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Homopolymerization and copolymerization studies of $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$. Part VII

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Abstract

The homopolymerization of $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$ (**1**) was carried out successfully using acid catalysts (BF_3, H_2SO_4, H_3PO_4) or a photo-initiated catalyst. In addition, copolymeric materials were produced using Cyracure UVR-6110, a cycloaliphatic diepoxide.

Introduction

The utilization of fluorocarbon sulfonyl fluorides as surface-active agents, ion-exchange resins and in the preparation of strong sulfonic acids continues to make them a subject of considerable interest [1–4]. Polymeric species such as Nafion (E.I. du Pont de Nemours & Co.) are currently employed commercially as ion-exchange resins and in brine electrolysis cells for the production of caustic soda. Solid polymer electrolyte (S.P.E.) fuel cells using Nafion or other fluorinated ionomeric materials have promise for use in electric vehicles [5].

In a previous paper, we reported the synthesis of the epoxide derivative, $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$ (**1**) which contains a fluorinated alkyl sulfonyl fluoride group [6]. Since epoxide resins possess rather unique combinations of properties (low viscosity, easy curing, low shrinkage, high adhesive strengths, high mechanical properties and good chemical resistance [7]), we have examined the homopolymerization of epoxide 1 and its copolymerization with a commercially available diepoxide crosslinking agent. We have obtained results which indicate the incorporation of the low surface energy and refractive index properties of the fluorinated alkyl sulfonyl fluoride group into these polymers.

Experimental

Materials

The sulfonyl fluoride-containing epoxide $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$ (**1**) was prepared according to the literature method [5]. The crosslinking agent, Cyracure UVR-6110, a cycloaliphatic diepoxide and the photoinitiator UVI-6974, a triarylsulfonium hexafluoroantimonate salt, were donated by the Union Carbide Chemicals and Plastics Co.

General procedures

Infrared spectra were obtained as capillary films on potassium bromide plates for liquid samples and as thin films for solid samples. NMR spectra were recorded with a Varian EM390 spectrometer operating at 90 MHz for proton and 84.7 MHz for fluorine resonances. TMS and $CFCl_3$ were used as internal standards. Elemental analyses were determined by Beller Microanalytical Laboratory in Göttingen, Germany. Contact angles were measured with distilled water using a Kayness model 1060 contact angle analyzer on films that were equilibrated at ambient humidity.

Photo-initiated polymerizations were performed using clean glass or brass substrates on which films of nominally 15 μm wet thickness were cast using a No. 10 Meyer rod. The coated substrates were irradiated in a horizontal position using a 450 W Hanovia mercury lamp under an aluminum reflector.

Homopolymerization of $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$ with boron trifluoride

Into a 10 ml round-bottom flask containing a Teflon-coated stirring bar and fitted with a septum cap was added 0.91 g (3.6 mmol) of $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$. After purging the vessel with dry nitrogen, gaseous BF_3 (5 ml) was injected via a gas syringe into the vessel while stirring the contents. Continued stirring for 5 min resulted in a thickening of the contents to which an additional amount of BF_3 (5 ml) was added.

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Stirring ceased after 30 min due to the viscosity of the contents. The flask was evacuated for 18 h to a final pressure of *ca.* 5 μmHg resulting in 0.89 g of a dark brown viscous liquid.

A portion (0.23 g) of the crude product was taken up in 2 ml of methylene chloride and washed five times with 2 ml of distilled water. The light honey-colored product was again placed under vacuum for 2.5 d to give 0.21 g of a nearly colorless viscous product in an 89% overall yield.

The infrared spectrum of $[CH_2CH(CH_2OCF_2CF_2SO_2F)O]_n$ exhibited the following bands (cm^{-1}): 2966, 2924, 2899 (w); 1455 (vs); 1406 (w); 1335 (s); 1244 (vs with sh at 1270); 1202 (vs); 1138 (vs); 1117 (vs); 1040 (m); 1005 (s); 995 (w); 815 (s); 794 (s); 653 (s); 611 (s).

The ^1H NMR spectrum in $CDCl_3$ showed two broad unresolved resonances (*c.* 40 Hz) at δ 4.3 ppm and δ 3.7 ppm downfield from TMS. In the ^{19}F NMR spectrum, resonances were present at δ 43.5 ppm downfield and δ 85.6 ppm and δ 112.1 ppm upfield from $CFCl_3$ with relative intensities of 1:2:2, respectively. Again, no coupling could be observed in the resonances which all had line widths of *c.* 50 Hz. (Analysis: Calc. for $[CH_2CH(CH_2OCF_2CF_2SO_2F)O]_n$: C, 23.45; H, 1.97; F, 37.1; S, 12.52%. Found: C, 23.53; H, 2.01; F, 36.6; S, 12.37%). The refractive index measured at 21 °C was 1.3847.

Homopolymerization of $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$ with H_2SO_4

To a 10 ml round-bottom flask containing a Teflon-coated stirring bar and fitted with a reflux condenser topped by a $CaCl_2$ drying tube was added 0.24 g of $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$ (0.94 mmol), 3.0 ml of CH_2Cl_2 and three drops of concentrated sulfuric acid. After heating to reflux with stirring for 2 h, the contents were cooled and washed ten times with 2 ml of distilled water. Removal of the CH_2Cl_2 via vacuum transfer resulted in 0.20 g of a honey-colored polymer in an 83% yield.

The NMR and infrared spectra were identical to those listed above. The refractive index measured at 21 °C was 1.3976.

Homopolymerization of $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$ with H_3PO_4

A mixture consisting of 0.75 g of $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$ (0.29 mmol) and 0.70 g of 83% phosphoric acid was stirred at 70–80 °C for 18 h in a 25 ml round-bottom flask containing a Teflon-coated stirring bar. The reaction mixture was added to 5 ml of distilled water and extracted twice with 25 ml of diethyl ether. Removal of the solvent and drying over anhydrous sodium sulfate resulted in 0.70 g of the viscous polymer in *c.* 100% yield.

The NMR and infrared spectra were identical to those listed above.

Homopolymerization of $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$ with photo-initiator UVI-6974

On a large clean watch glass was placed 0.88 g of $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$ (3.4 mmol) containing 2% by weight of photo-initiator UVI-6974. The sample was irradiated for 20 min with frequent swirling. The dark viscous product was taken up in 5 ml of CH_2Cl_2, washed five times with 3 ml of distilled water and placed under vacuum. A 0.81 g quantity (92% yield) of a honey-colored viscous liquid was obtained.

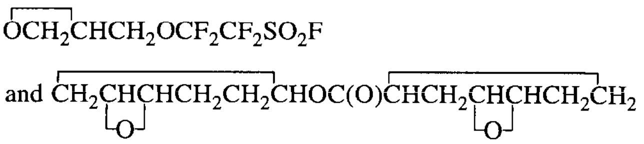
The NMR and infrared spectra were identical to those above. The refractive index measured at 21 °C was 1.3854.

Copolymerization of $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$ and Cyracure UVR-6110

Mixtures of Cyracure UVR-6110 and $\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$, containing 3–4% by weight of photo-initiator UVI-6974, were prepared in the ratios listed in Table 1. The cast films were irradiated for 2 min.

Infrared spectra of the copolymer films peeled from the glass substrates showed distinct bands at 3450, 1729 and 864 cm^{-1} which varied in intensity with composition. Also found were bands overlapping with the homopolymer **2** at 1455, 1398, 1363, 1258, 1181, 1089, 920 and 660 cm^{-1}. Subtraction of the bands attributable to the Cyracure UVR-6110 homopolymer resulted in spectra identical to homopolymer **2** listed above.

TABLE 1. Contact angles of distilled water on polymeric films composed of



$\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F$

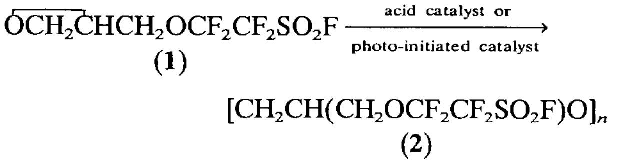
and $CH_2CHCHCH_2CH_2CHOC(O)CHCH_2CHCHCH_2CH_2$

Film sample	Composition (wt.% of **1**)	Contact angle (°)[a]	Optical clarity
A	67	66(2)	opaque
B	60	65(1)	opaque
C	50	66(1)	slightly opaque
D	33	65(2)	clear
E	17	63(1)	clear
F	0	41(0)	clear

[a] Average of three measurements (std. dev.).

Results and discussion

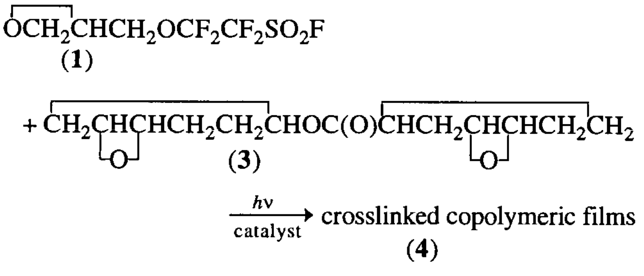
We have found that compound **1** undergoes cationic ring-opening polymerization in the presence of mineral acids, a Lewis acid and a photo-initiated catalyst to give viscous liquid polymers in very good yield.



$$\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F \xrightarrow[\text{photo-initiated catalyst}]{\text{acid catalyst or}} [CH_2CH(CH_2OCF_2CF_2SO_2F)O]_n$$

(1) (2)

Furthermore, photo-initiated-catalyzed copolymerization with Cyracure UVR-6110, a commercially available cycloaliphatic diepoxide **3**, gives copolymeric film coatings which can be formed *in situ*.



$$\overline{OCH_2C}HCH_2OCF_2CF_2SO_2F + \overline{CH_2CHCHCH_2CH_2C}HOC(O)\overline{CHCH_2CHCHCH_2CH_2} \xrightarrow[\text{catalyst}]{h\nu} \text{crosslinked copolymeric films}$$

(1) (3) (4)

The ^1H NMR spectrum of **2** consisted of two broad unresolved resonances at δ 4.3 ppm and δ 3.7 ppm downfield from TMS with linewidths of *c.* 40 MHz. This agrees closely with the corresponding spectra of derivatives of the epichlorohydrin polymers $[CH_2CH(CH_2Cl)O]_n$, where the polymer chain proton resonances appear as two broad unresolved bands at *c.* δ 4–3.5 ppm [8]. Also, characteristic epoxide absorbances [9] present in the infrared spectrum of **1** (3016, 907 and 764) were absent from the IR spectra of both the homopolymer **2** and copolymers **4**.

Polymerization of comonomers with sites of differing hydrophobicity often leads to phase separation [10]. The results listed in Table 1 indicate that phase separation may be occurring in the copolymeric films produced. Films D and E, containing lower proportions of **1**, were transparent and indicated that no major phase separation had occurred between the fluorinated and cycloaliphatic components. Films A and B, on the other hand, were opaque with film C being only slightly opaque. Analyses of the contact angle measurements show that all the copolymeric films possessed lower surface energies than film F which contained no fluorinated copolymer. A possible explanation is that in films D and E polymerization leads to a single phase in the bulk of the product and that the fluorinated groups are oriented along the air interface at the surface. In films A and B, phase separation is occurring in the bulk resulting in a significant loss of optical clarity.

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