

Novel Waterborne Polyurethanes Containing Short Fluoroalkyl Chains: Synthesis and Applications on Cotton Fabrics

Ming-Jie Zhu,¹ Feng-Ling Qing,^{1,2} Wei-Dong Meng^{1,2}

¹Key Laboratory of Science & Technology of Eco-Textiles (Ministry of Education), Donghua University, Shanghai 201620, People's Republic of China

²Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

Received 29 January 2007; accepted 26 June 2007

DOI 10.1002/app.27929

Published online 30 April 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two novel waterborne polyurethanes containing short fluoroalkyl groups [$-\text{CH}(\text{CF}_3)_2$ and $-\text{CH}_2\text{CF}_2\text{CF}_3$] were designed and synthesized. They were applied as surface modification agents on cotton fabrics. The treated cotton fabrics showed good water-repellent properties, and the contact angles for water were 146° for the fluorinated

polyurethane with the $-\text{CH}_2\text{CF}_2\text{CF}_3$ group and 132° for the fluorinated polyurethane with the $-\text{CH}(\text{CF}_3)_2$ group. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1911–1915, 2008

Key words: polyurethanes; short fluoroalkyl chains; hydrophobicity; cotton fabrics

INTRODUCTION

Fluorinated coatings are the most important class of water- and oil-repellent finishing agents for textiles because of their optimum performance in lowering the surface free energy¹ and improving both hydrophobicity and oleophobicity. Most of them contain long perfluoroalkyl chains ($\text{C}_n\text{F}_{2n+1}$, $n = 6-10$). In recent years, fluorocarbons containing long perfluoroalkyl chains have been facing problems such as persistence, bioaccumulation, and/or toxicity in the environment, and some of them have been banned from the market.² The use of perfluorooctyl-containing surfactants such as perfluorooctane sulfonates (PFOS) and perfluorooctanoic acid (PFOA) is going to be restricted in the international community.³ Thus, much research activity has been focused on searching for alternatives.⁴ Since Thomas et al.⁵ in 2002 prepared oxetane telechelics with short fluoroalkyl side chains (CF_3- or CF_3CF_2-) that showed positive results in surface activity, compounds containing decomposable short perfluoroalkyl chains have received much more attention.^{6,7}

In our previous study,⁸ we synthesized a waterborne polyurethane containing $-\text{CH}_2\text{CF}_3$, which

showed good hydrophobicity when it was applied to cotton fabrics. Continuing that project, we designed and synthesized two novel polyether diols containing $\text{CF}_3\text{CF}_2\text{CH}_2-$ and $(\text{CF}_3)_2\text{CH}-$ side chains (poly[3,3-bis(hexafluoroisopropyl)oxetane] glycol PFOX1 and poly[3,3-bis(pentafluoropropyl)oxetane] glycol PFOX2) on the basis of the ring-opening polymerization of oxetane.⁹ These fluorinated polyether diols were then condensed with isophorone diisocyanate (IPDI) to form fluorinated polyurethanes FPU1 and FPU2. The performance of these fluorinated polyurethanes (FPUs) on textiles was studied with cotton fabric, which is popular in our daily life, as a substrate by a conventional pad-dry-cure process. The treated fabrics showed good and durable water-repellent properties.

EXPERIMENTAL

Materials and instrumentation

Hexafluoroisopropanol was purchased from DuPont China Holding Co., Ltd. (Shanghai, China) Pentafluoropropanol was bought from Meryer Co. (Shanghai, China) Boron trifluoride etherate, diethylene triamine, epichlorohydrin, dibutyltin dilaurate (DBTDL), tetrabutylammonium bromide (TBAB), 2,2-dimethyl-1,3-propanediol, anhydrous magnesium sulfate, sodium hydroxide, sodium bicarbonate, sodium chloride, potassium hydroxide, acetone, acetic acid, tribromoneopentylglycol, and IPDI were used as purchased.

¹H-NMR spectra were recorded on a Bruker AM 300 (300-Hz) spectrometer (Bruker BioSpin AG, Swit-

Correspondence to: W.-D. Meng (wdmeng@dhu.edu.cn).

Contract grant sponsor: Program for Changjiang Scholars and Innovative Research Team in University; contract grant number: IRT0526.

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20325210.

zerland) with Me₄Si as an internal standard. ¹⁹F-NMR spectra were obtained on a Bruker AM 300 (282-Hz) spectrometer with CFCl₃ as the external standard. IR spectra were recorded on a Nicolet 380 Fourier transform infrared (FTIR) spectrometer (Thermo Electron Corporation, Madison, WI, USA). High-resolution mass spectrometry (HRMS) spectra were recorded on a Bruker APEXIII 7.0 instrument (Bruker BioSpin AG, Switzerland) with electrospray ionization (SEI) ionization. The molecular weights of the polyether diols were measured with a Waters 105C gel permeation chromatography instrument (Waters Corporation, Milford, USA) with tetrahydrofuran as the mobile phase.

Synthesis of fluorinated polyether diols

The fluorinated polyether diols were synthesized as shown in Scheme 1.

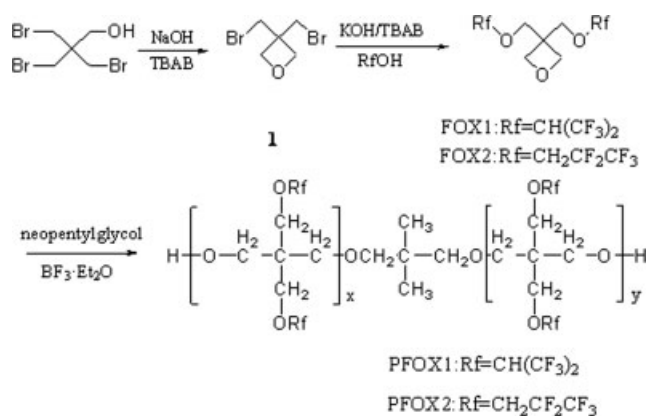
Synthesis of compound **1**¹⁰

A three-necked, 500-mL flask with a condenser and thermometer was charged with tribromoneopentylglycol (50.0 g, 0.154 mol), an aqueous solution of sodium hydroxide (10 wt %, 184.6 g, 0.461 mol), TBAB (1.984 g, 6.15 mmol), and dichloromethane (170 mL). The mixture was heated to 37°C and stirred for 12 h. After it was cooled to room temperature, the layers were separated. The aqueous phase was washed with CH₂Cl₂ (100 mL). The organic layers were combined, washed with brine, dried, and concentrated *in vacuo*. Compound **1** was collected as the fraction at 92–94°C and 2–4 mmHg by vacuum distillation in a 70% yield.

¹H-NMR (CDCl₃, δ): 3.86 (s, 4H), 4.44 (s, 4H).

Synthesis of 3,3-bis(fluoroalkyloxymethyl)oxetane (FOX) compounds (FOX1 and FOX2)

Under nitrogen, compound **1** (5.00 g, 20.5 mmol) was introduced into a three-necked, 100-mL flask



Scheme 1 Synthesis of PFOX.

with a thermometer, condenser, and addition funnel. The phase-transfer catalyst TBAB (12.2 wt %, 2.64 g, 0.001 mmol), hexafluoroisopropanol (6.88 g, 41.0 mmol), and a solution of KOH (45 wt %, 2.81 g, 22.55 mmol) were added to the vessel. After the addition, the reaction was heated to 65°C and stirred for about 24 h. Water (10 mL) was added, and the mixture was cooled to room temperature. The organic layer was separated and washed with brine and then dried. After removal of the solvent, the residue was distilled to give the crude monomer FOX1 in a 50% yield (82–84°C/2–4 mmHg).

¹H-NMR (CDCl₃, δ): 4.45 (t, 1H), 4.44 (s, 2H), 3.86 (s, 2H). ¹⁹F-NMR (CDCl₃, δ): –73.8 (s, 3F). IR (cm^{–1}, neat): 2961, 2877, 1431, 1373, 1290, 1237, 1194, 1103, 984, 881, 686, 656. HRMS (ES⁺): *m/z* 419.0512 [(M + H)⁺, calcd for C₁₁H₁₁O₃F₁₂: 419.0511].

Compound FOX2 was synthesized in the same way with pentafluoropropanol in a 78% yield.

¹H-NMR (CDCl₃, δ): 4.37 (s, 4H), 3.87–3.80 (t, 4H), 3.78 (s, 4H). ¹⁹F-NMR (CDCl₃, δ): –83.58 (m, 3F), –123.32 (m, 2F). IR (cm^{–1}, neat): 2960, 2878, 1433, 1201, 1144, 1101, 1028, 986, 984, 839, 728, 656. HRMS (ES⁺): *m/z* 383.0703 [(M + H)⁺, calcd for C₁₁H₁₃O₃F₁₀: 383.0700].

Synthesis of poly[3,3-bis(fluoroalkyloxymethyl)oxetane] glycol (PFOX) compounds (PFOX1 and PFOX2)

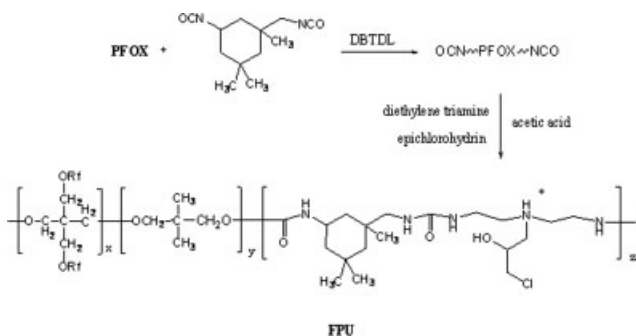
A dried three-necked, 100-mL flask with a thermometer, condenser, and addition funnel was charged with dried neopentylglycol (0.292 g, 2.79 mmol), BF₃ · Et₂O (0.238 g, 1.68 mmol), and CH₂Cl₂ (10 mL). The mixture was stirred at room temperature under nitrogen for 0.5 h, and then monomer FOX1 (7.0 g, 16.75 mmol) was added over 45 min. The reaction was allowed to stir for 5 h more. Residual BF₃ · Et₂O was removed through washing with 2.5 wt % sodium bicarbonate and a water rinse at 40°C. The solvent was removed under reduced pressure at 80°C. Polyether diol PFOX1 was obtained as a colorless, viscous liquid in a 90% yield.

IR (cm^{–1}, neat): 3469, 2961, 2877, 1431, 1372, 1290, 1194, 1104, 985, 898, 687.

The molecular weight was determined by gel permeation chromatography analysis (number-average molecular weight = 3298, weight-average molecular weight = 3412, polydispersity index = 1.03).

Polyether diol PFOX2 was synthesized in the same manner with FOX2 in a 90% yield.

IR (cm^{–1}, neat): 3465, 2962, 2878, 1485, 1367, 1198, 1104, 986, 944, 727, 660. Gel permeation chromatography analysis: number-average molecular weight = 2629, weight-average molecular weight = 2913, polydispersity index = 1.11.



Scheme 2 Synthesis of FPU.

Synthesis of cationic aqueous polyurethane FPU¹¹

The synthesis of FPU was carried out as shown in Scheme 2.

Under nitrogen, PFOX1 (11.3 g, 4.36 mmol), IPDI (2.04 g, 9.16 mmol), and DBTDL (1.89 g, 0.003 mmol) were added to a three-necked, 500-mL flask. The reaction mixture was stirred for 2 h at 45°C, and then dry acetone was added to dilute the prepolymer. At room temperature, this solution was added to a solution of epichlorohydrin (0.44 g, 4.79 mmol) and diethylene triamine (0.50 g, 4.79 mmol) in acetone slowly. After the addition, the mixture was heated at 45°C for 2.5 h. An aqueous solution of acetic acid (0.19 g) was added, and then acetone was removed under reduced pressure. A pale yellow emulsion was obtained as polyurethane FPU1.

IR (cm⁻¹, neat): 3327, 2897, 1713, 1521, 1479, 1274, 1127, 991, 969, 827, 670.

Polyurethane FPU2 was synthesized following the same procedure with PFOX2.

IR (cm⁻¹, neat): 3399, 2955, 1717, 1635, 1541, 1461, 1200, 1104, 1028, 727, 660.

Fabric, treatment, and test methods

Desized, scoured, bleached, and mercerized plain-weave 40 × 40 cotton weighed 118 g/m². Fabric samples were first immersed in an aqueous solution containing a finishing agent and then padded through two dips and two nips to reach a wet pickup of 90%. The samples were then dried at 80°C for 3 min and cured at 160 or 170°C for 3 min.

Two technological tests based on industrial standard methods were used to evaluate the water-repellent properties of the finished fabrics: the water/isopropyl alcohol test (3M water repellency test II and water/alcohol drop test) and the hydrocarbon resistance test method (AATCC test method 22-2001).

Water contact angles were measured on an OCA40 Micro automatic video contact-angle meter (Dataphysics Instruments GmbH, Filderstadt, Germany). For each sample, five water droplets were

placed on five different spots on the same fabric, and the measurement was performed; the arithmetical average of these five measurements was obtained as the result.

To test laundering durability, the treated fabrics were washed with soap flakes in a normal washing cycle according to AATCC 135-1987. Laundering involved a washing temperature of 50°C for 15 min, tumble drying for 15 min in an electric dryer, and tumbling for 10 min in air to cool the fabrics.

All measurements were performed at least in triplicate, and the arithmetical average of every experimental result was given.

RESULTS AND DISCUSSION

Synthesis and characterization of PFOX

As shown in Scheme 1, compound **1** was synthesized from tribromoneopentylglycol by an anion ring-closing reaction under a basic condition. Then, by a nucleophilic substitution reaction with corresponding fluorinated alcohols, FOX1 and FOX2 were obtained in 44 and 78% yields, respectively. The structures of compound **1**, FOX1, and FOX2 were confirmed by ¹H-NMR, ¹⁹F-NMR, FTIR, and HRMS spectra. The fluorinated oxetanes FOX1 and FOX2 were then initiated by trifluoroborane etherate and neopentylglycol for a ring-opening polymerization to form the polyether diols PFOX1 and PFOX2. The degree of polymerization could be controlled by the molar ratio of the monomer to the initiator. In this reaction, the molar ratio of FOX to neopentylglycol was 6:1, so the polymerization followed the active chain end mechanism mainly.¹² PFOX1 and PFOX2 contained a polyether backbone and were characterized with the FTIR spectra. The number-average mo-

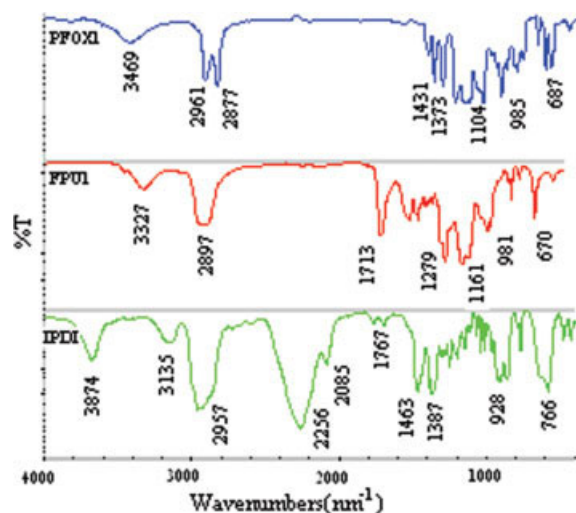


Figure 1 FTIR spectra of PFOX1, FPU1, and IPDI. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

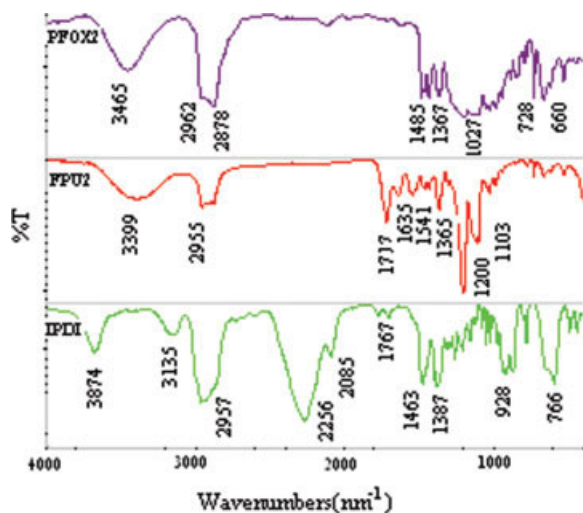


Figure 2 FTIR spectra of PFOX2, FPU2, and IPDI. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

molecular weights of PFOX1 and PFOX2 were 3298 and 2629, respectively, which were measured by gel permeation chromatography.

Synthesis and characterization of waterborne FPU

PFOX was then condensed with aliphatic diisocyanate IPDI in a ratio of $[IPDI]/[PFOX] = 2.1/1$ to afford polyurethane with two terminal isocyanate groups, and then the polyurethane with two terminal isocyanate groups was reacted with diethylene triamine to block the terminal isocyanate groups. As the crosslinking agent, epichlorohydrin was introduced into the polymer molecule by a ring-opening reaction with the hydroxyl group that formed. Some information on the chemical structures and linkages present in the polymer could be obtained by FTIR spectroscopy (Figs. 1 and 2).

The IR spectra for FPU1, PFOX1, and IPDI are shown in Figure 1. The 2256-cm^{-1} band observed in IPDI belonged to the —NCO group; the 3469-cm^{-1} band in PFOX1 indicated the —OH group. In the spectrum of FPU1, both peaks disappeared, and meanwhile, the bands standing for —NH at 3327 cm^{-1} and for C=O at 1713 cm^{-1} appeared. The band

around 1279 cm^{-1} came from the C—F bond. The IR spectra for FPU2, PFOX2, and IPDI are shown in Figure 2; the band for the —OH group in PFOX2 and the band for the —NCO group in IPDI both disappeared. Two peaks at 3399 and 1717 cm^{-1} standing for —NH and C=O , respectively, appeared; it was proved that carbamoyl NHCOO— was also formed in FPU2.

Finishing of cotton fabrics with FPU

The FPU emulsion, of which the solid content was about 30%, was diluted with water to 4, 8, and 12 wt % emulsions. The FPU was applied to the cotton fabric by a conventional pad-dry-cure process. The effects of the concentration of FPU and curing temperature on the water repellency were also examined. The water-repellent ratings under various conditions are listed in Table I.

All the samples treated by FPU1 reached grade 5 in the 3M water repellency test; some of the samples treated by FPU2 at a higher concentration reached grade 6. According to AATCC test results, the fabrics treated with a higher FPU concentration performed better in both series. As shown in Table I, the temperature in the curing process had no obvious influence on the repellency ratings. It seems that the concentration of FPU was the determining factor for the water-repellent rating.

Contact angles can also show the hydrophilicity or hydrophobicity of a fabric surface. The data for the contact angles are also listed in Table I. The biggest contact angle for FPU1 was 132° when the cotton fabric was treated with 12 wt % FPU1 at the curing temperature of 160°C . The contact angle reached 139° when the cotton fabric was treated with 4 wt % FPU2. The contact angle was 146° when 8 wt % FPU2 was used at the curing temperature of 170°C , which nearly reached the superhydrophobic level. Photographs of a water droplet placed on the treated cotton fabrics are shown in Figure 3. The data in Table I show that FPU2 possessed better hydrophobicity than FPU1. In combination with the results obtained for the polyurethane containing the $\text{—CH}_2\text{CF}_3$ group in our previous study,⁸ it seems that the polyurethane containing linear short fluoroalkyl chains possessed better hydrophobicity.

TABLE I
Water Repellency Ratings Under Different Conditions and with Different Contact Angles

	FPU1						FPU2					
	4 wt %		8 wt %		12 wt %		4 wt %		8 wt %		12 wt %	
Cure temperature ($^\circ\text{C}$)	160	170	160	170	160	170	160	170	160	170	160	170
3M water repellency test II	5	5	5	5	5	5	5	5	6	6	6	6
AATCC test method	50	50	70	70	80	80	70	70	80	80	80	80
Contact angle	122	119	127	126	132	123	139	139	139	146	146	140

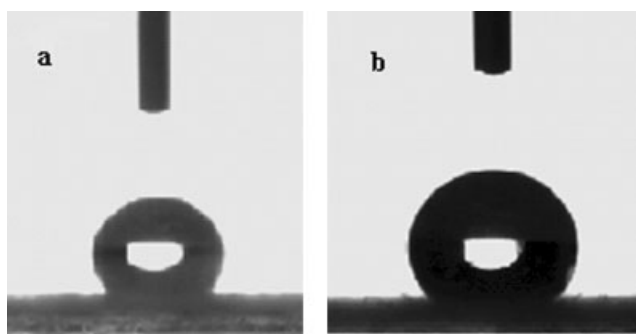


Figure 3 Water contact-angle measurements: (a) fabric treated with FPU1 and (b) fabric treated with FPU2.

As we know, the surface structures of fluorinated polymers are strongly influenced by the structures of the fluoroalkyl groups, and the surface properties of polymers are controlled by the orientation and packing of side groups.¹³ The short fluoroalkyl chains are assembled on the surface layer of treated cotton fabric, so the surface, protected by an array of pendant perfluoroalkyl groups, would make the water repellency maximum.¹⁴ The hexafluoroisopropyl has branches at its end, and the repulsive force between fluorine atoms causes our product to have a higher surface free energy than expected.¹⁵ As the pentafluoropropyl is a linear alkyl group, it can array closely and vertically on the surface of the coating to form a film that gives better water repellency.

After 10 washing cycles, all the water-repellent ratings had no obvious changes. This means that active groups such as chloro and hydroxyl groups in these FPU's can react with the hydroxyl groups of cellulose after the cure process to develop permanent covalent bonds with the cotton fabrics.

CONCLUSIONS

In this study, we designed and synthesized two novel polyether diols, PFOX1 and PFOX2, via a ring-

opening polymerization of oxetane monomers. After condensation polymerization with IPDI and successive ionization, two waterborne polyurethanes, FPU1 and FPU2, were synthesized successfully. They were applied as surface modification agent on cotton fabrics. FPU2 containing linear $\text{CF}_3\text{CF}_2\text{CH}_2-$ showed better hydrophobicity than FPU1. The contact angle of treated fabrics for water was 146° when 8 wt % FPU2 was used, and this nearly reached a superhydrophobic effect. The fabrics treated with FPU2 showed a water-repellent rating at grade 6 and scored 80. Studies on modifying the structure of FPU and improving the water-repellent property and even the oil-repellent property are currently under way in our laboratory and will be reported in due course.

References

1. Shafrin, E. G.; Zisman, W. A. *J Phys Chem* 1960, 64, 519.
2. Giesy, J. P.; Kannan, K. *Sci World* 2001, 1, 627.
3. (a) 2010/15 PFOA Stewardship Program. <http://www.epa.gov/opptintr/pfoa/pubs/pfoastewardship.htm>; (b) *Fed Regist* 2000, 65, 62318; Sigmund, A. *Off J Eur Union* 2006, C195, 10.
4. Rebecca, R. *Environ Sci Technol* 2006, 1, 12.
5. Kausch, C. M.; Leising, E. J.; Medsker, R. E.; Russell, V. M.; Thomas, R. R. *Langmuir* 2002, 18, 5933.
6. Makal, U.; Uilk, J.; Kurt, P.; Cooke, R. S.; Wynne, K. J. *Polymer* 2005, 46, 2522.
7. Fujiwara, T.; Makal, U.; Kenneth J. W. *Macromolecules* 2003, 36, 9383.
8. Jiang, W. C.; Huang, Y. G.; Gu, G. T.; Meng, W. D.; Qing, F. L. *Appl Surf Sci* 2006, 234, 2304.
9. Malik, A. A.; Archibald, T. G.; Carlson, R. P.; Wynne, K. J.; Kresge, E. N. U.S. Pat. 6,825,316 (2004).
10. Naokazu, I.; Toshiro, H. U.S. Pat. 5,886,199 (1999).
11. Lim, H.; Lee, Y.; Park, I. J.; Lee, S.-B. *J Colloid Interface Sci* 2001, 241, 269.
12. Kubisa, P.; Penczek, S. *Prog Polym Sci* 1999, 24, 1409.
13. Dreher, W. R.; Singh, A.; Urban, M. W. *Macromolecules* 2005, 38, 4666.
14. Takashi, N.; Yoshimasa, U.; Masashi, M.; Katsuhiko, N. *J Colloid Interface Sci* 2005, 283, 533.
15. Shafrin, E. G.; Zisman, W. A. *J Phys Chem* 1962, 66, 740.