Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 44 (2003) 6431–6434

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Synthesis and characterization of new fluorine-containing polyethers

John W. Fitch[a], Emilio Bucio[a,1], Lymari Martinez[a], Javier Macossay[a,2], Sreenu R. Venumbaka[a,*], Norman Dean[a,3], Diane Stoakley[b], Patrick E. Cassidy[a,*]

[a]*Shell Center for Polymer Science and Technology, Institute for Environmental and Industrial Science, Southwest Texas State University, San Marcos, TX 78666, USA*
[b]*NASA Langley Research Center, Hampton, VA 23681, USA*

Received 7 May 2003; received in revised form 4 August 2003; accepted 5 August 2003

Abstract

A highly fluorinated monomer, 1,3-bis(1,1,1,3,3,3-hexafluoro-2-pentafluorophenylmethoxy-2-propyl)benzene (12F-FBE), is obtained by reaction of the sodium salt of 1,3-bis(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)benzene with pentafluorobenzyl bromide. 12F-FBE reacts with diphenols to give soluble, hydrophobic, low dielectric (2.30–2.43 at 10 GHz) polyethers. Thermal stability as measured by TGA (10 wt% loss) is moderate and ranges from 445 to 464 °C in air. Glass transition temperatures are between 89 and 110 °C.

Keywords: Fluoropolymers; Low dielectrics; Polyethers

1. Introduction

Polymers containing the hexafluoroisopropylidene (HFIP) group are known to exhibit excellent properties such as increased solubility, flame resistance and thermo-oxidative stability along with decreased color, crystallinity, dielectric constant and water absorption. For this reason they have received extensive study and have been the subject of several reviews [1–3]. Most of the reported work relates to compounds in which the HFIP group is incorporated into the polymer backbone and is flanked by aromatic groups [1,2]. Considerably less work has been devoted to the preparation and characterization of polymers derived from hexafluoro-2-hydroxy-2-propylarenes such as 1,3- or 1,4-bis(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)-benzene (1,3- or 1,4-HFAB) [3].

Direct reaction of 1,3- or 1,4-HFAB in polycondensation reactions usually leads to the formation of low molecular weight polymers and oligomers due to the very poor nucleophilicity of the fluorinated alcohol or its derived alkoxy anion [4–7]. For this reason, much of the reported work involving HFABs has been on systems in which the hindered, electron-deficient hydroxyl groups have been first converted to more reactive species, such as conversion to acrylate or epoxy functions for example. This strategy has led to the preparation of reactive epoxy monomers, which yield tough, chemically resistant resins that are characteristically water repellant [8–19]. Conversion of hexafluoro-2-hydroxy-2-propylarenes to acrylate derivatives has also led to a variety of hydrophobic polymers [20–25]. Recently, we have prepared a new 1,3-HFAB-derived monomer, 1,3-bis(1,1,1,3,3,3-hexafluoro-2-pentafluorophenylmethoxy-2-propyl)benzene, 12F-FBE, which reacts readily with diphenols to give water repellant, low dielectric polyethers. We report the preparation and characterization of these materials at this time.

---

[*] Corresponding authors. Tel.: +1-512-245-2672; fax: +1-512-245-1892.

E-mail addresses: reddy@swt.edu (S.R. Venumbaka), pc03@swt.edu (P.E. Cassidy).

[1] Present address: Instituto de Ciencias Nucleares-UNAM, Ciudad Universitaria, 04510 Mexico, D.F., Mexico.

[2] Present address: Facultad de Ciencias Quimicas, Division de Estudios Superiores, Universidad Autonoma de Nuevo Leon, Apdo. Postal 1864 Monterrey, N.L., Mexico.

[3] Present address: Department of Chemistry, California State University Northridge, Northridge CA, USA.

0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00734-1

2. Experimental

2.1. Materials

Bisphenol AF, bisphenol F, bisphenol O, and 1,3-bis-(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl) benzene (1,3-HFAB) were kindly supplied by Central Glass, Japan. Bisphenol A, biphenol, *N*,*N*-dimethylacetamide (DMAc), and sodium hydride were obtained from Aldrich, and 2,3,4,5,6-pentafluorobenzylbromide was obtained from Oakwood Products, Inc. The diphenols were sublimed before use.

2.2. Measurements

^{19}F NMR spectra, which were observed at 282 MHz using a 300 MHz Varian Unity Plus Spectrometer, were referenced to Freon-11. Water absorption measurement was done gravimetrically; the films were immersed in water at room temperature for 24 h and then weighed. Sessile drop water contact angles were measured at ambient temperature using a Tantec CAM-Micro instrument. Thermogravimetric measurements were obtained using a Rheometric Scientific Model TGA 1000M instrument. Differential scanning calorimetry results were obtained using a Rheometric Scientific Model DSC Plus instrument. Gel permeation chromatography (GPC) was performed at 30 °C in tetrahydrofuron using Styragel HR5E and HR4E columns after calibration with standard polystyrene samples. Elemental analysis was performed by Desert Analytics of Tucson, Arizona, USA.

2.3. Synthesis of 1,3-bis(1,1,1,3,3,3-hexafluoro-2-pentafluorophenylmethoxy-2-propyl)benzene, 12F-FBE

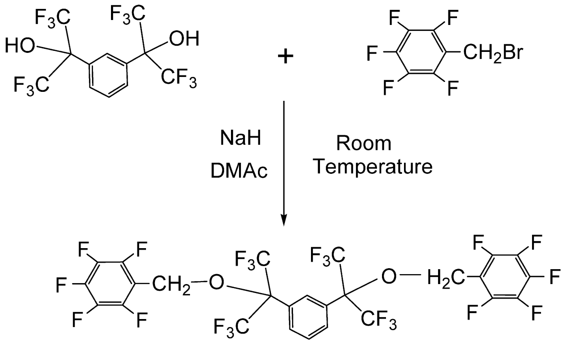
Sodium hydride (60% dispersion in oil) (2.68 g/1.61 g NaH, 0.067 mol) was freed of oil with dry hexane and was added to 70 ml of dry DMAc. The mixture was magnetically stirred, and 1,3-HFAB (11.0 g, 0.027 mol) was slowly added by syringe. The reaction was allowed to stir for 3 h. Pentafluorobenzyl bromide (15.4 g, 8.90 ml) was added rapidly to the reaction which was left stirring at room temperature overnight. The reaction mixture was then poured into 600 ml of stirring water. The water was extracted with 600 ml of diethylether (in three steps). Finally, the combined ether extract was washed three times with 175 ml of water, dried over magnesium sulfate and then evaporated under vacuum. The residue was taken up in hexane and cooled overnight at 0 °C to give white crystalline 12F-FBE (mp = 84.5–85.5 °C after drying at 40 °C in vacuo) in 91% yield (18.96 g). Anal. found: C, 40.43; H, 1.16. $C_{26}H_8F_{22}O_2$ calcd: C, 40.52; H, 1.04%.

2.4. Polymer synthesis

The diphenol (2.43 mmol) and potassium carbonate (0.6728 g, 4.87 mmol) were added to a mixture of 18 ml DMAc and 15 ml toluene in a round-bottom flask fitted with a Dean–Stark trap. The reaction was heated at reflux until no further water was collected in the trap. The toluene was removed by distillation, and the solution was cooled to room temperature. The monomer, 12F-FBE, (1.875 g, 2.43 mmol) was added, and the reaction was stirred at the appropriate temperature (40 °C for polymers **1**–**4**; 50 °C for **5**) for 24 h. The reaction mixture was cooled and poured into 500 ml of rapidly stirred water. The white fibrous polymer obtained was collected, dried, dissolved in chloroform and reprecipitated into methanol. After filtration the polymer was dried in vacuo for 15 h.

3. Results and discussion

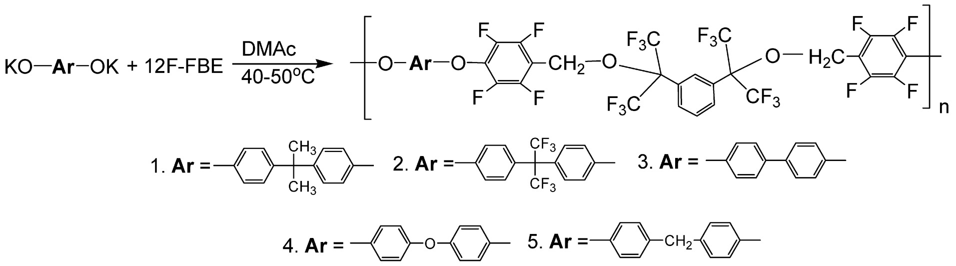
The new highly fluorinated monomer, 1,3-bis(1,1,1,3,3,3-hexafluoro-2-pentafluorophenylmethoxy-2-propyl)benzene, 12F-FBE, has been prepared in excellent yield from 1,3-HFAB and pentafluorobenzylbromide (Eq. (1)). The ^{19}F NMR spectrum of 12F-FBE is characterized by the three aromatic fluorine resonances centered at − 142.7 (4F, d), − 151.9 (2F, t) and − 161.7 (4F, m) ppm which are assigned, respectively, to the fluorine atoms which are *o*-, *p*- and *m*- to the $-CH_2$-groups in the monomer



(1)

12F-FBE

Polyethers were prepared as outlined in Eq. (2). Solutions of preformed potassium salts of the diphenols were reacted with 12F-FBE at 40–50 °C. Reaction at the higher temperatures customarily employed in aromatic nucleophilic displacement polymerizations [26] resulted in the formation of insoluble materials, which likely result from crosslinking. The orientation of fluorine displacement in the polymers was confirmed by the ^{19}F NMR spectrum of polymer **2**, which is characterized by two resonance signals of equal intensity in the aromatic region. The signal assigned to the *o*-fluorine atoms in the monomer remains essentially unchanged at − 142.9 ppm; however, the resonance assigned to the *m*-fluorines in the monomer is shifted to − 153.8 ppm in the polymer. Both resonance signals exist as doublets to the first order as expected for the proposed polymer structure (Eq. (2))

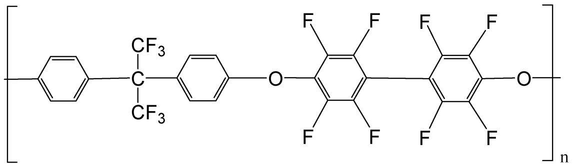


(2)

All of the polymers exhibit excellent solubility in common organic solvents from which clear, colorless, creasable films can be readily cast. Sessile drop water contact angles for these polymers ranged from 90 to 93° (Table 1), and film samples showed no measurable water absorption even after being submerged at room temperature for 24 h. The hydrophobic properties of the polymers are as expected from their high fluorine content; similar results have been reported for other polymers derived from HFAB [3].

Inherent viscosity values for polymers **1**–**4** range from 0.30 to 0.33 dl g^{-1} and M_w values range from 200 to 247 K with polydispersity values between 2.6 and 3.4. Polymer **5** exhibited a lower inherent viscosity of 0.20 dl g^{-1} which corresponded to a M_w of 64.1 K and a narrower molecular weight distribution (PD = 1.8). However, even at this lower molecular weight value, the properties of polymer **5** are comparable to those of polymers **1**–**4**.

The dielectric constants of the polyethers were uniformly low, measuring from 2.30 for **2** to 2.43 for **1** (Table 1). Excellent dielectric properties are expected of highly fluorinated polyethers and have been observed before for derivatives of decafluoro biphenol such as **6** [27–29].



6

Thermal decomposition temperatures of **1**–**5** (10 wt% loss) are as expected for a fluorinated polyether containing a methylene group in the backbone (Table 2). Decomposition temperatures in argon range from 445 °C for **5** to 464 °C for **1**, whereas **2** exhibits the greatest stability in air (10 wt% loss temperature = 456 °C) as measured by TGA. It is most interesting that in several cases the TGA data are similar (different by only 30 °C) or identical. This speaks either to the thermo-oxidative stability of these polymers or to the fact that the thermal weak link is in the 12F-FBE moiety in the backbone. Glass transition temperatures for the new polyethers are all considerably lower than observed for polymers such as **6** (T_g = 179 °C) [28] reflecting the greater flexibility of the monomer 12F-FBE incorporated into the current series of polyethers.

4. Conclusions

A new highly fluorinated monomer, 12F-FBE, has been prepared and characterized. Reaction of it with diphenols yields soluble low dielectric polyethers which show negligible water absorption. The new polymers have T_g values near 100 °C and exhibit moderate thermal stability in that the decomposition temperature ranges from 420 °C for **3** to 456 °C for **2**, the most stable polymer in air.

Acknowledgements

The authors wish to thank the National Aeronautics and Space Administration-Langley Research center, for financial support of this research. Also, the authors thank the National University of Mexico-DGAPA for financial support for Dr Bucio.

Table 1
Selected physical properties of polyethers

Polyether	η_{inh} ($CHCl_3$, dl g^{-1})	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	PD	Water contact angle (± 2°)	Dielectric constant (10 GHz)
1	0.30	75	250	3.2	93	2.43
2	0.31	84	220	2.6	91	2.30
3	0.33	66	230	3.4	90	2.40
4	0.32	78	200	2.6	90	2.42
5	0.20	35	64	1.8	92	2.34

Table 2
Thermal properties of polyethers

Polyether	TGA (10 wt% loss, °C)[a]		% Char yield (800 °C, Ar)	T_g (°C)[b]
	Argon	Air		
1	464	436	23	102
2	456	456	12	108
3	451	420	18	110
4	454	435	23	92
5	445	438	27	89

[a] Measured at 20 °C min^{-1}.
[b] Measured at 10 °C min^{-1}.

References

[1] Cassidy PE, Aminabhavi TM, Farley JM. JMS Rev Macromol Chem Phys 1989;C29(2 and 3):365.

[2] Bruma M, Fitch JW, Cassidy PE. JMS Rev Macromol Chem Phys 1996;C36(1):119.

[3] Cassidy PE, Aminabhavi TM, Reddy VS, Fitch JW. Eur Polym J 1995;31:353.

[4] Keller TM. J Polym Sci, Polym Chem Ed 1984;22:2719.

[5] Keller TM. J Polym Sci, Polym Chem Ed 1985;23:2557.

[6] Holmes BS, Keller TM. Polym Prepr 1984;25:338.

[7] Reddy VS, Cassidy PE, Fitch JW, Lunceford BD, Person D. Polymer 1996;37:4873.

[8] Griffith JR, O'Rear JG. Am Chem Soc Div Org Coat Plast Chem Prep 1979;40:781.

[9] O'Rear JG, Griffith JR. Am Chem Soc Div Org Coat Plast Chem Prep 1973;33:657.

[10] O'Rear JG, Griffith JR. US Patent 3,879,430; 1975.

[11] Donald EF, Falls CV, Griffith JR. US Pat. 3,852,222; 1974.

[12] Griffith JR, Field DE, O'Rear JG. Am Chem Soc Div Coat Plast Chem Prep 1974;34:709.

[13] Griffith JR. Canadian Patent 956,398; 1974.

[14] Field DE, Griffith JR. Ind Engng Chem Prod Res Dev 1975;14:52.

[15] Griffith JR, O'Rear JG, Reardon JP. Polym Sci Technol (Adhes Sci Technol) 1975;9A:429.

[16] Griffith JR, O'Rear JG. US Pat. 4,045,408; 1977.

[17] Soulen RL, Griffith JR. J Fluor Chem 1989;44:203.

[18] Brady RF, Sikes AM. Macromolecules 1991;24:688.

[19] Sikes AM, Brady RF. Polym Prepr 1990;31:358.

[20] Griffith JR, O'Rear JG. US Pat. 4,356,296; 1982.

[21] Griffith JR. Am Chem Soc Polym Mater 1984;50:422.

[22] Griffith JR, O'Rear JG. US Pat. 4,578,508; 1986.

[23] Gupta D, Reddy VS, Cassidy PE, Fitch JW. Polymer 1993;34:4173.

[24] Reddy VS, Weikel WJ, Arbaugh J, Fitch JW, Cassidy PE, St. Clair AK. Polymer 1996;37:4653.

[25] Reddy VS, Lunceford BD, Cassidy PE, Fitch JW. Polymer 1997;38:703.

[26] Tullos GL, Cassidy PE, St. Clair AK. Macromolecules 1991;24:6059.

[27] Mercer FW, Goodman TD. Polym Prepr 1991;32:189.

[28] Irvin JA, Neef CJ, Kane KM, Cassidy PE, Tullos G, St. Clair AK. J Polym Sci, Part A: Polym Chem 1992;30:1675.

[29] Mercer F, Duff D, Wojitowiez J, Goodman T. Polym Mater Sci Engng 1992;66:98.