Synthesis and Flame Retardant Potential of Polyols Based on Bisphenol-S

Mark F. Sonnenschein,[1] Justin M. Virgili,[1]* David A. Babb,[2] Bruce M. Bell,[1] Brian C. Nickless[1]

[1]Corporate Research and Development, Midland, Michigan, 48674
[2]Polyurethanes Research and Development, Freeport, Texas, 77541
Correspondence to: M. F. Sonnenschein (E-mail: mfsonnenschein@dow.com)

Received 11 January 2016; accepted 3 February 2016; published online 8 March 2016
DOI: 10.1002/pola.28077

ABSTRACT: Polyether polyols based on bisphenol-S were prepared by alkoxylation and compared with analogs based on bisphenol-A, as well as standard aromatic polyester, and polyether polyols for viscosity and temperature stability. Thermo-oxidative stability was determined by thermo-gravimetric analysis, pyrolysis gas chromatography/mass spectroscopy, and evolved gas analysis mass spectroscopy. Incorporation of the sulfone moiety was found to dramatically improve the thermo-oxidative stability of the neat polyol. Significant char formation was observed with gas phase evolution of flame retardant SO_2 and aromatic sulfone only apparent at about 600 °C. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *54*, 2102–2108

KEYWORDS: double-metal cyanide catalyst; flame retardance; polyethersulfone

INTRODUCTION Environmental, health, and safety regulations are creating increasing demand for halogen-free flame retardants (FRs).[1,2] In addition, there is increasing scrutiny of other FRs based on phosphorous. Acceptable FR are expected to mitigate flame initiation and inhibit post ignition behavior such as heat release rate, smoke obscuration, and evolved gas toxicity. Many FR additives are utilized for polyurethane, polycarbonate, and polyester containing products.[3] These plastics are produced by addition or condensation polymerizations, and hydroxyl functional polymer building blocks are commonly employed.[4] There is growing exploration of reactive FR agents that can be incorporated in the polymer network.[5,6] These can be useful compared with small molecule FR additives which may become fugitive in the environment, or expose unsuspecting consumers by touch or ingestion. Polymerizable FR feedstocks that contain hydroxyl functional materials become part of the main polycarbonate, polyurethane, or polyester polymer network, and are held captive in the plastic until such time as its FR function is required.

Polysulfones are well known to possess outstanding thermo-oxidative stability,[7,8] resistance to burning, and low smoke emission.[9–11] Their use as selective FR agents however, is apparently missing from the literature. This article will explore the first alkoxylation of bisphenol-S, a commercially available feedstock for making hydroxyl functional polymerizable building blocks. A detailed procedure for producing alkoxylated bisphenol-S is presented. Bisphenol-S is alkoxylated with propylene oxide to various useful molecular weights. Thermo-oxidative performance of these new building blocks are assessed versus comparable materials produced from the non-sulfone functional bisphenol-A, and conventional polyether and aromatic polyester polyols, the latter of which could be used for FR resistant PU rigid insulation foams.

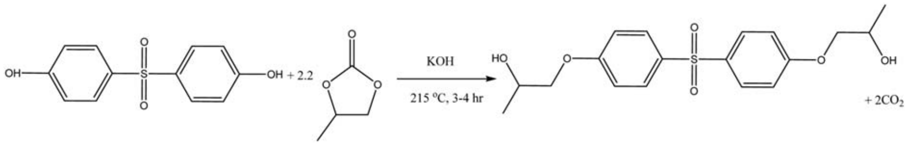
EXPERIMENTAL

Materials

Bisphenol-S (98%), bisphenol-A (97%), propylene carbonate (99.7%), and all other reagents were purchased from Sigma-Aldrich and used as received. Aromatic polyester polyol IP 9001, propylene oxide, and polypropylene oxide (725 Da) were obtained from Dow Chemical. DMC catalyst (Arcol 3^{TM}) was obtained from Bayer Material Science (Covestro). DMC catalyst (double metal cyanide) is a compound of zinc hexacyanocobaltate and tert-butyl alcohol useful for epoxide polymerizations.[12] IP 9001 is an aromatic polyester polyol; the reaction product of terephthalic acid with diethylene glycol and 200 g/mol polyethylene glycol with functionality 2.0 and polymerized to result in OH number of 205–220, and a viscosity at 25 °C of 2000 cps.

Present address: Justin M. Virgili, Tactus Technology Fremont, California, 94555.

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Synthesis of HPPS by reaction of bisphenol S with propylene carbonate.

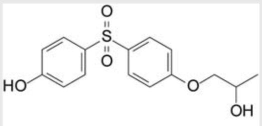
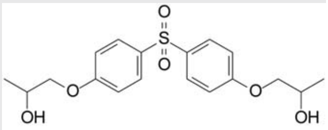
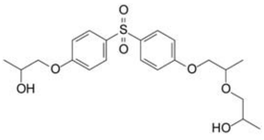
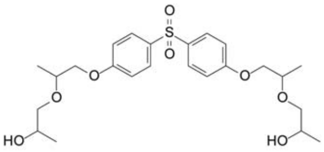
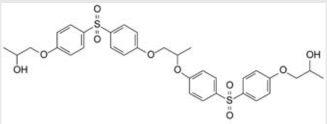
Synthesis of Polyols

Synthesis of HPPS [1,1′-((Sulfonylbis(4,1-phenylene))bis(oxy))bispropan-2-Ol)] and HPPA [1,1′-((Propane-2,2-Bis(4,1-phenylene))bis(oxy))bis(propan-2-Ol)]

The method utilized for the synthesis of HPPS is an adaptation of that published by Liaw et al.[13] and is here expanded to the synthesis of HPPA. As illustrated in Scheme 1, bisphenol-S (125 g, 0.5 mol) and anhydrous propylene carbonate (112.6 g, 1.1 mol) were introduced to a 500 mL three-neck flask with stirring, and heated to 215 °C under N_2 and reflux. The bisphenol-S dissolved in the propylene carbonate between 150 °C and 170 °C and catalytic KOH (0.59 g, 0.01 mol) was added to the flask.

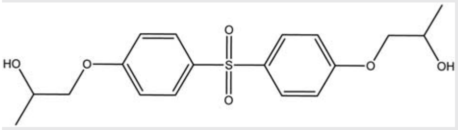
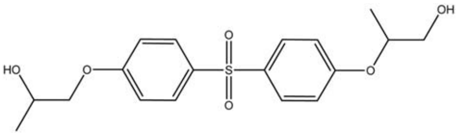
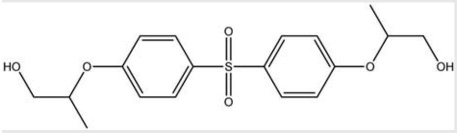
The crude product was dissolved in warm methylene chloride, washed with brine three times, and dried over $MgSO_4$. HPPS was isolated by rotary evaporation followed by vacuum drying overnight. Yield of a transparent yellow viscous liquid was 90.3% of theoretical. Composition was verified by ^{1}H-NMR (98+% apparent purity) in d6-acetone. While ^{1}H-NMR was found to be sensitive to the disappearance of two distinct aromatic resonances ($\delta = 7.7$ ppm and 6.85 ppm)

TABLE 1 Identification of HPPS Components by ESI/LC/MS Analysis

Peak	Assignments	Peak	Assignments
A	 $C_{15}H_{16}O_5S$ 308.34 308.071845 or isomer **0.6%**	B	 $C_{18}H_{22}O_6S$ 366.42 366.113710 or isomer mixture of three isomers **88%**
C	 $C_{21}H_{28}O_7S$ 424.50 424.155575 or isomer several possible isomers **9%**	D	 $C_{24}H_{34}O_8S$ 482.58 482.197440 or isomer several possible isomers **0.2%**
E	 $C_{33}H_{36}O_{10}S_2$ 656.76 656.174991 or isomer several possible isomers **2.3%**		

Molar percentages are rounded on nearest significant figure.

TABLE 2 Relative Molar Percentages of Primary–Primary, Primary–Secondary, and Secondary–Secondary Hydroxyl Species in HPPS

Isomers of Peak B in Table 1	Compositional Abundance
	45.8
	44.1
	10.1

present in neat bisphenol-S, and the appearance of two distinct aromatic resonances ($\delta = 7.85$ ppm and 7.05 ppm) in the HPPS product, the technique was unable to distinguish between products with greater than one propylene oxide unit added per phenol group of the bisphenol-S.

LC/ESI/MS (liquid chromatography/electro-spray ionization/mass spectrometry) analysis[14] was utilized to establish the product composition and the relative abundance of each species estimated from the UV peak absorption obtained following liquid chromatographic separation. All reaction products (Table 1, hereafter termed HPPS) possess two hydroxyl groups with average molecular weight 378 g/mol and 8.5 wt % sulfur. This product is used as a polyol itself and as an initiator to make higher equivalent weight polyols as subsequently described.

The distribution of isomers with primary versus secondary hydroxyl groups in the major product corresponding to peak B in Table 1 was analyzed via GC/MS and GC FID after HPPS was derivatized with bis(trimethylsilyl)trifluoroacetamide. The relative molar percentages of primary–primary, primary–secondary, and secondary–secondary hydroxyls are given in Table 2.

HPPA was synthesized following a similar procedure to that used to synthesize HPPS. Bisphenol-A (25.0 g, 0.11 mol) and anhydrous propylene carbonate (24.7 g, 0.24 mol) were added to a 250 mL three-neck flask with stirring and heated to 200 °C under N_2 and reflux for 3–4 h (Scheme 2). As the bisphenol-A dissolves in propylene carbonate, catalytic KOH (0.13 g, 0.0023 mol) was added to the reaction at room temperature.

Upon cooling, the crude product was dissolved in warm methylene chloride, washed with brine 3×, and dried with $MgSO_4$. HPPA was isolated by removal of methylene chloride by rotary evaporation, followed by vacuum drying overnight. Yield of a clear, yellow near-glass liquid was 77% of theoretical, and the composition was verified by ^{1}H-NMR (96+% apparent) in d6-acetone. As in the case of HPPS, ^{1}H-NMR was found to be sensitive to the disappearance of two distinct aromatic resonances ($\delta = 7.05$ and 6.75 ppm) present in neat bisphenol-A, and the appearance of two distinct aromatic resonances ($\delta = 7.15$ and 6.85 ppm) in the HPPA product, but unable to distinguish between products with greater than one propylene oxide unit added per phenol group of bisphenol-A.

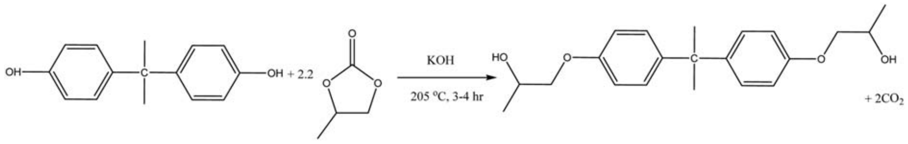
LC/ESI/MS analysis was utilized to establish the product composition and the relative abundance of each species estimated from UV peak absorption area from the LC analysis. In Table 3 all major reaction products are observed to possess two hydroxyl groups with an average product (hereafter called HPPA) molecular weight of 347 g/mol. The distribution of isomers with primary versus secondary hydroxyl groups present in the species corresponding to peaks B, C, and D in Table 3 was further analyzed by GC/MS analogously to the analysis on HPPS and the results shown in Table 4. This product is used as a polyol itself and as an initiator to make higher equivalent weight polyols as subsequently described.

It is worth noting from comparing Tables 2 and 4, that the choice of bisphenol-S or bisphenol-A appeared to have exercised substantial influence on the distribution of primary and secondary hydroxyl produced from the reactions with propylene carbonate. The cause of this director effect is ambiguous, but may be due to the difference in inductive electronic effects between the sulfone and the isopropylidene bridges altering the nucleophilicity of the phenol.

Synthesis of BIS-S and BIS-a Containing Polyols by Propoxylation with DMC Catalyst

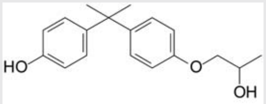
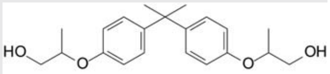
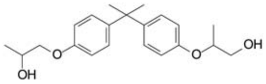
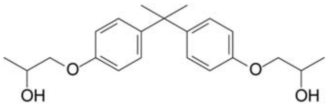
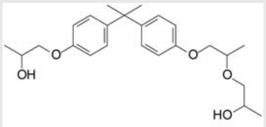
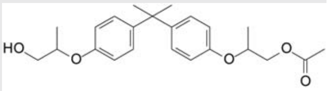
Alkoxylation of HPPS

Direct alkoxylation of bisphenol-S is not practical using DMC catalysis since the diphenol monomer is a high melting solid (m.p. = 245 °C–247 °C) that is incompatible with the alkoxylation process.[15] Instead, the viscous product (polyol) obtained by reacting bisphenol S with propylene carbonate (Table 1) was used as an initiator for DMC catalyzed



SCHEME 2 Synthesis of HPPA.

TABLE 3 Constituents of HPPA Determined by ESI/LC/MS

Peak	Assignments	Peak	Assignments
A	 $C_{18}H_{22}O_3$ 286.37 286.156894 or isomer two isomers **2.1%**	B	 $C_{21}H_{28}O_4$ 344.45 344.198759 or isomer **1.6%**
C	 $C_{21}H_{28}O_4$ 344.45 344.198759 or isomer **21.6%**	D	 $C_{21}H_{28}O_4$ 344.45 344.198759 or isomer **68.4%**
E	 $C_{24}H_{34}O_5$ 402.53 402.240624 or isomer several possible isomers **4.9%**	F	 $C_{23}H_{30}O_5$ 386.48 386.209324 or isomer two isomers **1.4%**

Molar percentages are rounded on nearest significant figure.

alkoxylation. HPPS initiator (45.8 g, 0.125 mol) was added to a 500 cc Zipperclave^{TM} reactor along with aqueous phosphoric acid (0.15 M, 1.21 μl) followed by DMC catalyst (0.0125 g)[16] and aluminum isoproxide (0.095 g). The mixture was heated to 145 °C with a N_2 purge for 2 h to dry the mixture. The N_2 purge was stopped, the reactor sealed and then heated to 150 °C. Propylene oxide (PO) (99.29 g, 116.8 ml) was added at a rate of 1 mL/min up to an internal reactor pressure of 20 psig, and then added at a rate of 0.75 mL/min to maintain 20 ± 1 psig reactor pressure. Following residual PO digestion, the reactor was cooled and the product (140.5 g, 96.9% yield) was isolated. GPC analysis of the alkoxylated product indicated a polyether product with M_n of 1265 g/mol and a polydispersity (M_w/M_n) of 1.03.

In a second alkoxylation reaction, a polyol with $M_n = 700$ g/mol was targeted. The HPPS initiator was combined with phosphoric acid followed by DMC catalyst and aluminum isopropoxide as above. Following drying, the reactor was sealed, heated to 150 °C, and PO (54.2 g, 66.1 mL) was added to the reactor to maintain a reactor pressure ≤ 14 psig. The residual PO was digested, the reactor cooled, and

TABLE 4 Relative Molar Percentages of Primary–Primary, Primary–Secondary, and Secondary–Secondary Hydroxyl Species in HPPA

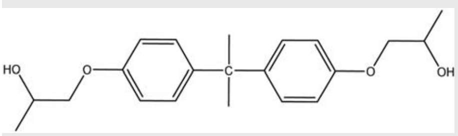
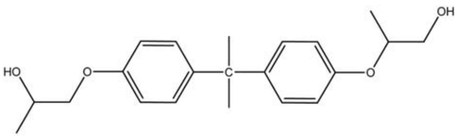
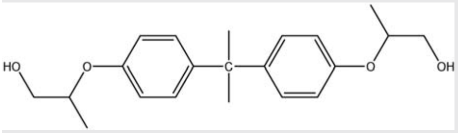
Isomers Distribution in HPPA Peaks B, C,D in Table 1	Compositional Abundance
	74.6 (UV) 78.1 (GC/MS)
	23.6 (UV) 21.0 (GC/MS)
	1.7(UV) 0.1 (GC/MS)

TABLE 5 Viscosity of Bisphenol-S and Bisphenol-A Based Polyols at Three Temperatures and Comparison to Aromatic Polyester Polyol (IP-9001)

Polyol (g/mol)	35 °C (cps)	60 °C (cps)	80 °C (cps)
HPPS 378	1.2×10^7	8×10^5	7×10^3
HPPS 847	3.5×10^3	7×10^2	3×10^2
HPPS 1,265	1.3×10^3	3×10^2	1×10^2
HPPA 347	3.7×10^4	1×10^3	1.5×10^2
HPPA 794	7.2×10^2	1×10^2	$<10^2$
HPPA 1,271	4.9×10^2	1×10^2	$<10^2$
PTA polyol 492	1×10^3	1.3×10^2	$<10^2$

the product (97.8 g, 87.8% yield) collected for analysis. GPC analysis of the reaction product indicated a polyol with $M_n = 847$ g/mol and polydispersity of 1.05.

Alkoxylation of HPPA Monomer

The viscous product (polyol) obtained by reacting bisphenol A with propylene carbonate (Table 3) was used as an initiator for DMC catalyzed alkoxylation. Alkoxylation of HPPA initiator (Table 3) to produce a 1200 g/mol polyol was carried out in a similar manner to alkoxylation of HPPS initiator described previously. HPPA initiator (43.1 g) was added to the alkoxylation reactor along with phosphoric acid (0.15 M, 1.1 μL) followed by DMC catalyst (0.0125 g) and Al isopropoxide (0.094 g). The reactor was heated and dried as before. After drying, the N_2 purge was stopped, the reactor heated to 150 °C and then sealed. PO was added at a rate sufficient to maintain reactor pressure less than 15 psig throughout the addition, until a total of 106.9 g (130.4 mL) was added. The residual PO was digested to a constant reactor pressure, the reactor cooled, and the product (153.5 g) collected for analysis. GPC analysis indicated a polyol with $M_n = 1271$ g/mol and polydispersity of 1.03.

In a second preparation, the HPPA initiator was alkoxylated based on a design to produce a polyol with $M_n = 800$ g/mol. HPPA initiator (43.1 g), phosphoric acid (0.15 M, 1.1 μL), DMC catalyst (0.005 g) and Al isopropoxide (0.019 g) was reacted with 56.9 g PO (69.4 mL) using a similar procedure as outlined above. A total of 96.4 g of polyol was obtained (96% yield) with a $M_n = 794$ g/mol and a polydispersity of 1.05.

Viscosity of the Polyols

Viscosity is a practical, but critical property of polyols since for many applications process equipment limitations dictate acceptable flow properties. The inability to adequately adjust polyol viscosity to meet prosaic issues such as flowability and mixing requirements can result in an innovation that is little more than a laboratory curiosity. For instance, polyurethane process equipment for rigid insulation foams usually set a room temperature viscosity limit of between 5000 and 20,000 cps at room temperature.[12,17]

Temperature dependant viscosities were measured using a Rheometrics ARES II rheometer with a cone-and-cup geometry ($\omega = 1$ rad/sec, 2 °C/min ramp rate). The bisphenol-S polyols possessed the highest viscosity among all the comparatives at any particular molecular weight and at any particular temperature. HPPS initiator (polyol from reacting bisphenol S with propylene carbonate) with molecular weight 378 g/mol was a glass at room temperature so all viscosity measurements were begun at 35 °C. Table 5 provides the viscosity of the bis-S polyols and the comparatives at several temperatures. Two trends are observed, (1) the increased hydrogen bond potential of bisphenol-S versus

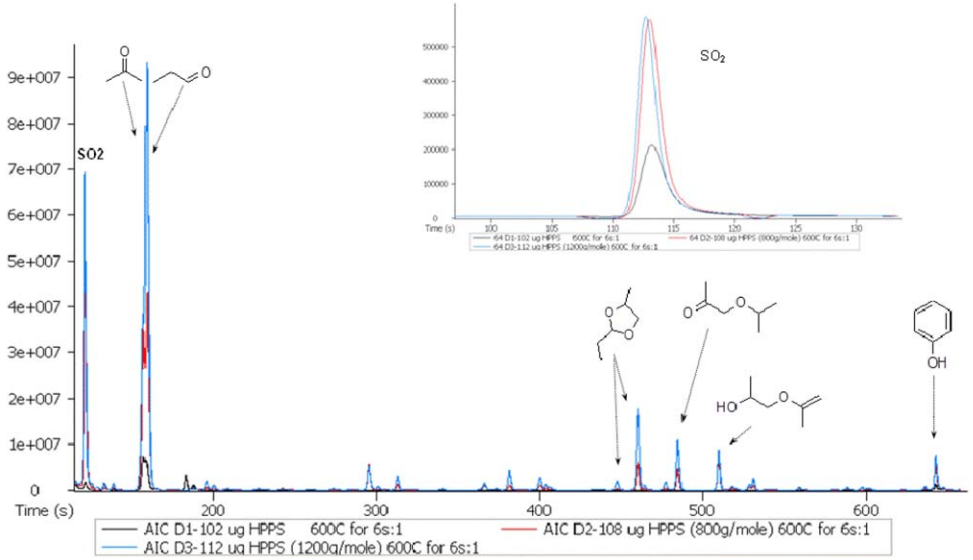


FIGURE 1 Total ion response versus retention time from pyrolysis of sulfone polyols of varying molecular weight heated ballistically to 600 °C. Inset shows detail of SO_2 response with lowest response for polyol having highest percentage sulfur content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 6 $T_{d,5\%}$ Determined Using Thermogravimetric Analysis for Conventional Aromatic Polyester Polyol, Polyether Polyols, and Polyols Produced by Functionalization of Bisphenol-A and Bisphenol-S

Sample	% Aromatic	% Sulfur	$T_{d,\ 5\%}$ (°C)
IP 9001 (492 g/mol)	12	0	132
PPG (425 g/mol)	0	0	153
PPG (725 g/mol)	0	0	260
HPPA (347 g/mol)	43.9	0	184
HPPS (378 g/mol)	41.3	8.5	305
HPPS (847 g/mol)	18	4	344
HPPS (1,265 g/mol)	12	2.7	331

All percentages are based on weight.

bisphenol-A moieties leads to higher viscosity at comparative molecular weights, (2) the addition of racemic propylene oxide to bisphenol-S and bisphenol-A moieties disrupts the strong intermolecular interactions leading to reduced polyol viscosity as molecular weight increases. The beneficial viscosity reduction effect of propoxylation is leveled at high equivalent weight as all polyols converge to 100 cps at the highest molecular weight. Thus, with increasing molecular weight conventional polymer rheology effects dominate over inter- and intramolecular hydrogen bonding interactions.[18]

Thermo-Oxidative Stability of Sulfone Polyols

Pyrolysis gas chromatography/mass spectroscopy[19,20] was performed using an Agilent 7890 GC coupled to a Frontier Labs PY-2020iD pyrolyzer. Analyses were performed on about 100 μg samples, solvent (methylene chloride) deposited into a sample cup under varying heating conditions. The samples were selectively sampled by temperature range (100 °C–400 °C and 375 °C–400 °C) and also ballistically heated to 600 °C for 6 sec. Species thermally desorbed were transported to a GC and focused with a cryotrap at −195 °C. GC parameters were injection port 320 °C, with a GC oven program set to ramp from 40 °C to 100 °C at 8 °C/min followed by 100 °C–320 °C at 20 °C/min followed by isothermal condition at 320 °C for 8 min. The column was 30 M × 0.25 mm, 1.0 μm 5% phenyl methylsilicone, with a He column flow rate of 0.6 mL/min at 5.0 psi. Mass spectral parameters were an electron energy of −70 V, electron current −71 μA, ion source temperature 250 °C acquisition rate 20 spectra/sec, acquisition delay of 60 sec, and a mass range from 14 to 600.

For pyrolyzed HPPS and alkoxylated HPPS polyols, sulfur-containing degradation species were only observed for samples heated to 600 °C and in each example SO_2 was the only detectable S containing degradation species (Fig. 1). Samples heated to 400 °C showed evidence only of polyether degradation products, primarily propanal and dioxane derivatives (data not shown). Samples heated to 600 °C evolved SO_2, but the amount was inversely correlated to polyol sulfur content suggesting that char layer formation impedes thermoxidative formation of volatile degradation products.[21,22] In addition to SO_2, phenol is also observed upon heating to 600 °C. The dependence of degradation products on thermoxidative path reflects the complexity of thermo-oxidative pathways involved.

For thermogravimetric analysis (TGA), 5–10 mg samples were weighed into platinum sample pans, dried overnight under vacuum, and analyzed under N_2 purge with a 10 °C/min temperature ramp rate using a TA Q5000 instrument. Table 6 documents the dramatic increase in the temperature

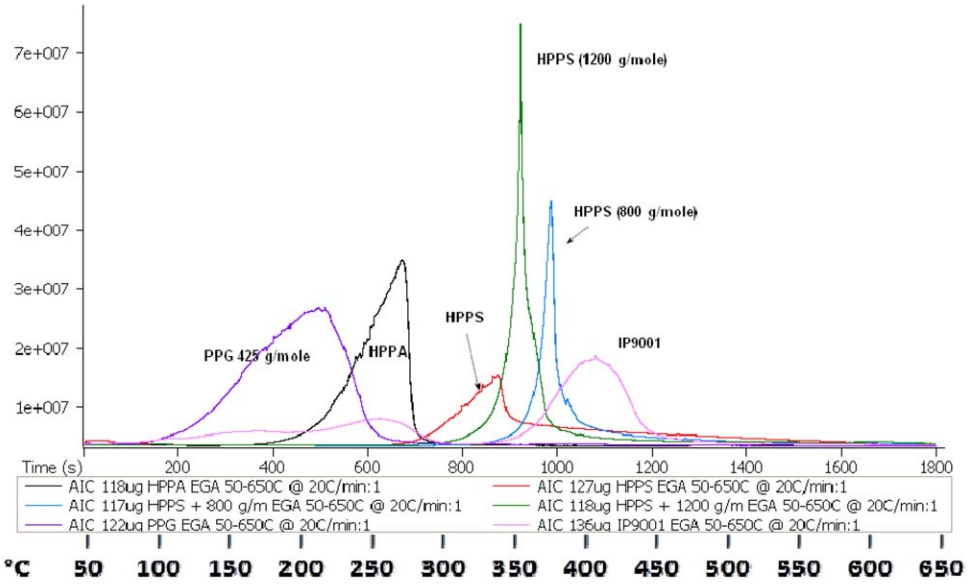


FIGURE 2 Total ion response versus temperature from evolved gas analysis (EGA/MS) of HPPS, HPPA, aromatic polyester, and polyether polyols. Samples were heated at 20 C/min from 50 °C to 650 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at which HPPS 5% weight loss is observed ($T_{d,5\%}$), compared with the bisphenol-A analogue and polyether and polyester comparatives (TGA curves are supplied in Supporting Information). Along with the substantial retarding effect of sulfone on thermal degradation, the 5% degradation temperature also shows that higher molecular weight polypropylene oxide polyols possess greater thermal stability than lower molecular weight homologs, which complicates quantitative estimation of the effect of sulfone moiety by this measurement technique.

In Figure 2, the cumulative total ion current (CTIC) EGA/MS[23] from sulfone polyols, HPPA, polyester polyol (IP-9001) and PPG (425 g/mol) heated 20 °C/min from 50 °C to 650 °C is shown. In agreement with the TGA and pyrolysis results, the polyester polyol, PPG and HPPA-based polyols are observed to degrade at lower temperatures compared with the sulfone polyols. The IP-9001 aromatic polyester polyol exhibits three distinct degradation events corresponding to the polyether and aromatic components produced via condensation polymerization.[24] Differences among the three HPPS polyols were observed and are likely due to the interplay between molecular weight and sulfur content on thermo-oxidative stability.

CONCLUSIONS

The synthesis of alkoxylated bisphenol-S polyols was accomplished and FR potential compared with bisphenol-A analogs and standard polyether and terephthalic acid based aromatic polyester polyols. The sulfone polyols are viewed as offering a potential alternative to halogen- or phosphorous-based FRs. Bisphenol-S polyols possessed higher viscosities than bisphenol-A and terephthalic acid analogues of similar molecular weight, presumably due to the increased interchain hydrogen bonding potential afforded by the sulfone moiety. The sulfone polyols exhibited significantly better thermo-oxidative stability relative to the comparatives as measured by gas evolution, and pyrolysis GC mass spectroscopic techniques. Sulfur dioxide is only evolved at temperatures above 600 °C presumably due to prior incorporation into a char.

ACKNOWLEDGMENTS

The authors would like to thank Bruce Gerhart for the evolved gas measurements, and Ganesh Kailasam for helpful discussions. The Dow Chemical Co. is thanked for its support of this work.

REFERENCES AND NOTES

1 A. Morgan, C. WIlkie, Non-Halogenated Flame Retardant Handbook; Wiley-Scrivener: Hoboken, NJ, **2014**.

2 T. Hull, R. Law, A. Bergman, In Polymer Green Flame Retardants; C. Papaspyrides, P. Kiliaris, Eds.; Elsevier: Amsterdam, **2014**, pp 119–180.

3 Y. Wang, Y. Xia, S. Luo, *Makromol. Chem. Macromol. Symp.* **1993**, *74*, 295–298.

4 M. Sonnenschein, Polyurethanes: Science Technology, Markets, and Trends; Wiley: Hoboken, NJ, **2014**.

5 R. Yang, W. Hu, Y. Song, J. Li, *Polym. Degrad. Stabil.* **2015**, *122*, 102–109.

6 F. Luo, K. Wu, J. Zheng, H. Guo, *J. Appl. Polym. Sci.* **2015**, *132*, 41829.

7 F. Gardea, J. Garcia, D. Boday, K. Bajjuri, M. Naraghi, J. Hedrick, *Macromol. Chem. Phys.* **2014**, *215*, 2260–2267.

8 M. Mao, S. Das, R. Turner, *Polymer* **2007**, *48*, 6245.

9 I. Blanco, G. Cicala, A. Latteri, A. Mamo, A. Recca, *J. Therm. Anal., Calorim.* **2013**, *112*, 375–381.

10 H. Ohtani, S. Tsuge, In Applied Pyrolysis Handbook, 2nd Ed.; T. Wampler, Ed; CRC Press: Boca Raton, Fl, **2007**, pp 249–269.

11 C. Libanati, L. Broadbelt, C. Iamarca, M. Klien, S. Andrews, R. Cotter, *Mol. Simul.* **1993**, *11*, 187–204.

12 M. Sonnenschein, Polyurethanes: Science, Technology, Markets, and Trends, John Wiley and Sons: Hoboken, NJ, **2015**, Chapter 3.

13 D. Liaw, W. Shen, *Angew. Makromol. Chem.* **1992**, *199*, 171–190.

14 W. Bodnar, R. Blackburn, J. Krise, M. Moseley, *J. Am. Soc. Mass Spectrom.* **2003**, *14*, 971–979.

15 N. Almora-Barrios, S. Pogodin, L. Bellarosa, M. Garcia-Melchior, G. Revilla-Lopez, M. Garcia-Rates, A. Vazquez-Garcia, P. Hernandez-Ariznavarreta, N. Lopez, *ChemCatChem* **2015**, *7*, 928–935.

16 J. Sebastian, D. Srinivas, *Appl. Catal A: Gen.* **2015**, *506*, 163–172.

17 S. Singh, J. Fife, S. Dubs, P. Coleman, In Proceedings of API Polyurethanes Technical Conference Salt Lake City, American Chemical Council Pubs, Troy, MI, September 25–27, **2006**; pp 819–833.

18 J. Ferry, Viscoelastic Properties of Polymers, 2nd ed.; John Wiley and Sons: New York, **1970**; Chapter 10.

19 R. Menescal, J. Eveland, R. West, M. Blazso, *Macromolecules* **1994**, *27*, 5893–5899.

20 P. Bradna, J. Zima, *J. Anal. Appl. Pyrolysis.* **1991**, *21*, 207–220.

21 G. You, Z. Cheng, Y. Tang, H. He, *Ind. Eng. Chem. Res.* **2015**, *54*, 7309–7319.

22 F. Mohaddes, L. Wang, R. Shanks, S. Fergusson, *Green Chem. Lett. Rev.* **2014**, *7*, 184–190.

23 S. Materazzi, R. Risoluto, *Appl. Spectrosc. Rev.* **2014**, *49*, 635–665.

24 K. Erickson, *J. Therm. Anal. Calorim.* **2007**, *89*, 427–440.