Perfluorocyclobutane Aromatic Ether Polymers. III. Synthesis and Thermal Stability of a Thermoset Polymer Containing Triphenylphosphine Oxide

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ABSTRACT: The preparation of a novel triaryl phosphine oxide thermoset polymer containing the perfluorocyclobutane linkage is described. The synthetic methodology involves the formation of a Grignard reagent from 4-bromotrifluorovinyloxybenzene and reaction with phosphorous trichloride to form the triaryl phosphine trifluorovinyl ether monomer. Oxidation of the phosphine monomer with hydrogen peroxide in ethanol provides quantitative conversion of the phosphine to the phosphine oxide. Analysis of the thermal decomposition of the resulting polymer in both nitrogen and air indicates improvement in thermal and thermal/oxidative stability with respect to the previously reported polymer prepared from 1,1,1-tris(4-trifluorovinyloxy)phenyl ethane. Differences in thermal and thermal/oxidative performance still exist, indicating that oxidative processes contribute to the polymer decomposition in air. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2005–2012, 1998

Key words: perfluorocyclobutane polymers; PFCB; fluoropolymers; high-performance polymers; high-temperature polymers; polyarylate polymers

INTRODUCTION

The phosphine oxide group has often been incorporated into polymers to enhance the thermal and thermal/oxidative stability and ignition resistance of polymer matrices. Polymers containing triphenylphosphine oxide or aryl alkyl phosphine oxide have been extensively evaluated for their thermal stability and ignition resistance.[1–16] These polymers include some of the first examples of thermoset polymers containing the triphenylphosphine oxide structure as a crosslinking agent.[17–21] In the majority of cases, the authors report improvements in the thermal/oxidative performance or improvements in resistance to atomic oxygen upon incorporation of phosphine oxide into the polymer matrix.

Our recent work into the preparation of hexafluorocyclobutane ring-containing polyarylene ethers[22–26] led us into a study of the thermal stability of the polyether polymers containing this fluorocarbon linkage. Preparation of the thermoset polymer from 1,1,1-tris(4-trifluorovinyloxyphenyl)ethane (**1**) produced a thermoset polymer (**2**) with good thermal and thermal/oxidative stability.[23] This polymer is illustrated in Figure 1.

While the thermal decomposition of this polymer in an inert atmosphere appears to involve a single chemical process involving homolysis of the oxygen-to-fluorocarbon ring bond, the thermal/
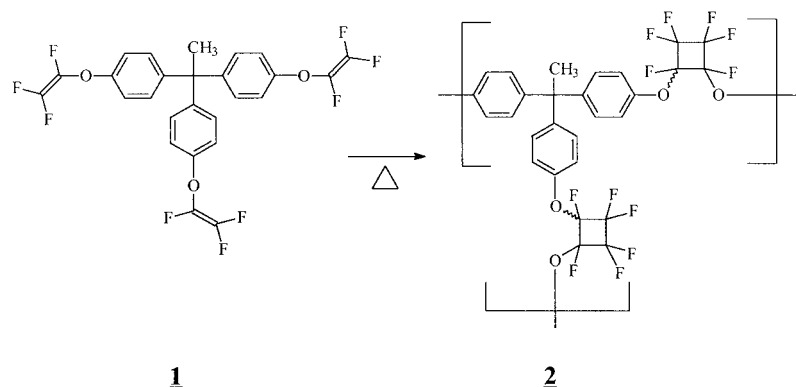
Figure 1 Thermoset polymer **2** of the previous study.

oxidative decomposition of the polymer is more complex and involves at least two separate processes. Homolysis of the ether linkage is still prevalent, as is evidenced by the identification of C_4 fluorocarbons in the evolved gas analysis.[23] In addition, the presence of CO_2 indicates that oxidative processes are also active in the decomposition. Infrared spectral analysis of the polymer indicates that the primary site of oxidation of the polymer is the methyl group which is pendant to the quaternary carbon.

In an effort to prepare a polymer with enhanced thermal and thermal/oxidative stability, a polymer containing phosphine oxide in place of the ethylidene group in the polymer of Figure 1 was designed. The goal was to prepare a polymer with a significantly reduced thermal/oxidative contribution to the rate of thermal degradation and ideally to prepare a new polymer which would exhibit very little difference in the rates of thermal and thermal/oxidative decomposition.

A synthetic route was devised using the Grignard reagent prepared from 4-bromotrifluorovinyloxybenzene (**3**) (Fig. 2). This versatile trifluorovinyl ether intermediate is prepared in excellent yields from 4-bromophenol, as we have previously reported in the preparation of siloxane-containing fluoropolymers.[24] By reaction with trichlorophosphine, this reagent gives tris(4-trifluorovinyloxy)phenyl phosphine (**4**). Reaction of the triaryl phosphine with one equivalent of hydrogen peroxide in alcohol gives quantitative conversion to tris(4-trifluorovinyloxy)phenyl phosphine oxide (**5**), which is readily isolated by the evaporation of the aqueous alcohol followed by crystallization and vacuum drying of the phosphine oxide monomer. Thermal polymerization of

5 under an inert atmosphere gives the phosphine oxide-containing thermoset polymer **6**.

Analysis of the thermal stability of the triphenylphosphine oxide polymer prepared from **5** was performed in both air and nitrogen, in a side-by-side comparison to polymer **2** of the previous study. Significant reductions in the rates of thermal and thermal/oxidative degradation were noted; however, differences still are evident in the thermal performance of the new polymer under inert and oxidative environments.

EXPERIMENTAL

Mass spectrometric analysis was carried out on a Varian Saturn GC/MS equipped with a 30-m RSL-150 capillary column, 0.25-mm i.d., 0.25-μm coating. Infrared analysis was performed on a Mattson Genesis FTIR using Winfirst software provided with the instrument. Spectra were collected at 4-cm^{-1} resolution, with 16 scans per spectrum, using a nitrogen-purged sample chamber as a background.

^{1}H-NMR 400-MHz, ^{13}C-NMR 100-MHz, ^{19}F-NMR 376-MHz, and ^{31}P-NMR 160-MHz spectra were obtained on a Varian Unity Plus spectrometer. The chemical shifts reported are internally referenced to tetramethylsilane and $CFCl_3$ for ^{1}H and ^{19}F nuclei, respectively.

Differential scanning calorimetry (DSC) data were obtained from a Mettler TA4000 system under a nitrogen atmosphere at a scan rate of 10°C/min. Thermogravimetric analysis (TGA) data were obtained on a Perkin–Elmer TGA7 with an attached 7 series/Unix thermal analyzer. The TGA was ramped from 100 to 900°C at 5°/min
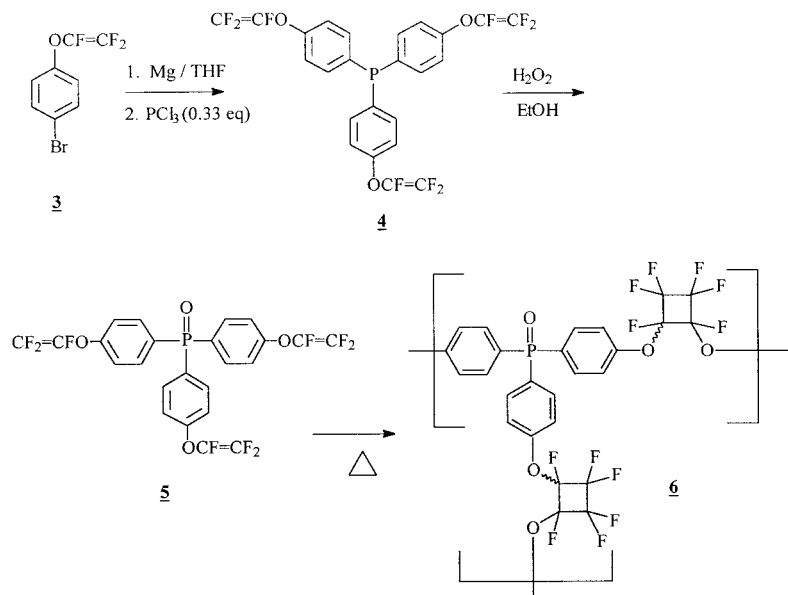
Figure 2 Synthesis of the triphenylphosphine oxide perfluorocyclobutane polyether **6**.

with programmed heating in nitrogen and anhydrous air with a flow rate of 60 mL/min. The anaerobic isothermal TGA kinetic experiments were obtained by placing a ground polymer sample into a platinum boat, loaded into the TGA furnace which was then purged with nitrogen and ramped to the desired temperature at 100°C/min. Isothermal TGA in nitrogen were obtained with a flow rate of 55 mL/min. This procedure was repeated with a fresh polymer sample at each temperature. Isothermal TGA in anhydrous air was obtained using a flow rate of 60 mL/min and similar sample preparation conditions as anaerobic conditions.

X-ray data was collected with a Rigaku AFC5R, using Cu Kα radiation, with a 12-kW rotating anode, at -100°C; trigonal, P-3; $a = 14.755(4)$, $c = 6.122(6)$A; $V = 1154(1)$A^3. Full details are provided in Table I. The structure geometry was solved by TEXSAN[27] using neutral atom scattering factors[28] with anomalous dispersion included.[29,30] The solution was derived from MITHRIL/DIRDIF.[31,32] Nonhydrogens were refined anisotropically; hydrogens from difference Fourier were refined positionally; $R = 0.106$, $Rw = 0.132$, and $S = 4.51$.

Chemical reagents were used as received without further purification. Aldrich Chemical Co. was the supplier of the 4-bromophenol. Dimethyl sulfoxide was purchased from Gaylord Chemical and was drum grade. Acetonitrile was purchased from

Fisher Scientific. Freon 114B2 was purchased in bulk from Great Lakes Chemical.

1,1,1-Tris(4-trifluorovinyloxy)phenyl Phosphine (4)

A 1.0-L jacketed five-necked flask was oven-dried and fitted with a mechanical stirrer and a dry reflux condenser. Dry tetrahydrofuran (250 mL) and fresh magnesium (6.07 g, 0.25 mol) were added to the flask and the flask was cooled to 15°C by circulating a coolant through the jacket. The 4-(trifluorovinyloxy)bromombenzene **4** (55.4 g, 0.22 mol) was placed in a dry addition funnel along with 50 mL of dry THF. A small portion (about 6 mL) of this solution was added to the magnesium in THF at 15°C along with a small grain of iodine to initiate the Grignard reaction. When the reaction had started, the starting material in THF was added to the reaction mixture slowly to form the Grignard reagent. After the conversion of the bromoaryl compound to the Grignard reagent, a solution of phosphorus trichloride (10.07 g, 0.073 mol) in 25 mL of THF was added very slowly over about 1 h. This reaction was very exothermic. The resulting reaction mixture was stirred at 15°C for 14 h (overnight), then filtered to remove solids. The filtrate was evaporated and redissolved in hexane (50 mL). This solution was deposited on a bed of alumina

Table I Crystal and Experimental Details

Empirical formula	$C_{24}H_{12}F_9PO_4$
Formula weight	566.32
$F(000)$	568
Crystal color, habit	Colorless, rod
Crystal dimensions (mm)	$0.35 \times 0.07 \times 0.09$
Crystal system	Trigonal
Space group, space group no.	P-3, no. 147
Z value (no. molecules/cell)	02
No. reflections for unit cell	
($2q$ range)	14, 51.5–72.7
Average peak half-width (w)	0.31
Cell parameters	
a	14.755 (4)
$b =$	a
c	6.122 (6)
a (°)	90
b (°)	90
g (°)	120
V (Å^3)	1154 (1)
d calc (g/cm^3)	1.629
m (CuKα) (cm^{-1})	20.28
No. data collected	1356
No. averaged data	204
R_{int} for averaged data	0.078
No. observations ($I > 3.0$ s(1))	703
% Reflections observed	61.0
No. variables	127
Data-to-variable ratio	5.5
p-Factor	0.03
Absorption correction	psi scans
Residual, R	0.106
Weighted residual, Rw	0.131
Goodness-of-fit indicator	4.51
Maximum shift error in last	
cycle	0.39
Max peak in final difference	
Fourier	0.37 e/Å^3
Min peak in final difference	
Fourier	-0.40 e/Å^3
Diffractometer	Rigaku AFC5R
Radiation	CuKα
Wavelength (Å)	1.54078
Temperature (°C)	-100
Attenuator (Zr foil) factors	3.5, 12.2, 42.3
Take-off angle (°)	6.0
Detector aperture	
(horizontal/vertical)	6.0 mm
Crystal-to-detector distance	40.0 cm
Data collection scan type	w
Scan rate, (°/min w)	8.0
Rescan of weak data	3 maximum
Scan width (°w)	$A + 0.14 \tan q$
A, peak width (°w)	1.52
$2q$ maximum for data (°)	120.2

in a 600-mL coarse grain sintered glass funnel and eluted with hexane. The phosphine monomer 1,1,1-tris(4-trifluorovinyloxy)phenylphosphine (12.63 g, 0.023 mol, 31.4% yield) was isolated as a light yellow oil. A second fraction of the product was isolated as the phosphine oxide (3.87 g, 0.0068 mol, 9.3% yield) by eluting the alumina bed with dichloromethane, bringing the overall conversion to Grignard coupled products to a 40.7% yield.

IR (cm^{-1}): 782, 829 (Ar); 1014, 1093, 1106, 1139, 1170, 1203, 1278, 1317 (C—O, C—F, P—Ar); 1492, 1590 (Ar); 1832 (CF=CF$_2$). Mass spec, m/e (%): 107 (4.1), 183 (5.0), 280 (3.4), 377 (9.4), 550 (100), 551 (21.9). ^{1}H-NMR (CDCl$_3$) δ 7.23 (d, 2H), 7.32 (t, 2H). ^{31}P-NMR (CDCl$_3$) δ −9.36 (s). ^{19}F-NMR(CDCl$_3$) δ −120.10 (dd, cis—CF=CF$_2$, F$_a$), −126.80 (dd, $trans$-CF=CF$_2$ F$_b$) − 134.80 (dd, CF=CF$_2$, F$_c$).

1,1,1-Tris-(4-trifluorovinyloxy)phenylphosphine Oxide (5)

A solution of 1,1,1-tris-(4-trifluorovinyloxy)phenylphosphine (6.34 g, 0.0115 mol) in absolute ethanol (50 mL) was placed in a 100-mL three-necked jacketed round-bottomed flask. The solution was cooled to 5°C. Hydrogen peroxide (30%, 1.31 g, 0.01156 mol) was placed in a 3-mL plastic syringe and added to the phosphine solution over 5 min through a plastic canula tube. The solution was stirred at 5°C for 10 min, then analyzed by gas chromatography. All the phosphine starting material had been converted, and a large peak associated with the phosphine oxide had appeared. The reaction mixture was evaporated to remove alcohol, then evaporated under a high vacuum (2 mmHg) at 60°C to remove water. Upon cooling, the phosphine oxide monomer crystallized. This crystalline product was washed twice with 25 mL of hexane and then filtered and air-dried. A total of 5.02 g of material was isolated in this fashion for a 77.1% yield. A melting point of 104–105°C was measured for this material.

IR(cm^{-1}): 783, 822, 833 (Ar), 1014, 1090, 1114, 1141, 1169, 1204, 1268, 1287, 1316, 1401 (C—O, C—F, P—Ar, P=O), 1494, 1582, 1593 (Ar), 1834 (CF=CF$_2$). Mass spec, m/e (%): 152 (5.8), 468 (15.8), 469 (13.8), 565 (5.1), 566 (100), 567 (75.4). ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.22 (t, 2H), 7.67 (t, 2H). ^{31}P-NMR (CDCl$_3$) δ 26.6 (s). ^{13}C-NMR (100 MHz, CDCl$_3$) 118.8, 125 (^{31}P—Ar, d, J = 1800 Hz), 127.7, 128.8, 132.7 (ddd, CF=CF$_2$, ^{1}J = 49 Hz, ^{2}J = 48, ^{2}J = 262

Hz), 146.5 (ddd, CF$=$CF$_2$, ^{1}J $=$ 59 Hz, ^{1}J $=$ 273, ^{2}J $=$ 279 Hz), 157.9. ^{19}F-NMR (376 MHz, CDCl$_3$) δ -118.9 (1F, dd, cis—CF$=$CF$_2$, F$_a$), -125.6 (1F, dd, $trans$—CF$=$CF$_2$ F$_b$), -135.3 (1F, dd, CF$=$CF$_2$, F$_c$) (J$_{ab}$ $=$ 85.3 Hz, J$_{bc}$ $=$ 110 Hz, J$_{ac}$ $=$ 60.9 Hz).

Triphenylphosphine Oxide Perfluorocyclobutane Polyether (6)

Monomers **1** and **5** were thermally polymerized by placing **1** (0.36 g, 0.66 mmol) and **5** (0.34 g, 0.60 mmol) into separate aluminum pans and heating in a nitrogen-blanketed oven to 225°C for 48 h. Postcuring of the polymers was accomplished by heating the individual polymers to 300°C for 3 h in a nitrogen-blanketed oven. The polymers were removed from the oven, cooled to room temperature in air, and ground to powder using a mortar and pestle. Infrared analysis of **2** was consistent with that which was previously reported.[22] Infrared analysis of polymer **6** is reported below:

IR (cm^{-1}): 829 (Ar), 960 (perfluorocyclobutane), 1014, 1114, 1141, 1170, 1203, 1268, 1317 (1403 (C—O, C—F, P$=$O), 1496, 1595 (Ar).

RESULTS AND DISCUSSION

Monomer Synthesis

The synthetic method involved the preparation of the fluoroolefin compound 4-(trifluorovinyloxy)-bromobenzene **3** from 4-bromophenol via the conventional preparative route.[24] Compound **3** was then coupled with phosphorus trichloride (PCl$_3$) via Grignard chemistry to form the trifunctional phosphine monomer **4**, followed by oxidation of **4** to the phosphine oxide monomer **5** under mild conditions.

The preparation of the phosphine oxide monomer was carried out through the corresponding phosphine monomer because of problems with the purification of the monomer in the phosphine oxide form. A synthetic route involving the preparation of **6** by first preparing the compound 1,1,1-tris(4-hydroxyphenyl)phosphine oxide[33,34] followed by fluoroalkylation and olefin formation in the classical reaction scheme[22] was unsuccessful due to difficulties in purifying the final phosphine oxide monomer which contained the typical reaction by-products. When using the reaction scheme outlined in Figure 2, it was found that the phos-

phine monomer **4** could be purified by chromatography or by solvent extraction in the typical fashion.[22] The phosphine monomer could then be quantitatively converted to the phosphine oxide monomer **5** by treatment with hydrogen peroxide in ethanol, without destruction of the fluorinated olefins. The product thus isolated usually required little if any purification.

X-ray Crystallography

Bond distances and angles in the trifluorovinyl end group indicate that the terminal carbon is relatively more sp^3, rather than sp^2-hybridized. A very short olefinic bond distance [1.12(2) Å] is the result of an increased s-character and a reduced p-character for this bond. The molecule packs in columns of like orientation along the c-axis. Adjacent columns have reverse orientation. The C—α-F distance is 1.42(2) Å; terminal C—F average 1.31(2) Å. The fluoroolefin bond distances are typical of these types of structures.[35] The X-ray crystal structure of **5** is depicted in Figure 3.

Polymerization

The cyclodimerization of tetrafluoroethylene was reported to proceed with a $\Delta H = -50$ kcal/mol.[36] The exothermic polymerization of trifluorovinyl ether monomers prepared in our laboratories to date reached a measurable rate (dynamic DSC at 10°C/min) near 140°C, and polymerizations are
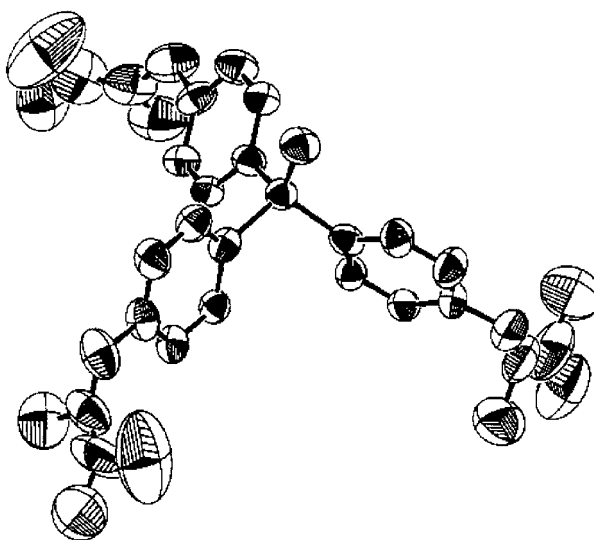

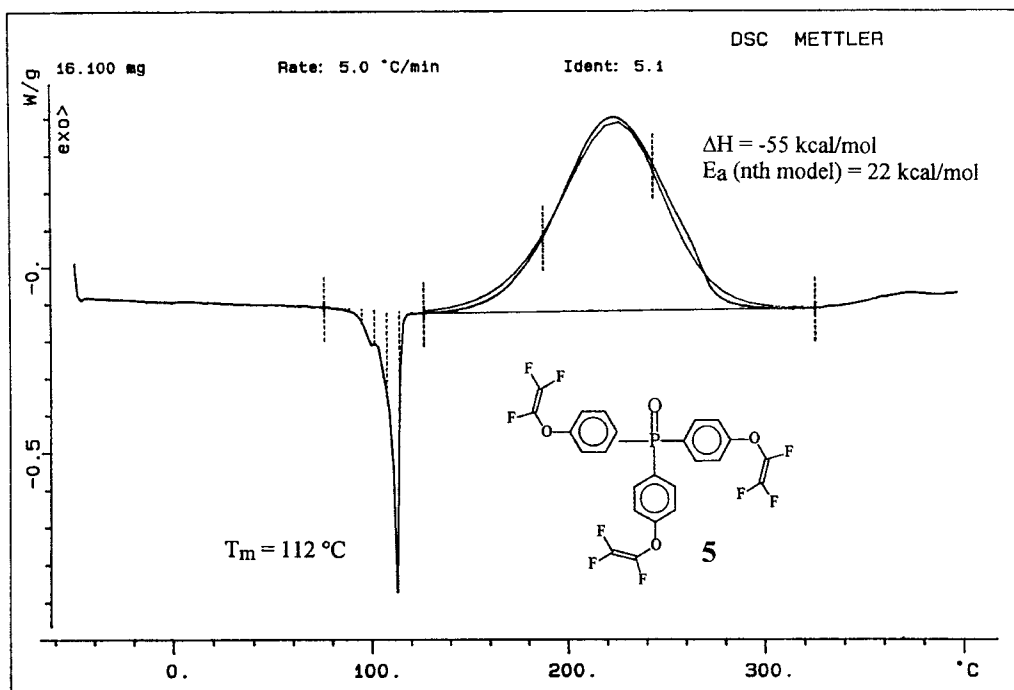**Figure 3** X-ray structure of monomer **5**.

Figure 4 Polymerization of monomer **5** by dynamic DSC (5°C/min).

typically carried out at temperatures between 150 and 250°C. Figure 4 depicts the bulk polymerization of monomer **5**, giving a $\Delta H = -55$ kcal/mol and an nth-order model $E_a = 22$ kcal/mol. In contrast, the isothermal DSC kinetic treatment gives lower activation energies for the polymerization of monomer **5**, yielding an $E_a = 18$ kcal/mol.[37] Significant differences in the polymerization rate have not been observed for the variety of trifluorovinyl ether monomers studied to date.

Thermal Stability

The kinetics of thermal and thermal/oxidative decomposition for the triphenylphosphine oxide polymer **6** were compared to the decomposition kinetics of the polymer **2** prepared under identical conditions. Slight differences between the thermal analysis data reported for **2** in this article as compared to the previous report[22] may be attributed to differences in sample preparation and the data being collected on different instruments with different sample chamber configurations.

As can be seen from the graph in Figure 5, measurable improvements were noted for the thermal stability of polymer **6** compared to **2**. While the polymer does appear to exhibit a slightly lower rate of weight loss under oxidative conditions, the rates of weight loss in air and in nitrogen are still markedly different, indicating that oxidative processes still play a significant role in the decomposition of the polymer. In all cases, the data converge at temperatures above 400°C, where rates of decomposition become relatively rapid. The rate data for the four experi-
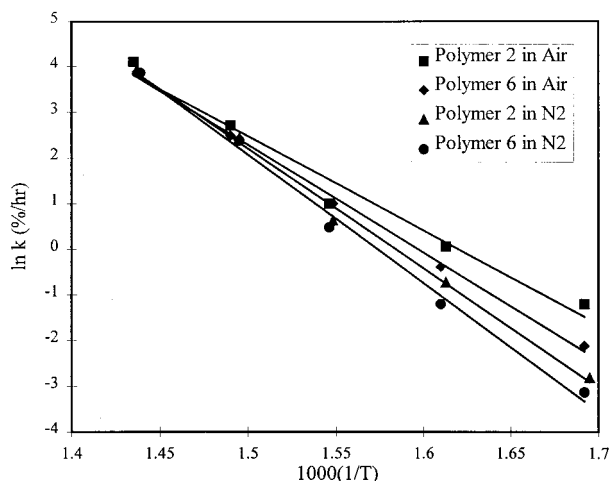

Figure 5 Arrhenius plot of thermal decomposition data for **2** and **6**.

Table II   Thermal Decomposition Data for Polymers 2 and 6

Nitrogen				Air			
Temp (°C)	$1/T$ (1000/K)	k (%/h)	ln k (%/h)	Temp (°C)	$1/T$ (1000/K)	k (%/h)	ln k (%/h)
Polymer 2[a]							
423	1.437	51.00	3.932	424	1.435	60.75	4.107
396	1.495	11.40	2.434	398	1.490	15.00	2.708
373	1.548	1.86	0.621	374	1.546	2.70	0.993
347	1.613	0.48	−0.734	347	1.613	1.06	0.058
317	1.695	0.06	−2.813	318	1.692	0.30	−1.240
Polymer 6[b]							
422	1.439	48.00	3.871	423	1.437	49.00	3.892
396	1.495	10.80	2.380	398	1.490	12.00	2.485
374	1.546	1.62	0.482	373	1.548	2.72	1.001
348	1.610	0.30	−1.204	348	1.610	0.68	−0.393
318	1.692	0.04	−3.124	318	1.692	0.12	−2.120

[a] $E_a/R = 26.131$, $E_a = 51.920$ kcal/mol.
[b] $E_a/R = 27.626$, $E_a = 54.900$ kcal/mol.

ments are tabulated in Table II. As before,[23] Arrhenius parameters are not calculated for the cases of decomposition in air because of the inability to exclude competing weight-gain processes from the zeroth-order calculations.

CONCLUSIONS

While some improvements in thermal and thermal/oxidative performance were seen in the perfluorocyclobutane thermoset polymer system by replacing the alkyl crosslinking structure in polymer **2** with a phosphine oxide group in polymer **6**, this change did not result in the desired performance optimization in which the thermal and thermal/oxidative performances of polymer **6** are identical. Further minimization of the oxidative contribution to thermal/oxidative degradation of these poly(phenylene ether) polymers may be possible with other structural modifications.

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