 4 h at room temperature and then quenched by the addition of 100 mL of glacial acetic acid. Water was added, and the liquid phase was decanted from the solid. The solid was treated with 2 L of 1,1,2-trichlorotrifluoroethane and filtered. The filtrate was concentrated to about 700 mL and poured slowly into 4 L of pentane. The precipitated polymer was isolated and dried under vacuum at room temperature, affording 39 g of a light tan solid. The solid was suspended in 900 mL of acetone and heated to reflux. Hydrogen peroxide (30 mL, 30%) was added and the mixture refluxed overnight. Another 10 mL of hydrogen peroxide was added, and reflux was continued overnight. The mixture was cooled and the now white polymer was isolated, washed with water and dried under vacuum at room temperature giving 35.7 g of white rubbery polymer. Unlike the TFE-grafted polymers, this material was found to be insoluble in acetone, THF, and DMSO but soluble in 1,1,2-trichlorotrifluoroethane. ^{19}F NMR (1,1,2-trichlorotrifluoroethane): δ −82.6 (3F), −85.8 (2F), −88.0 and −88.5 (2F), −131.1 (2F) and −144.8 (1F). Proton NMR (1,1,2-trichlorotrifluoroethane) showed peaks at δ 5.8 (assigned to CFH), 4.6 (assigned to H−C−OCF$_2$) in a 1:1 ratio plus a weak peak at 3.9 (assigned to H−C−OH). T_g (DSC): −15.6 °C. Anal. Found: C, 27.84; H, 1.47; F, 53.63. From the % C analysis, it was calculated that 77% of the OH groups were converted to OCF$_2$CHFOC$_3$F$_7$.

References and Notes

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(8) Numerous patents list olefins CH$_2$=CHOR$_f$, where R$_f$ is a fluoroalkyl group, as components in various copolymers, although no examples of the specific copolymers described in this paper have been found. References to copolymers of **4** as a minor component with other fluorinated monomers include: Crawford, G. H.; Low, E. S. U.S. Patent 2975164, 1961 (*Chem. Abstr.* **1961**, 15999f) and British Patent 823974, 1959 (*Chem. Abstr.* **1961**, 9368h). Monomer **4** has been used as a minor component with several comonomers for the production of plastic lenses (Yuzawa, Y. Jpn. Kokai Tokkyo Koho JP 03287201, 1991 (*Chem. Abstr.* **1992**, 201166)).

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