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Synthesis and properties of poly[3-chloromethyl-3-(1,1,2,2-tetrahydro-perfluoro-octyl-oxy)methyl oxetane]

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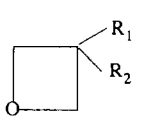
Abstract

The synthesis of poly[3-chloromethyl-3-(1,1,2,2-tetrahydro-perfluoro-octyl-oxy)methyl oxetane] has been performed in four steps. Chlorination of pentaerythritol produced a mixture of halogenated alcohols, which, in an alkaline medium, led to a mixture of hydroxylated and chlorinated oxetanes. Of these, the bis(3-chloromethyl) oxetane (BCMO) was etherified with $C_6F_{13}C_2H_4OH$ via phase-transfer catalysis to yield the mono- and di-substituted fluorinated oxetanes. In a last step, the mono-substituted oxetane was cationically polymerized using $BF_3 \cdot OEt_2$ as the catalyst, and was characterized by ^1H and ^{13}C NMR spectroscopy. Finally, several physical properties have been determined such as the viscosity, glass transition and decomposition temperatures, and surface properties.

Introduction

The synthesis and polymerization of halogenated oxetanes have been well known for several years [1–3]. The chlorinated compounds have been mainly studied because of their valuable properties, such as corrosion resistance. Bis(chloromethyl) oxetane (BCMO) has been extensively investigated, particularly its polymerization [4–9] which has led to the development of an industrial product Penton [10–12].

Several oxetanes containing fluorine atoms have been synthesized [13, 14], but such atoms have been introduced mainly on the ring. Furthermore, the substituent in the 3-position has normally been of short chain-length [13, 15, 16], despite the interesting investigations of Vakhlavoma *et al.* [17] who isolated the following oxetanes:

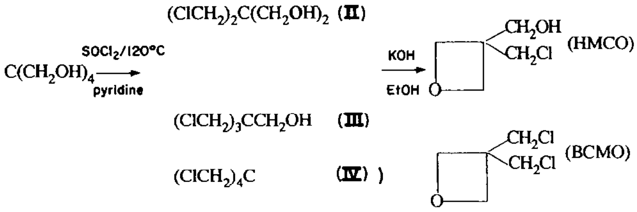


with $R_1 = R_2 = CH_2OCH_2C_2F_4H$ or $R_1 = CH_2Cl$ and $R_2 = CH_2OCH_2C_2F_4H$.

Most fluorinated polyethers which have been synthesized are semi-crystalline solids [11] with poor surface properties. In order to avoid such drawbacks, new oxetanes containing perfluorinated groups (e.g. C_6F_{13} and C_8F_{17}) have been prepared by chemical modification of bis(chloromethyl) oxetane. In this paper, the synthesis and cationic polymerization of such fluorinated cyclic ethers, and their physical properties are presented.

Results and discussion

The synthesis and cationic polymerization of the new fluorinated oxetanes were performed in four steps as summarized below. Synthesis of chlorinated and/or hydroxylated oxetanes was carried out by chlorination of pentaerythritol, followed by the cyclization of the chlorinated alcohols in an alkaline medium:



The amounts of each product were determined by the initial $[SOCl_2]/[C(CH_2OH)_4]$ molar ratio (R_0) employed. After optimization, the best conditions were obtained for $R_0 = 3$, which produced 10, 75, 8 and 0% of the chlorinated products **IV**, **III**, **II** and **I**, respectively [18].

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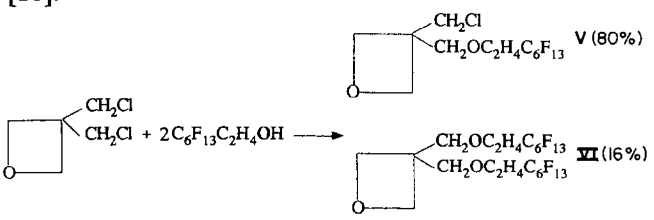
TABLE 1. Polymerization of 3-chloromethyl-3-(1,1,2,2-tetrahydro-perfluoro-octyl-oxy)methyl oxetane and the physical properties of the corresponding oligomers

$\frac{[BF_3\cdot OEt_2]}{[\text{oxetane}]}$	% Oxetane conversion	$\overline{DP}_n$	$\overline{M}_n$	T_g (°C)	η (dl g^{-1})	γ_s (dyn cm^{-1})
10:1	75	6	3000	−45	0.0225	14
7:1	87	8	3900	−40	0.0259	12

The oxetanes were obtained by cyclization of the chlorinated alcohols with yields higher than 80%. It is best to cyclize the mixture of halogenated alcohols before distilling the oxetanes, rather than purifying the alcohols before their cyclization. 2,6-Dioxaspiro-[2,3]heptane produced by cyclization of 3-(hydroxymethyl)-3-chloromethyl oxetane (HMCO) was only obtained in low yield.

Bis(chloromethyl) oxetane (BCMO) was obtained with very high purity. Its ^{1}H NMR spectrum exhibits two singlets at 4.44 and 3.93 ppm, characteristic of the cyclic methylene group and that of the substituent, respectively. In the ^{13}C NMR spectrum, the signal for the quaternary carbon is at 45.60 ppm and signals at 76.51 and 46.61 ppm correspond to the cyclic and substituted methylene groups, respectively.

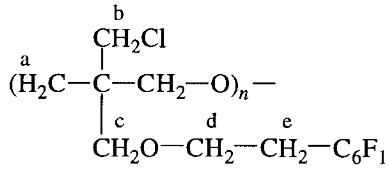
Synthesis of the fluorinated oxetanes was carried out by phase-transfer catalysis in the presence of tetrabutylammonium hydrogen sulphate (TBAH), as follows [18]:



The monochloroperfluoro oxetane **V** was purified by distillation and was characterized by ^{19}F, ^{13}C and ^{1}H NMR spectroscopy [18] (see Experimental section).

Cationic polymerization was performed at −15 °C in dried methylene chloride using 7–10% of $BF_3\cdot OEt_2$ as catalyst (Table 1) and was stopped by adding methanol and then left to stir for 10 min at room temperature. After evaporation of the solvent and volatile compounds, the product was dried under vacuum to constant weight. The resulting polymer was very viscous and its GPC chromatogram exhibited a sharp peak centred at 14.2 ml (whereas that of the monomer appeared at 21.1 ml under the same chromatographic conditions). This shows that an oligomer was produced. As expected, the lower the catalyst/monomer molar ratio, the higher the molecular weight.

The ^{1}H NMR spectrum of the oligomer showed the absence of the singlet at 4.4 ppm, which confirms that ring-opening had occurred. The different signals observed for the oligomer so formed may be explained as follows:



$$(\overset{a}{H_2C}-\overset{\overset{b}{CH_2Cl}}{\underset{\underset{c\quad\ d\quad\ e}{CH_2O-CH_2-CH_2-C_6F_{13}}}{C}}-CH_2-O)_n-$$

^{1}H NMR	a	b	c	d	e
δ (ppm)	3.30	3.60	3.45	3.75	2.40
Signal shape	d	s	t	dt	m

The physical properties of the oligomers prepared are collected in Table 1.

The intrinsic viscosities determined in chloroform were 0.0225–0.0259 dl g^{-1}, confirming the low molecular weight which was also demonstrated by hydroxy end-group titration ($\overline{M}_n$ = 3000–4000 g mol^{-1}). The glass transition temperatures of such oligomers were *c.* −40 °C, whereas that of the poly[3,3-bis(chloromethyl) oxetane] polymerized under the same conditions was +14 °C. The fluorinated compound started to decompose from 200 °C with total decomposition at 350 °C. The measured surface tensions were *c.* 13 dyn cm^{-1} as would be expected for a polymer with a long perfluorinated chain.

Experimental

General comments

Pentaerythritol was purchased from Aldrich and was used without further purification. 1,1,2,2-Tetrahydro-perfluoro-octanol was kindly supplied by Elf Atochem.

After reaction, the products were worked-up and analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with an FFAP column, 1 m × 1/8 in. (i.d.). The nitrogen pressure at the entrance to the column was maintained at 0.6 bar, and the detector and injector temperatures were 260 °C and 255 °C, respectively. The temperature program started from 50 °C and attained 220 °C at a heating rate of

15 °C min^{-1}. The GC apparatus was connected to a Hewlett Packard integrator (model 3390) which automatically calculated the area of each peak on the chromatogram.

The products were analyzed at the CNRS Microanalysis Laboratory of ENSCM and characterized by ^{1}H, ^{19}F and ^{13}C NMR spectroscopy, all undertaken at room temperature. The ^{19}F and ^{1}H NMR spectra were recorded on a Bruker CW 60 apparatus, with $CFCl_3$ and TMS as internal references, respectively, or at higher resolution on a Bruker AC 250 or Bruker WM 360 instrument, using deuterated chloroform as the solvent and the internal reference. The letters s, d, t, q and m designate singlet, doublet, triplet, quartet and multiplet, respectively. The ^{13}C NMR spectra were performed on a Bruker WP 80 apparatus and the compounds were usually diluted in $CDCl_3$ (reference).

Polymerizations were monitored by gel permeation chromatography (GPC) using a Waters Associates M 590 apparatus equipped with a set of four Styragel columns whose pore diameters were 100, 100, 500 and 1000 Å, respectively. THF was used as the eluent (flow rate, 1.5 ml min^{-1} at 30 °C). The detector was a Waters R 401 Series differential refractometer.

Intrinsic viscosities were calculated from an automatic capillary viscometer AMTEC. The hydroxy end-groups were titrated by acetylation with an acetic anhydride/pyridine mixture. Differential scanning calorimetry (DSC) measurements were conducted with a Perkin-Elmer DSC-4 apparatus equipped with a TADS microcomputer; the apparatus was calibrated with indium and with n-decane. After insertion into the DSC apparatus, the sample was first cooled to −100 °C for 15 min. A first scan was made at a heating rate of 40 °C min^{-1} up to 100 °C, where the sample was held for 2 min. It was then quenched to −100 °C at a cooling rate of 320 °C min^{-1}, and again left for 10 min at that temperature before a second scan at a heating rate of 20 °C min^{-1} was taken. This gave the T_g values reported in this paper, taken at the half-height of the jump in the heat capacity at the glass transition. Thermogravimetric analysis curves were executed with a TGS 2 Perkin-Elmer apparatus at a heating rate of 10 °C min^{-1}.

Surface property measurements were determined from samples prepared by spin-coating on a microscope slide from a dilute solution of the fluorinated oligomer in chloroform (0.5–1.0 g l^{-1}) (thickness c. 50 μm). The contact angle of a drop of a polar (water) or non-polar (di-iodomethane) liquid on the film was measured using an ERMA contact angle goniometer at 25 °C. Fowkes' law [19] was applied to calculate the dispersive and polar components, the sum of which led to values of the superficial surface energy γ_s.

Synthesis of chlorinated polyols

The chlorination of pentaerythritol was performed according to the method developed by Mooradian and Cloke [2]. The addition of 3 mol (357 g) of thionyl chloride to 1 mol (136 g) of pentaerythritol stirred with 3 mol (237 g) of pyridine was carried out in a three-necked round-bottom flask equipped with a condenser and a mechanical stirrer. The first third of the thionyl chloride was added dropwise and the rest was added quickly. The mixture was refluxed for at least 14 h to ensure that no sulphur dioxide remained in the reaction medium. The pyridinium salt and unreacted pentaerythritol were extracted three times with water. The organic phase was dried over magnesium sulphate and after filtration the orange-coloured liquid remaining was distilled.

2,2-Bis(chloromethyl)-1,3-propanediol (II): b.p. 95–99 °C/0.01 Torr, m.p. 80 °C (white crystals). [Analysis: Found: C, 35.03; H, 5.96; Cl, 40.52%. $C_5H_{10}O_2Cl_2$ (F.W. 173.04) requires: C, 34.71; H, 5.82: Cl, 40.98%]. ^{1}H NMR ($CDCl_3$) δ: 3.64 (s, 2H); 3.75 (s, 2H); 3.95 (s, 2H) ppm, the latter signal being shifted with Cl_3CNCO. ^{13}C NMR (CD_3OD) δ: 45.25; 47.39; and 61.31 ppm.

2,2-Bis(chloromethyl)-3-chloropropanol (III): b.p. 80–83 °C/0.01 Torr, m.p. 64 °C (white crystals). [Analysis: Found: C, 31.72: H, 4.89; Cl, 55.12%. $C_5H_9Cl_3O$ (F.W. 191.48) requires: C, 31.36; H, 4.74; Cl, 55.54%]. ^{1}H NMR ($CDCl_3$) δ: 3.64 (s, 6H); 3.72 (s, 2H) ppm. ^{13}C NMR (CD_3OD) δ: 43.95; 46.45; and 60.58 ppm.

2,2-Bis(chloromethyl)-1,3-dichloropropane (IV): b.p. 65–67 °C/0.01 Torr, m.p. 93 °C (white crystals). [Analysis: Found: C, 29.04; H, 3.97; Cl, 67.09%. $C_5H_8Cl_4$ (F.W. 209.93) requires: C, 28.61; H, 3.84; Cl, 67.55%]. ^{1}H NMR ($CDCl_3$) δ: 3.65 (s) ppm. ^{13}C NMR ($CDCl_3$) δ: 43.46; and 44.00 ppm.

Synthesis of non-fluorinated oxetanes

These oxetanes were obtained from the cyclization of the corresponding chlorinated alcohols by refluxing with an equimolar ratio of potassium hydroxide in 6 mol of ethanol for 5 h. After filtration of potassium chloride and evaporation of the ethanol, the oxetanes were distilled. The yields obtained were greater than 80%.

3,3-Bis(chloromethyl) oxetane (BCMO): b.p. 40–43 °C/0.05 Torr (colourless liquid). [Analysis: Found: C, 43.53; H, 5.89; Cl, 32.08%. $C_5H_8O_2Cl_2$ (F.W. 139.02) requires: C, 43.20; H, 5.80; Cl, 32.35%]. ^{1}H NMR ($CDCl_3$) δ: 3.93 (s, 4H); 4.44 (s, 4H) ppm. ^{13}C NMR ($CDCl_3$) δ: 45.60; 46.61; and 76.51 ppm.

3-(Hydroxymethyl)-3-chloromethyl oxetane (HMCO): b.p. 72–76 °C/0.05 Torr (colourless liquid). ^{1}H NMR ($CDCl_3$) δ: 3.76 (s, 4H); 4.36 (s, 4H); 4.71 (s, 1H) ppm, the latter signal being shifted on dilution.

^{13}C NMR ($CDCl_3$) δ: 45.63; 46.69; 63.37; and 76.70 ppm.

2,6-Dioxaspiro[2,3]heptane (obtained as white crystals from the cyclization of HMCO): b.p. 62–66 °C/0.1 Torr. [Analysis: Found: C, 60.19; H, 7.91%. $C_5H_8O_2$ (F.W. 100.12) requires: C, 59.98; H, 8.05%]. ^{1}H NMR (CCl_4) δ: 4.65 (s) ppm. ^{13}C NMR ($CDCl_3$) δ: 43.62; and 80.25 ppm.

3,3-Bis(hydroxymethyl) oxetane (BHMO): b.p. 109–114 °C/0.01 Torr, m.p. 75 °C. ^{1}H NMR (CD_3OD) δ: 3.28 (s, 4H); 4.00 (s, 4H); 4.32 (s, 2H) ppm, the latter signal being shifted with Cl_3CNCO. ^{13}C NMR (CD_3OD) δ: 46.70; 64.14; and 76.65 ppm.

The syntheses of the above oxetanes were also performed by cyclization of a mixture of the chlorinated alcohols under similar conditions.

Synthesis of fluorinated oxetanes

In a 250 ml three-necked round-bottom flask, equipped with a condenser and a mechanical stirrer, was placed a mixture consisting of 0.13 mol (20 g) of 3,3-bis(chloromethyl) oxetane (BCMO), 0.26 mol (95 g) of $C_6F_{13}C_2H_4OH$, 0.026 mol (9 g) of tetrabutylammonium hydrogen sulphate and 150 ml of 20 N NaOH and stirred for 10 h at 70 °C. After cooling, 300 ml of methylene chloride was added. The mixture was washed several times with water and the organic phase was concentrated and distilled. The conversion of BCMO was quantitative.

3-Chloromethyl-3-(1,1,2,2-tetrahydro-perfluoro-octyloxy)methyl oxetane (V): b.p. 85–87 °C/0.02 Torr (clear yellow liquid). [Analysis: Found: C, 32.56: H, 2.64; Cl, 7.08; F, 51.58%. $C_{13}H_{12}F_{13}ClO_2$ (F.W. 482.67) requires: C, 32.35; H, 2.51; Cl, 7.35; F, 51.17%]. ^{1}H NMR ($CDCl_3$) δ: 2.37 (m, 2H, $J = 18.6$ Hz, $J = 6.5$ Hz); 3.74 (s, 2H); 3.77 (t, 2H, $J = 6.5$ Hz); 3.83 (s, 2H); 4.42 (s, 4H) ppm. ^{13}C NMR (CD_3OD) δ: 31.34; 44.60; 46.54; 63.27; 71.74; 76.19; 90–135 ppm. ^{19}F NMR ($CDCl_3$) δ: −82.20; −113.28; −122.25; −123.34; −124.02; and −126.29 ppm.

Residue (obtained after chromatography over silica): ^{1}H NMR ($CDCl_3$) δ: 2.38 (m, 2H, $J = 18.7$ Hz, $J = 6.5$ Hz); 3.74 (s, 2H); 3.77 (t, 2H, $J = 6.5$ Hz); 4.42 (s, 4H) ppm. ^{13}C NMR ($CDCl_3$) δ: 31.96; 44.48; 63.39; 71.85; 76.35; 90–135 ppm. ^{19}F NMR ($CDCl_3$) δ: −82.52; −113.49; −122.15; −123.10; −123.85; and −126.42 ppm.

Polymerization of fluorinated oxetanes

Methylene chloride and the fluorinated oxetane were dried over calcium hydride for *c.* 8 h and then distilled under nitrogen prior to use. Polymerizations of these oxetanes were performed in a one-necked round-bottom flask equipped with a three-way valve covered with a septum connected to a vacuum line and to a nitrogen flow.

First, 10 ml of solvent were introduced into the flask by means of a pipette, followed by 0.02 mol (10 g) of oxetane **V**. The flask was immersed in cold acetone at −15 °C, the contents stirred magnetically and 0.0021 mol of $BF_3 \cdot OEt_2$ introduced via a syringe under nitrogen.

The reaction medium was kept at −15 °C for 6–8 h and then left to stir up to room temperature over *c.* 10 h. Termination was performed by adding methanol. After evaporation of the solvent, the oligomer was dried under vacuum to constant weight. The poly[3-chloromethyl-3-(1,1,2,2-tetrahydro-perfluoro-octyl-oxy)methyl oxetane] was a sticky orange wax whose physical properties are listed in Table 1. ^{1}H NMR ($CDCl_3$) δ: 2.40 (m, 2H); 3.30 (d, 4H); 3.45 (t, 2H); 3.60 (s, 2H); 3.75 (dt, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 31.45; 44.75; 46.62; 63.54; 71.59; 76.25; 90–135 ppm. ^{19}F NMR ($CDCl_3$) δ: −83.02; −113.51; −122.18; −123.19; −124.10; −126.59 ppm.

Conclusions

The synthesis of new fluorinated oxetanes can be achieved by etherification of 3,3-bis(chloromethyl) oxetane with commercially available fluorinated alcohols. The synthesis is quite rapid and leads to high yields. Such oxetanes can be polymerized with $BF_3 \cdot OEt_2$ to produce low molecular weight polymers. Good surface properties and normal thermostability allow these compounds to be used in interesting applications such as polyurethane or polyester coatings which are under investigation.

Acknowledgments

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