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Notes

Poly(ether ether ketone)s and Poly(ether sulfones) with Pendent Adamantyl Groups

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Introduction

Adamantane has been incorporated into many polymers over the past several years due, in part, to the unusual physical and thermal properties this multicyclic cage structure imparts. Its rigid, spherical structure results in a very high melting point for the parent molecule (269 °C) and excellent thermal stability for a hydrocarbon.[1] When it replaces other aliphatic groups in the main chain of a polymer, increases in glass transition (T_g), melting (T_m), and decomposition (T_{dec}) temperatures are generally observed.[2] Many examples of adamantane-containing polymers have been reported that describe adamantane incorporation into the backbone using 1,3- or 2,2-disubstituted derivatives. Examples include aliphatic and aromatic polyesters, polyamides and imides, and polycarbonates.[2] Recently, adamantane-containing polysulfones were reported in which the adamantane was used as the bridgehead for Bisphenol A analogs.[3] The physical properties and gas permeation behavior of both the 2,2-bis(4-hydroxyphenyl)- and the 1,3-bis(4-hydroxyphenyl)adamantane-containing polysulfones were reported. They displayed high T_g's (297 and 242 °C, respectively) when compared to the commercial Bisphenol A derived polysulfone (T_g 190 °C), thus providing an indication of the greater resistance to segmental motion caused by the bulky and rigid adamantane segment, especially for the 2,2-disubstituted species.

When adamantane is incorporated into a polymer as a pendent group, even more dramatic increases in T_g's were observed. For example, poly(1-adamantyl acrylate) and poly(1-adamantyl methacrylate) displayed increases in T_g of over 140 °C compared to their methyl ester analogs.[4] In addition, these polymers showed increased hardness but were reported to form brittle films. We observed similar T_g increases for adamantyl-pendent derivatives of linear polymers and cyclopolymers based on α-hydroxymethyl acrylate[5] and its ether dimer; these polymers also formed brittle films.[6]

Our group is currently interested in the synthesis of other adamantane-containing polymers to develop a better understanding of the generic effect adamantane has on the physical properties of polymers.[7−10] Recently, we have focused on incorporating pendent adamantane groups.[11,12]

Poly(aryl ether)s such as poly(ether ether ketone) (PEEK, **1**) and poly(ether sulfone) (PES, **2**) (Figure 1) are well established as commercially important, high performance engineering thermoplastics. These polymers are readily synthesized via nucleophilic aromatic substitution (NAS) between a bisphenolate salt and an activated aromatic dihalide.[13] They display outstanding toughness but, compared to thermosets, have relatively low use temperatures.

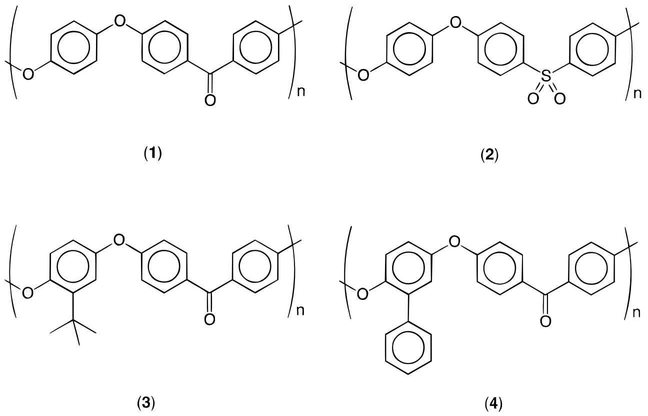

Figure 1. Parent PEEK (**1**) and PES (**2**) and *tert*-butyl (**3**) and phenyl (**4**) substituted PEEK derivatives.

Several approaches have been taken in attempts to manipulate the properties of ether ketone and ether sulfone polymers. Structural modifications have included varying the para\meta connectivity,[14] changing the ether-to-ketone ratio,[15] and introduction of pendent groups onto the polymer.[16,17] Several substituted PEEK polymers with pendent alkyl and phenyl groups have been reported. Polymers containing *tert*-butyl and phenyl groups have been prepared and found to be completely amorphous and readily soluble in common organic solvents.[16,17] For example, including one *tert*-butyl group per repeat unit (**3**) increased the glass transition temperature by 24 °C (151 to 175 °C) whereas the phenyl group (**4**) resulted in a minor change of only 3 °C. Generally, the incorporation of pendent groups results in amorphous materials with increased solubility in common organic solvents.

Here we report the synthesis and characterization of adamantane-containing poly(ether ether ketone)s (ADPEEK) and poly(ether sulfone)s (ADPES) derived from adamantyl-substituted resorcinol, **5**, along with PEEK and PES copolymers of **5** with hydroquinone and Bisphenol A comonomers.

Experimental Section

Solvents and reagents were purchased from the Aldrich Chemical Co. and used as received except as noted. DMAc was vacuum distilled from CaH_2. 4,4′-Difluorobenzophenone was recrystallized from ether. 4,4′-Dichlorophenyl sulfone was recrystallized from toluene and sublimed. 4,4′-Difluorophenyl sulfone was recrystallized from toluene and sublimed. 2,2-Bis(4-hydroxyphenyl)propane (Bisphenol A) was recrystallized from toluene. 1,4-Hydroquinone was recrystallized from ethanol and sublimed.

Intrinsic viscosities were determined in $CHCl_3$ at 30 °C. Size exclusion chromatography (SEC) was performed in THF

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Table 1. Synthesis Conditions and Polymerization Results

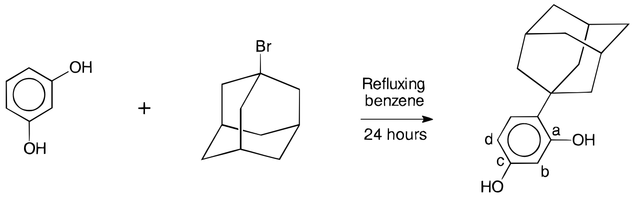
	feed ratio (mole fraction)					mol wt	
polymer	ADRES	BPA	HQ	DFBP	DFPS	[η], dl/g	SEC 10^{-3} M_n
P1	0.50			0.50		0.62	55
					0.50[a]	0.20	
P2	0.50				0.50	0.88	
P3	0.25		0.25	0.50			
P4	0.125		0.375	0.50			
P5	0.05		0.45	0.50			
P6	0.25	0.25		0.50		0.97	
P7	0.125	0.375		0.50		1.51	
P8	0.25	0.25			0.50	0.99	
P9	0.125	0.375			0.50	0.47	

using four AM gel mixed-bed 7.5 mm × 300 mm, 10 μm particle diameter columns (American Polymer Standard Corp., Mentor, OH). ^{13}C and ^{1}H NMR spectra were obtained in $CDCl_3$ or DMSO-d_6 using a Bruker AC-300 operating at 75.469 MHz for carbon and 300.019 MHz for proton. Differential scanning calorimetry (DSC) was performed using a TA DSC 2920 module (TA 2100 controller) at a heating rate of 10 °C/min in a nitrogen atmosphere. Thermogravimetric analysis was conducted on a TA SDT 2960 module (TA 2100 controller) at a heating rate of 20 °C/min in nitrogen and air environments. Dynamic mechanical analysis was performed on a Polymer Labs DMTA Mark III in tensile mode at a ramp rate of 4 °C/min in a nitrogen environment. Wide angle X-ray diffraction data were collected on polymer films using a Siemens XPD-700 polymer diffraction system equipped with a two-dimensional, position sensitive area detector. Elemental analyses were carried out by MHW Laboratories, Phoenix, AZ.

4-(1-Adamantyl)-1,3-benzenediol. Bromoadamantane (100 g, 0.46 mol), resorcinol (55.1 g, 0.50 mol), and benzene (500 mL) were combined in a reaction flask equipped with a nitrogen inlet, a condenser fitted with a caustic scrubber, and a mechanical stirrer. The mixture was heated to reflux and allowed to react for 72 h under a constant nitrogen purge to assist in the removal of HBr formed. The reaction mixture was cooled to ambient temperature and the adamantyl-substituted resorcinol **5** crystallized from solution. Residual resorcinol was removed by precipitating a solution of **5** in methanol into warm water followed by filtering and washing with water. Purification to polymerization quality monomer was accomplished by vacuum drying to remove residual water, recrystallizing from toluene, and finally subliming; yd 77%; mp 249−250 °C. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.70, H, 8.30. Found: C, 79.00; H, 8.17. ^{1}H NMR (DMSO-d_6): δ 8.36 (s, 1H), 8.29 (s, 1H), 6.93 (d, 1H), 6.35 (d, 1H), 6.25 (d, 1H), 2.07 (s, 6H), 2.02 (s, 3H), 1.73 (s, 6H). ^{13}C NMR: δ 156.36, 155.22, 127.32, 126.30, 105.36, 103.65, 40.24, 36.64, 35.42, 28.57.

Adamantane-Containing Poly(aryl ethers). Polymerizations were performed by following published procedures.[18] For example, adamantylresorcinol (5 g, 20.5 mmol) and 4,4'-difluorobenzophenone (4.468 g, 20.5 mmol) were dissolved in DMAc (35 mL) and toluene (10 mL) in a reaction flask fitted with a nitrogen blanket, mechanical stirrer, and a Dean-Stark trap. K_2CO_3 (2.969 g, 21.48 mmol) was added and the stirring mixture heated to reflux. Reflux was held (130 °C) for 1 h followed by the gradual removal of toluene from the reaction flask until the flask temperature reached 160 °C (ca 2 h). The reaction mixture was maintained at 160 °C for 10 h and then cooled to ambient temperature. The polymer solution was diluted with chloroform, filtered to remove the inorganic salts, acidified, and then precipitated into methanol. Filtration and drying of the product at 120 °C under vacuum gave essentially quantitative yields of the homopolymer **P1**. ^{13}C NMR ($CDCl_3$): δ 194.1, 161.1, 161.0, 155.7, 154.2, 138.1, 132.3, 132.28, 128.7, 117.5, 117.1, 115.6, 113.1, 41.3, 36.8, 36.8, 28.9.

Copolymerizations were carried out with the mole ratios given in Table 1 using either DMAc or tetramethylene sulfone (sulfolane) as solvent. Isolation of the products was carried out in the same manner as for the homopolymer. Copolymers with hydroquinone were prepared in tetramethylene sulfone and were Soxhlet extracted with methanol to remove solvent and salts from the insoluble polymer.



(**5**)

Figure 2. Synthesis of adamantylresorcinol (**5**).

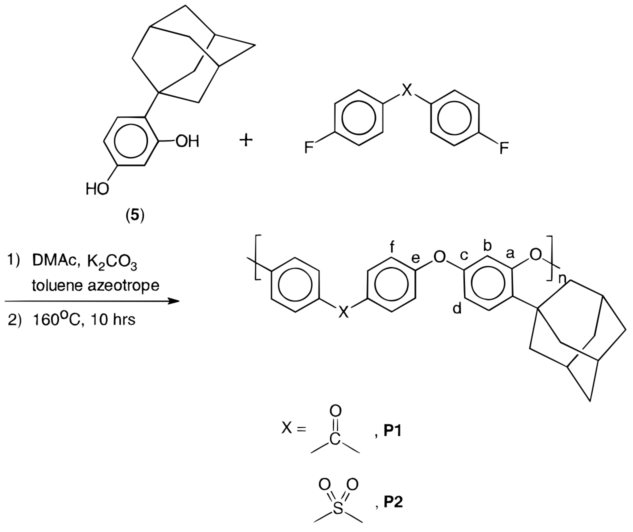


Figure 3. Synthesis of poly(aryl ether)s from adamantylresorcinol (**5**).

Results and Discussion

Adamantylresorcinol **5** was prepared in 77% purified yield in a manner similar to that previously reported (Figure 2).[19] It was readily synthesized by the alkylation of resorcinol with bromoadamantane without added catalyst. After recrystallization from toluene and drying at 120 °C under vacuum, NMR indicated that solvent (0.5−2.0 wt %) was still present in the needles that were collected. Sublimation of the recrystallized compound resulted in a purity of >99.9%, as determined by gas chromotagraphy.

Adamantane and its derivatives are known to form solid solutions and inclusion compounds with a variety of organic small molecules.[1] It appears that adamantylresorcinol also traps solvent within its crystal lattice and effectively prevents it from being removed without subliming or melting the sample. This solid state behavior apparently revolves around the bulky and nonsymmetrical nature of the substituted adamantane derivatives. We believe this behavior also controls the properties of the polymers described below.

Homopolymers. Poly(aryl ether)s with pendent adamantyl groups were prepared from adamantylresorcinol using conventional NAS conditions in DMAc. Figure 3 illustrates the general polymerization scheme that was employed. The reaction was followed qualitatively by a reduction in red color from the phenolate ion as the reaction proceeded and an increase in reaction viscosity near the end of the reaction. The NAS synthesis using adamantylresorcinol resulted in viscous reaction solutions when 4,4′-difluorobenzophenone or 4,4′-difluorophenyl sulfone was used. However, hardly any increase in viscosity was observed with 4,4′-dichlorophenyl sulfone.

Polymer molecular weights were estimated using dilute solution viscosity (intrinsic viscosity or IV) and SEC. For the polymers prepared from the bis(aryl fluorides), IV values of 0.6−1.0 dL/g were observed, indicating high molecular weight polymers were formed. However, reactions using 4,4′-chlorophenyl sulfone resulted only in low molecular weight polymer with typical IVs of ca. 0.2 dL/g, suggesting that an alternative reaction pathway competes with the NAS polymerization (discussed below).

SEC results indicated that polymer **P1** had hydrodynamic volumes comparable to a 55 000 number average molecular weight (M_n) polystyrene standard (with a dispersity of 2.5) for an IV of 0.62 dL/g. SEC results for the sulfone polymer, **P2**, with an IV of 0.90 dL/g, showed an M_n of 152 000. For the polymer formed from 4,4′-dichlorophenyl sulfone, SEC indicated an M_n of <10 000.

These results suggest that the steric hindrance from the adamantane around the adjacent OH, in combination with the less activated aryl chloride group, led to side reactions that effectively competed with polymerization. It has recently been shown that a single electron transfer pathway can effectively compete with nucleophilic substitution reactions when less activated halide groups are employed. For example, when 4,4′-dichlorobenzophenone was used instead of the more reactive fluorine analog in the synthesis of poly(aryl ether ketone), molecular weights were significantly lower and benzophenone end groups were identified.[20,21] Three of the factors described that influence the extent of competition of the reduction pathway are degree of activation by the leaving group, steric hindrance of the nucleophile, and oxidation potential of the nucleophile. Phenolate nucleophiles with bulky ortho substituents have been shown to increase the occurrence of side reactions (such as single electron transfer) that lead to unreactive chain ends and low molecular weights.[21]

Another consequence of the adamantane pendent groups on the polymerization process, in conjunction with meta diol substitution on the resorcinol ring, was the formation of an insoluble crystalline product (ca. 5−15% by weight) during the synthesis of high molecular weight polymers. The materials were first noted due to their insolubility in good solvents for the polymer; in fact, this led to facile separation of these materials by repeated extraction. Their solid state ^{13}C NMR spectrum showed resonances consistent with adamantane, aryl ethers, and ketone groups (but no end groups), suggesting crystalline macrocycle formation. The isolated cyclics displayed a broad melting transition with a peak temperature of 378 °C. Cyclic oligomer formation was minimized by using more concentrated solutions (25 wt % monomer), which resulted in polymer formation in high yields.

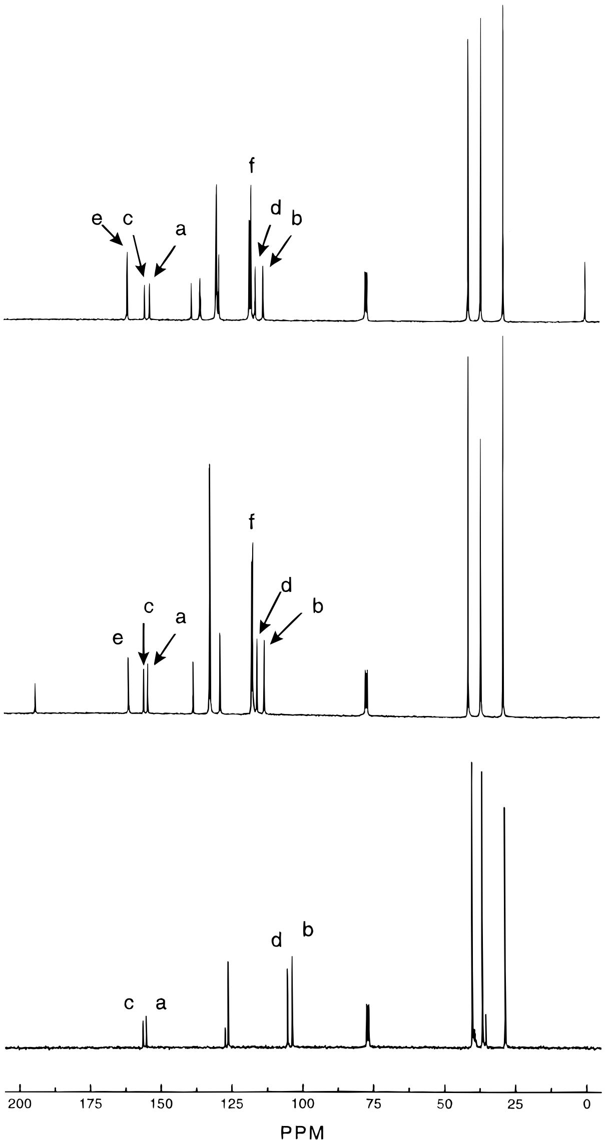


Figure 4. ^{13}C NMR spectra of adamantylresorcinol (**5**, bottom trace), ADPEEK (**P1**, middle trace), and ADPES (**P2**, top trace).

The solution ^{13}C NMR spectrum of **P1** and **P2** corroborates the SEC data, showing only peaks consistent with the proposed repeat unit structures (Figure 4) and no evidence of end groups, which would be difficult to detect at the <1% concentration level estimated for this MW. Chemical shift assignments were consistent with those predicted from additivity tables. Assignments for some of the key carbons of the repeat unit have been made for ADPEEK (**P1**) and ADPES (**P2**), as shown in Figure 4. Though the potential steric hindrance of the adamantyl group ortho to the phenolic OH was not great enough to prevent polymerization under NAS conditions using the highly activated fluoro monomers, its asymmetric placement in the polymer resulted in splitting that was observed for the resonances assigned to the benzophenone carbons ortho to the ether, suggesting that the adamantyl group has an influence on the environment several atoms away, most likely by through-space effects and restricted rotational mobility.

The adamantyl-substituted homopolymers **P1** and **P2** were soluble in many common organic solvents such as chloroform, methylene chloride, THF, and NMP. Surprisingly, upon cooling the reaction mixture, **P1** gelled from the DMAc reaction mixture and became insoluble. The isolated polymer was soluble in hot DMAc, but again gelled as the temperature returned to ambient.

Copolymers. Two series of ether ketone copolymers were prepared using either hydroquinone or Bisphenol A as comonomer with **5** in order to better understand the effects of adamantane on polymer properties. The copolymers were prepared using the monomer feeds shown in Table 1. The hydroquinone copolymers were prepared for comparison to the commercial polymer and to determine how **5** would modify the physical properties at low levels of incorporation. For these copolymers, tetramethylene sulfone was required as the reaction

Table 2. Solubility Behavior of the Adamantyl-Substituted Poly(aryl ether)s

	polymer solubility				
polymer	$CHCl_3$	THF	DMAc	NMP	sulfolane
P1	+	+	±	+	+
P2	+	+	+	+	+
P3	−	−	+	+	+
P4	−	−	−	−	+
P5	−	−	−	−	+
P6	+	+	+	+	+
P7	+	+	+	+	+
P8	+	+	+	+	+
P9	+	+	+	+	+

Table 3. Thermal Properties of Adamantyl-Substituted Polymers

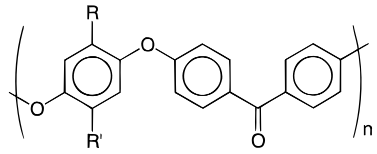
		TGA results 5% loss		DMTA results	
polymer	T_g (°C)	N_2	air	T_γ, °C	film properties
P1	225	505	486	−89	strong, brittle
P2	258	480	470		clear, brittle
P3	193	466	410		strong, flexible
P4	173				translucent, strong, flexible
P5	165				
P6	191	509	483	−91	clear, strong, flexible
P7	173	500	481	−97	clear, strong, flexible
P8	239	470	474	−102	clear, strong, flexible
P9	223	476	467	−104	clear, strong, flexible

solvent so that polymer solubility was maintained throughout the reaction. Even with this solvent, a reaction temperature of 230 °C was needed to maintain polymer solubility for polymers **P4** and **P5**. Upon cooling, the reaction mixtures gelled for all the copolymers and the products were isolated by Soxhlet extraction with methanol and then chloroform (24 h each) to remove inorganic salts and trapped solvent. The Bisphenol A copolymers were prepared in DMAc using the method described for the homopolymer. Intrinsic viscosities for these copolymers were all greater than 0.9 dL/g, indicating high molecular weight polymers were formed in all cases. No macrocyclic oligomer formation was apparent, although solubility differences between polymer and macrocycles may not be great enough to allow ready detection in the copolymers.

The solubility behavior (Table 2) of the hydroquinone copolymers was markedly different than ADPEEK and more like that of the commercial material. The 50:50 copolymer, **P3,** showed the broadest solubility of the HQ copolymers, dissolving in DMAc, NMP, and tetramethylene sulfone. **P4** and **P5** only dissolved in hot tetramethylene sulfone at >200 °C. The copolymers based on Bisphenol A (similar to **P1** and **P2**) were soluble in common organic solvents such as polar aprotic and chlorinated solvents.

Thermal Behavior. The T_g's of the adamantyl-substituted polymers were determined by DSC, and the results are given in Table 3. The homopolymer **P1** displayed a T_g of 235 °C with no indication of a melting transition. This is an increase of over 100 °C compared to the unsubstituted polymer (120 °C[22]) made from resorcinol and is considerably higher than the value reported for commercial PEEK (154 °C). In comparison, several poly(ether ether ketone)s based on substituted hydroquinones (Table 4) have been reported.[16,17,18] Methyl and phenyl groups have little effect on the glass transition temperature but do decrease crystallinity. The more bulky *tert*-butyl group does increase the T_g, but to a lesser extent than pendent adamantyl moieties. The combination of side-chain rigidity and size for the latter, along with ortho interaction with the adjacent backbone unit, appears to require much more energy to develop the segmental mobility needed to reach T_g.

Table 4. Pendent group effect on T_g for Hydroquinone-based PEEK



R	R′	T_g, °C
		152.2[18]
CH_3		154.5[18]
tert-butyl		175[17]
tert-butyl	*tert*-butyl	206[17]
phenyl		154[17]

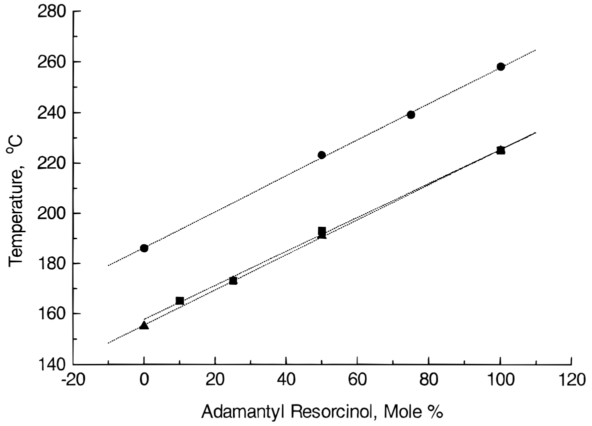


Figure 5. T_g as a function of composition for ADRES/BPA PEEK copolymers (▲), ADRES/HQ PEEK copolymers (■), and ADRES/BPA PES copolymers (●).

The adamantane-containing polysulfones were also prepared in order to better establish the relationship between backbone rigidity and the degree to which pendent adamantane groups affect T_g. The sulfone linkage provides a more polar rigid backbone compared to the ketone moiety of PEEK polymers, and the homopolymer **P2** made here with **5** has a T_g of 258 °C, which is 60 °C higher than the polysulfone based on Bisphenol A and falls in between the polysulfones possessing backbone adamantane moieties derived from 1,3-bis(4-hydroxyphenyl) and 2,2-bis(4-hydroxyphenyl)-adamantane (242 and 297 °C).[3]

For all three copolymer series synthesized here, glass transition temperatures varied linearly with composition (Figure 5), suggesting random incorporation of **5** with the other bisphenols. Surprisingly, the effect of the adamantyl content is experimentally the same for all three series; the slope of the best fit line acquired from linear regression is 0.7 for each. Increasing the parent backbone rigidity only translates the curve along the *Y* axis. This behavior suggests that a well-defined segment contribution exists for pendent adamantanes, at least when they are directly bound to backbone phenylene groups.

TGA was performed to measure the effect that adamantane has on the thermooxidative stability of these new polymers. Temperatures of onset of weight loss and 5% weight loss for the families of polymers are given in Table 3. These new aryl ethers all display thermal stability to greater than 400 °C by TGA, indicating that the inherent short-term stability of the parent polymers has not been significantly reduced by incorporation of

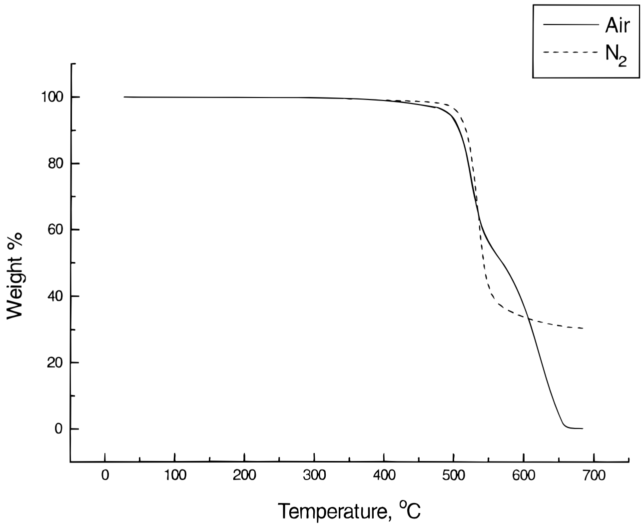


Figure 6. TGA trace for **P1** in air and N_2.

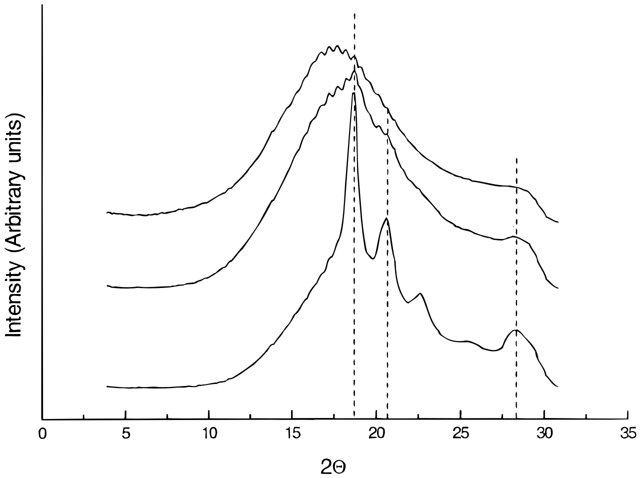


Figure 7. WAXD patterns for **P3** (upper), **P4** (middle), and **P5** (lower).

such a large aliphatic substituent. The TGA trace for polymer **P1** (Figure 6), the system that contains the highest adamantane content, is an example of the behavior of the entire series. Onset of decomposition occurred above 400 °C in both air and nitrogen with a 5% weight loss value of >490 °C in air. Considering that adamantane is aliphatic, these polymers have excellent short-term stability in N_2 and air. Long-term aging studies in air at elevated temperatures should show differences, however; such studies have not yet been done.

X-ray Analysis. The hydroquinone copolymers demonstrate the effects of adamantyl groups on the solid-state packing properties of the commercially produced PEEK (believed to be made from HQ and DFBP). One of the important properties of PEEK is that it is semicrystalline. The copolymers made here represent a progressively increasing amount of defect in the polymer in the form of meta linkages containing a bulky pendent moiety. Not surprisingly, the 50:50 copolymer (**P3**) displayed no crystalline X-ray reflections, only a broad amorphous halo centered around 5 Å, as shown in Figure 7. The 25:75 copolymer, **P4**, was found to display weak crystalline reflections at the same 2Θ values as the much more crystalline 10:90 copolymer. This polymer, however, only displayed crystallinity after melt-pressing at ~270 °C. DSC indicated a relatively small amount of crystallinity, with a heat of fusion of 10 J/g at a T_m of 285 °C compared to PEEK's T_m at 338 °C reported for virgin material on the first scan.[17] The reflections that were observed are also consistent with those reported for PEEK.[23]

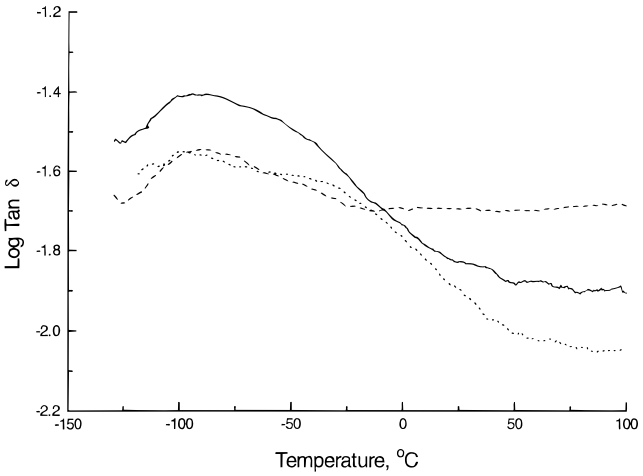


Figure 8. tan δ at 1 Hz as a function of temperature for **P1** (---), **P6** (—), and **P7** (···).

Film Properties. Films of the different polymer samples were prepared by solution casting from $CHCl_3$ at 250−270 °C or (for the hydroquinone copolymers) melt-pressing at ~50 °C above the T_g. All films were off-white to tan in color. Based upon visual inspection, the quality of the films were ranked from brittle to strong, flexible, and creasible, as listed in Table 3. In addition to increasing T_g, adamantane incorporation caused brittleness in the thin films. Films of **P1** were transparent and strong, but brittle. However, the copolymers with hydroquinone or Bisphenol A formed films that were transparent, strong, and flexible. The sulfone homopolymer, **P2**, was even more brittle and had very poor mechanical integrity, but again, the copolymers with Bisphenol A yielded strong, flexible, and creasible films.

With these variations in film properties with composition, dynamic mechanical analyses (DMA) were performed to probe the sub-T_g relaxation behavior of the adamantyl-substituted polymers (Figure 8). For the copolymer series, a single broad and weak γ relaxation for each polymer was observed (Table 3). All the relaxations were observed at low temperature (−100 °C to −85 °C) with no discernible correlation with copolymer composition. The sub-T_g relaxation was observed for polymer **P7**, but again no direct correlation between adamantane content in the polymer and peak temperature could be made.

Conclusions

New adamantane-containing aryl polyethers were synthesized from adamantylresorcinol. The hindered ortho-substituted phenolic group did allow polymerization and copolymerization under NAS conditions with highly active monomers to give high molecular weight products. Steric inhibition was sufficient, however, to cause side reactions with a less-active monomer, likely SET reductions, that reduced MW. Thermal behavior of the polymers was affected greatly by incorporation of adamantyl groups, with increases of T_g of over 100 °C for homopolymers compared to unsubstituted analogs. This is significant in light of the fact that only one in three phenyl rings in the backbone is substituted with adamantane. The polymers also displayed thermal stability (by TGA) to greater than 400 °C, indicating that the adamantane units do not greatly decrease the inherent thermal stability of the PEEK backbone. T_g–composition plots of all three families of copolymers examined gave identical slopes, suggesting that copolymers are random and that there is a well-defined segment contribution for the pendent adamantanes.

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