Phenylethynyl End-Capped Polyimides Derived from 4,4′-(2,2,2-Trifluoro-1-phenylethylidene)diphthalic Anhydride, 4,4′-(Hexafluoroisopropylidene)diphthalic Anhydride, and 3,3′,4,4′-Biphenylene Dianhydride: Structure−Viscosity Relationship

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ABSTRACT: The synthesis and characterization of phenylethynyl (PE) end-capped polyimides derived from 4,4′-(2,2,2-trifluoro-1-phenylethylidene) diphthalic anhydride (3FDA), 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), and 3,3′,4,4′-biphenylene dianhydride (s-BPDA) are described in this paper, with particular emphasis on the glass transition temperatures and viscosities. The phenylethynyl end-capped 3FDA- and 6FDA-containing oligomides demonstrate much lower minimum complex melt viscosities than s-BPDA-containing oligomides. The PE-3F and PE-6F oligomers also show greater viscosity stability at elevated temperature (310 °C) than s-BPDA oligomides. The lower viscosities can be explained by the presence of the bulky groups CF_3 and phenyl on 3FDA and 6FDA relative to the planar configuration of the s-BPDA dianhydride. The greater viscosity stability of the PE-3F and PE-6F oligomers over the s-BPDA oligomers at 310 °C may be explained by the decreased electron density and hence lower reactivity of the ethynyl group in the PE-3F and PE-6F oligomers due to the influence of fluorine in the polymer chain.

Introduction

Polyimides have acquired importance in the past 20 years as promising macromolecules for high technology applications in new materials. Their good thermooxidative stability is well-known as well as their high glass transition temperatures. Polyimides are versatile polymers, which can be utilized for a wide range of applications: i.e., as matrices for high-performance advanced composite materials, as thin films in electronic applications, as structural adhesives and sealants, as high-temperature insulators for aircraft wire coatings, and as membranes for gas separation.[1] Polyimides present several advantages over other high-temperature materials. They can be used in the soluble polyamic acid form, from which films can be prepared. The outstanding chemical resistance and thermostability have been attributed to interchain interactions due to the stiffness of the aromatic backbone and charge-transfer interactions.[2]

Although the aromatic thermoplastic polyimides exhibit excellent thermooxidative stability, the high melt viscosity of these materials requires that high pressure be used in processing to fabricate structural composites and adhesive joints. A considerable amount of research has been carried out to address this problem. The introduction of the phenylethynyl group as an end-capping agent in low molecular weight imide oligomers has greatly improved processability,[3−7] but additional improvements are required to reduce the melt viscosities for composite and adhesive applications without compromising other properties. Considerable work in this regard has been done by several researchers,[8−17] and additional work is in progress.

Researchers at NASA have demonstrated that modification of a phenylethynyl (PE)-terminated imide (PETI) oligomer, which was designated PETI-5 (Figure 1) (where 5 refers to a number-average molecular weight of 5000 g/mol), has led to improvements in minimum melt viscosity of the imide oligomers. These improvements include introduction of a triamine[12,13,17] within the phenylethynyl (PE)-terminated imide oligomer network (PETI) and also the addition of low-viscosity reactive diluents[10,11] to PETI structures.

Reducing the number-average molecular weight, by control of stoichiometry and diamine composition of s-BPDA PETI oligomers, has a profound effect on the viscosity of the uncured oligomers and on the cured glass transition temperature (T_g).[20−25] This approach has led to the development of resin transfer moldable (RTM) phenylethynyl end-capped oligomers with cured T_g's which varied from 258 to 320 °C (by DSC) and minimum melt viscosities in the range 0.1−1.0 Pa s at 260−280 °C. AS4-8HS carbon fiber/resin laminates have been fabricated by the RTM technique from a novel PETI composition. The laminates contained no microcracks and exhibited excellent thermal ($T_g \sim 287$ °C) and mechanical properties.[22−24]

It has been further demonstrated that replacement of the symmetrical dianhydride s-BPDA in PETI-5 with asymmetric a-BPDA decreases the minimum melt viscosity and also increases the glass transition temperature (T_g) relative to PETI-5.[26,27] Adhesive properties using titanium adherents show good tensile lap shear strengths and excellent retention of room temperature strength at 260 °C.[27]

More recently,[28,29]studies to improve processing of phenylethynyl end-capped imide oligomers by replacement of this end-cap with naphthyl and anthracenyl end-caps have led to a lower cure temperature (by 80 °C), with no sacrifice in cure rate, and glass transition temperature. Subsequent studies[30] on the phenylethynyl and naphthylethynyl end-capped phthalimide or naphthalimide PETI-5 type oligomers showed that the naphthylethynyl group did not afford any advantage

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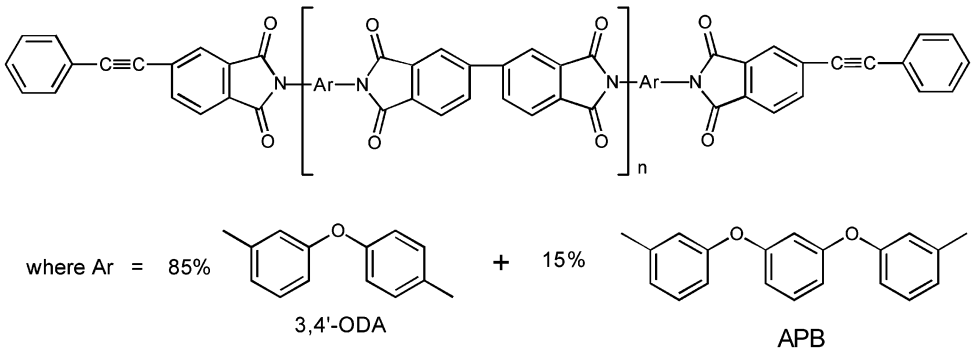

Figure 1. PETI-5K structure (M_n, 5000 g/mol).

over the phenylethynyl end-cap, based on mechanical properties of films cured at 340 and 370 °C.

In the present research, in efforts to further overcome the strong enthalpic interactions inherent in polyimide structures, structural modifications of the polymer backbone with bulky lateral substituents, noncoplanar phenylene moieties, and kinked comonomers are under investigation. It was reasoned that introduction of the dianhydrides 3FDA and 6FDA, containing bulky trifluoromethyl and phenyl groups to replace the linear rigid symmetrical biphenylene dianhydride (s-BPDA) in PETI oligomides, could lower the interchain interaction or reduce the stiffness of the polymer backbone. Kinked comonomers such as 1,3-phenylenediamine or noncoplanar monomers such as 2,2′-trifluoromethylbiphenylenediamine could have similar effects.

Experimental Section

Materials. 4,4′-(2,2,2-Trifluoro-1-phenylethylidene)diphthalic anhydride (3FDA), mp 201−202 °C, was prepared according to a published technique.[31] 3,4′-Diaminodiphenyl ether (3,4′-ODA), mp 84 °C (DSC), was purchased from Wakayama Seika Kogyo Corp., Ltd., and recrystallized from a 2/1 ratio of ethanol/water before use. 2,2-Bis[4-(aminophenoxy)phenyl]hexafluoropropane (4-BDAF), mp 162 °C (DSC), was recrystallized from absolute ethanol before use. 3,3′,4,4′-Biphenylenetetracarboxylic dianhydride (s-BPDA), mp 305−308 °C, was purchased from ChrisKev Co., Inc., and dried at 200 °C for 2 h in a vacuum before use. 4-Phenylethynylphthalic anhydride (PEPA), mp 152 °C (DSC), and 1,3-bis(3-aminophenoxy)benzene (APB), mp 107−109 °C, were purchased from Imitec Inc. and recrystallized from absolute ethanol. *N*-Methyl-2-pyrolidinone (NMP) and methanol were purchased from Fisher and used as received. 4,4′-(Hexafluorosiopropylidene)-diphthalic anhydride (6FDA), mp 246.5 °C (DSC), was purchased from ChrisKev Co., Inc., and dried at 100 °C/2 h in a vacuum before use. 1,4-Phenylenediamine, mp 89−91 °C, was purchased from Aldrich and used as received. 2,2′-Bis(trifluoromethyl)benzidene, mp 181−182 °C, was purchased from Ken Seika Corp. and used as received. With the exception of the last two materials, the melting point listed for each material is the melting point after purification.

Characterization. *Differential Scanning Calorimetry (DSC).* DSC of the imide oligomers was performed by a Perkin-Elmer DSC 7 series analysis system at a heating rate of 20 °C/min under a nitrogen atmosphere at a flow rate of 20 cm^3 min^{-1}. The glass transition temperature (T_g) was taken at the inflection point of the heat flow vs temperature curve.

Thermogravimetric Analysis (TGA). TGA of cured imide film specimens was performed by a Perkin-Elmer TGA 7 series analysis system at a heating rate of 20 °C/min under nitrogen and oxygen atmospheres at a flow rate of 20 cm^3 min^{-1}.

Gel Pemeation Chromatography (GPC). A Millipore model 150-C GPC system was applied to determine the molecular weight of the amic acid oligomers. NMP with 0.05 M LiBr was used as the mobile phase. The results were calibrated by standard poly(methyl methacrylate).

Infrared Spectroscopy (IR). IR spectra of the imide oligomers were taken using a Nicolet Magna 560 FT-IR system. Spectra of cured specimens were obtained by transmission IR microscopy using a compression cell fitted with type IIa diamond windows.

Inherent Viscosity. Inherent viscosities $[\eta]^{25}_{NMP}$ were obtained by dissolving the imide oligomer powder in NMP at a concentration of 0.5% (w/v) and measuring the elution time using a Ubbelohde viscometer in a thermostatted 25 °C water bath.

Complex Viscosity. Rheological measurements were conducted on a Rheometric Scientific ARES mechanical spectrometer. Sample specimen disks, 2.54 cm in diameter and ∼1.5 mm thick, were prepared by press-molding the imide powder at room temperature. The compacted resin disk was subsequently loaded in the rheometer fixture equipped with 2.54 cm diameter parallel plates. The lower plate was oscillated at a fixed strain of 5% and a fixed angular frequency of 10 rad s^{-1} while the upper plate was attached to a transducer which recorded the resultant torque. Autotension was used which was set at 50 g (compression) with a sensitivity set at 10 g. The initial temperature, 200 °C, was set, and the parallel plates and sample were equilibrated at this temperature for 20 min. The complex viscosity (η^*) as a function of temperature was measured from 200 to 390 °C at a rate of 4 °C min^{-1}, but only the data between 300 and 390 °C are plotted because this is within the viscosity/temperature range of the minimum viscosity of these materials.

Synthesis. Examples of the synthetic procedures used in the synthesis are given for three oligomides, as described below. A table for the stoichiometry used for the other 11 oligomers synthesized is shown in Table 1. In all cases NMP solvent was used to give a solution containing 20−30 wt % of oligomer.

Linear PETI-2K, -3K, and -5K Oligomers. Example 1: PETI-2K. To a dried three-neck 100 mL flask equipped with Dean−Stark trap, condenser, nitrogen or argon inlet, and magnetic stir bar were added APB (0.5832 g, 1.995 mmol), 3,4′-ODA (2.2636 g, 11.305 mmol), and 10 mL of NMP. The mixture was stirred at ambient temperature until the diamines were completely dissolved. Next, BPDA 2.883 g (9.8 mmol) was gradually added as a solid over a 20 min period. An additional 10 mL of NMP was added at this point. The reaction was then left to stir under nitrogen at ambient temperature for 6 h. A solution of PEPA (1.738 g, 7.0 mmol) dissolved in NMP (9.8 mL) was added to the reaction mixture, resulting in a 20% (w/w) solution. The reaction was then left to continue stirring at room temperature for 24 h. Toluene (20 mL) was added to the reaction solution to remove water due to the imidization step, by azeotropic distillation. This required approximately 10 h to complete the reaction (130−140 °C), after which the temperature was increased to 180 °C to ensure removal of toluene. The flask was removed from the heat, cooled in an ice−water bath, and poured into a high-speed laboratory blender containing 200 mL of a 1:1 methanol/deionized water mixture to precipitate the oligomer. The fine powder was

Table 1. Stoichiometry of PETI, PE-3F, and PE-6F Oligomides Synthesized[a]

oligomer	M_n (calc)	BPDA (g, mmol)	3FDA (g, mmol)	6FDA (g, mmol)	diamine (g, mmol)	PEPA (g, mmol)	yield (g, %)
PETI-3K	3000	(4.64, 15.8)			3,4′-ODA (3.24, 16.2) APB (0.83, 2.85)	(1.59, 6.40)	(9.34, 97)
PETI-5K	5000	(8.09, 27.5)			3,4′-ODA (5.19, 25.9) APB (1.34, 4.57)	(1.49, 6.00)	14.5, 97)
PE-3F-PETI-3K	3000		(4.17, 9.23)		3,4′-ODA (1.99, 9.97) APB (0.519, 1.76)	(1.24, 5.00)	(6.4, 91)
PE-3F-PETI-5K	5000		(3.72, 8.23)		3,4′-ODA (1.61, 8.02) APB (0.407, 1.38)	(0.596, 2.40)	(5.5, 92
PE-3F-4,4′-ODA-5K	5000		(5.09, 11.3)		4,4′-ODA (2.57, 12.9)	(0.794, 3.20)	(7.7, 96)
PE-3F-3,4′-ODA-5K	5000		(4.46, 9.85)		3,4′-ODA (2.25, 11.3)	(0.695, 2.80)	(6.32, 90)
PE-3F-APB-5K	5000		(3.79, 8.39)		APB (2.86, 9.79)	(0.694, 2.80)	(6.45, 92)
PE-3F-TFMB-5K	5000		(3.00, 6.60)		TFMB (2.51, 7.80)	(0.596, 2.40)	(5.16, 86)
PE-3F-p-PDA-5K	5000		(4.48, 9.90)		*p*-PDA (1.21, 11.1)	(0.598, 2.40)	(5.7, 95)
PE-6F-PETI-3K	3000			(3.86, 8.70)	3,4′-ODA (1.88, 9.38) APB (0.48, 1.65)	(1.16, 4.66)	(6.44, 92)
PE-6F-PETI-5K	5000			(4.32, 9.70)	3,4′-ODA (1.89, 9.46) APB (0.488, 1.67)	(0.695, 2.80)	(6.39, 91)

[a] In *N*-methylpyrrolidone (NMP) solvent to give a final solution of 20−30 wt %.

filtered, washed with copious amounts of deionized water and methanol, and dried in vacuo for 20 h at 150 °C to yield an off-white powder in 97% yield (6.9 g). IR (KBr, cm^{-1}): 3073 (aryl C−H str), 2202 (C≡C str).

PE-3F-PETI-2K, -3K, and -5K. Example 1: PE-3F-PETI-2K. 4,4′-(2,2,2-Trifluoro-1-phenylethylidene) diphthalic anhydride (3FDA) was prepared according to a published technique.[31] To a dried three-neck 100 mL flask equipped with a Dean−Stark trap, condenser, nitrogen or argon inlet, and magnetic stir bar were added 3,4′-ODA (2.007 g, 10.0 mmol), APB (0.5171 g, 1.768 mmol), and NMP (7 mL). The mixture was stirred at ambient temperature until the diamines were completely dissolved. 3FDA 4.6592 g (10.3 mmol) was then gradually added as a solid over a 20 min period. An additional 10 mL of NMP was added at this point. The reaction was allowed to stir under nitrogen at ambient temperature for 10 h. A solution of PEPA (0.7447 g, 3.0 mmol) in 2.0 mL of NMP and subsequently added to the reaction mixture, resulting in a 30% (w/w) solution. The reaction was allowed to continue stirring at room temperature for 24 h. Toluene (20 mL) was added to the reaction solution to remove water by azeotropic distillation. Then, the reaction was maintained at reflux for 12 h, after which most of the toluene was removed by distillation. The reaction mixture was cooled in an ice−water bath and poured into a high-speed laboratory blender containing 200 mL of warm methanol to precipitate the oligomer. The fine powder was filtered, washed with copius amounts of deionized water and methanol, and dried in vacuo for 20 h at 150 °C to yield an off-white powder in 97% yield (6.9 g). IR (KBr, cm^{-1}): 3073 (aryl C−H str), 2202 (C≡C str), 1772 (C═O asym str), 1723 (C═O sym str), 1368 (C−N str), 733 (C═O bend).

Linear Oligomers with 3FDA Backbone Modification. Example 2: PE-3F-BDAF-5K. To a dried three-neck 100 mL flask equipped with a Dean−Stark trap, condenser, nitrogen inlet, and magnetic stir bar were added 4-BDAF (3.848 g, 7.422 mmol) and NMP (20 mL). The mixture was stirred at ambient temperature until the diamines were completely dissolved. Next, 3FDA (2.724 g, 6.02 mmol) was gradually added as a solid over a 20 min period. An additional 10 mL of NMP was added at this point. The reaction was allowed to stir under nitrogen at ambient temperature for 6 h. PEPA (0.695 g, 2.8 mmol) was dissolved in 8.3 mL of NMP, and the solution was subsequently added to the reaction mixture, resulting in a 20% (w/w) solution. The reaction was allowed to continue stirring at room temperature for 24 h. Toluene (20 mL) was added to the reaction solution; the temperature was raised to provide for a steady reflux to remove water by azeotropic distillation. The reaction was maintained at reflux for 12 h, after which most of the toluene was removed by distillation. The flask was cooled in an ice−water bath, and the contents were poured into a high-speed laboratory blender containing 200 mL of a 1:1 methanol/deionized water mixture to precipitate the oligomer. The fine powder was filtered, washed with copious amounts of deionized water and methanol, and dried in vacuo for 20 h at 150 °C. A light beige powder obtained was isolated in 93% yield (6.5 g). IR (KBr, cm^{-1}): 3047 (aryl C−H str), 2202 (C═C str), 1777 (C═O asym str), 1721 (C═O sym str), 1373 (C−N str), 738 (C═O bend).

Results and Discussion

In the present investigation we wish to report on our work to lower the viscosity of PE end-capped imide oligomers by replacement of the rigid biphenylene imide (BPDA) repeat unit in the PETI-5 structure (Figure 1), with a bulky fluorinated dianhydride, 4,4′-(2,2,2-trifluoro-1-phenyl (ethylidene)diphthalic dianhydride (3FDA), and in a few cases with the bulky fluorinated dianhydride 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA). In addition, the influence of replacement of 3,4′-ODA and APB diamines in PETI-5 with other aromatic amines such as 2,2-bis[4-(4,4′-aminophenoxyphenyl]hexafluoropropane (4-BDAF), 2,2′-trifluoromethylbiphenylenediamine, and *p*- and *m*-phenylenediamines was also investigated. A series of phenylethynyl (PE) end-capped 3FDA/diamine imide oligomers, herein defined as PE-3F imide oligomers (Figure 2), were synthesized and characterized for thermal and rheological characteristics.

Selected PE end-capped 6FDA imide oligomers (PE-6F) were also synthesized for thermal and rheological properties (Figure 3). The fluorinated dianhydride, 4,4′-(2,2,2-trifluoro-1-phenylethylidene)diphthalic dianhydride (3FDA), was synthesized by a published method.[31] PETI-2, PETI-3, and PETI-5 imide oligomers modifications were synthesized according to published methods,[8,9] with selected modifications described herein. The modification includes addition of PEPA end-cap 6 h after polyamic acid formation to allow for longer reaction time for polyamic acid formation due to the lower reactivity of the fluorinated dianhydrides. In this manner, the PE-3F oligomides and PE-6F oligomides were obtained in nearly quantitative yields. The PE-3F and PE-6F oligomides investigated with molecular weights, and thermal characterization data are listed in Table 2.

Molecular Weight Characterization. Molecular weights of polyamic acid oligomers as determined by gel permeation chromatography (GPC) are shown in Table 2. The number-average molecular weights (M_n) agree

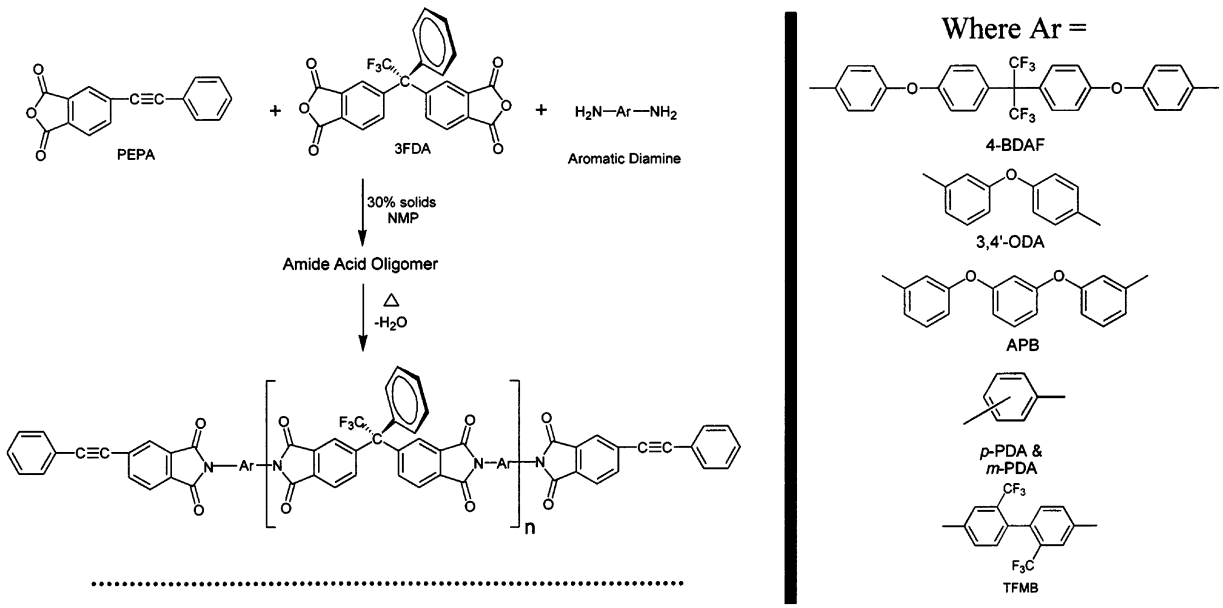

Figure 2. Phenylethynyl (PE) end-capped 3FDA oligomides synthesized.

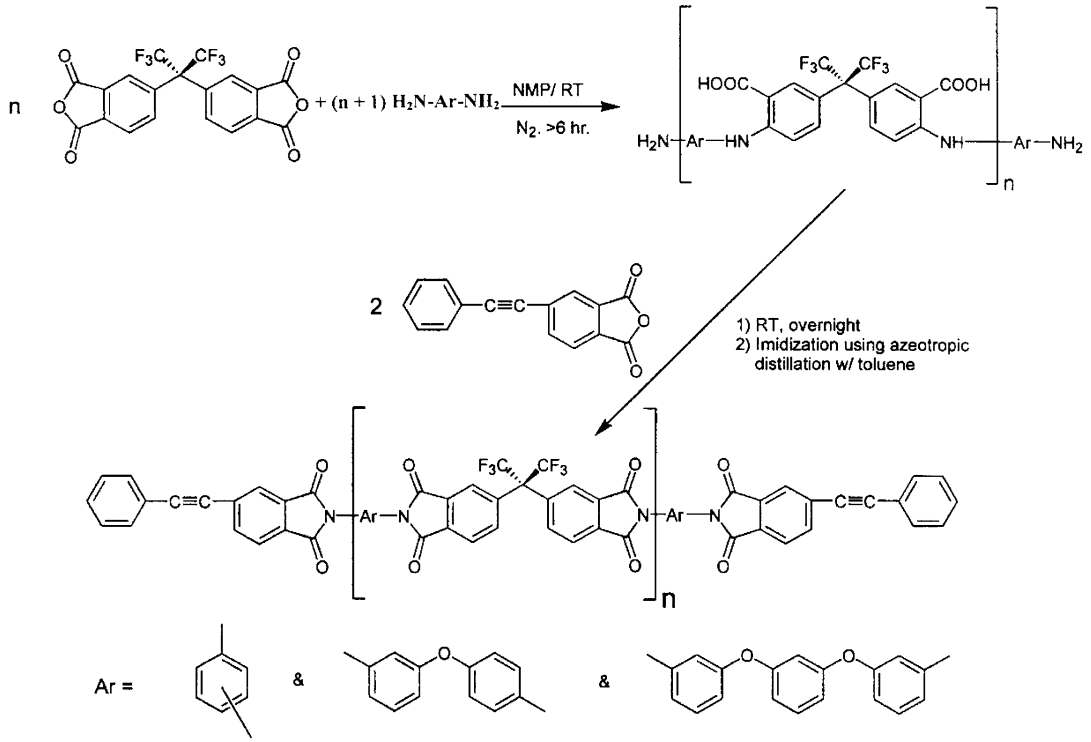

Figure 3. Phenylethynyl (PE) end-capped 6FDA oligomides synthesized.

very well with the stoichiometric calculated molecular weights (M_n), expect for PETI-5K, which gave a much higher M_n (8383) relative to the calculated M_n (5000). Smith et al.[9] report similar differences in the calculated and measured molecular weights of PETI-5K. However, polydispersities of the 3F-PI's are in agreement with the reported values for PETI-2.5K and PETI-5K.[9] The inherent viscosities of all oligomides are what may be expected on the basis of molecular weights. The oligomides with number-average molecular weights M_n 5000 fall in the range 0.26−0.28 dL/g, while those with M_n 3000 are ∼0.17 dL/g, which is in agreement for values reported for PETI-5K and PETI-2.5K.[9]

Thermal Properties. An important aspect of this study is the influence of the structural changes on the uncured glass transition temperature. Typical DSC curves for several systems are shown in Figure 4a−c. In one-to-one comparison of PETI-3K and PETI-5K with PE-3F-PETI-3K, PE-6F-PETI-3K, 3F-PETI-5K, and PE-6F-PETI-5K, the uncured T_g's of the PE-3F and PE-6F oligomides are lower than the PETI-3K and PETI-5K materials (Table 2). This would be expected in view of the fact that each of these oligomides exhibited lower viscosities than PETI-3K and PETI-5K. This would suggest that the bulky groups in the 3FDA and 6FDA units increase free volume between polymer chains, therefore leading to lower T_g's. It should be mentioned that the number-average molecular weight (M_n) measured for the PE-3F series are lower than the value measured for the PETI-5K material (∼5500 vs 8400),

Table 2. Molecular Weight and Thermal Data of Phenylethynyl End-Capped PE-3F and PE-6F Imide Oligomers

		GPC analysis				uncured oligomer		cured oligomer
sample	theor M_n	M_n	M_w	PDI	η_{INH} (dL g^{-1})	T_g (°C)	T_m (°C)	T_g* (°C)[b]
PE-3F-PETI-3K[a]	3000	3215	5 855	1.82	0.17	190		302
PE-3F-PETI-5K[a]	5000	5301	11 769	2.16	0.27	218		272
PE-3F-4,4′-ODA-5K	5000	5703	11 161	1.96	0.28	235		330
PE-3F-3,4′-ODA-5K	5000	5207	10 830	2.07	0.27	226		288
PE-3F-APB-5K	5000	5406	11 055	2.11	0.23	184		217
PE-3F-TFMB-5K	5000	5691	11 609	2.04	0.25	213		267
PE-3F-BDAF-5K	5000	6532	13 263	2.03	0.26	237		279
PE-3F-*p*PDA-5K	5000	5621	11 017	1.96	0.28	221		273
PE-6F-PETI-3K[a]	3000	3491	6 667	1.91	0.16	195		279
PE-6F-PETI-5K[a]	5000	5367	11 056	2.06	0.28	212		268
PETI-2K	2000					188	320	282
PETI-3K	3000	3491	6 796	1.94	0.17	195	319	275
PETI-5K	5000	8383	14 496	1.73	0.28	225	349	270

[a] Contains 3,4′-ODA and APB diamines in same ratio as PETI-5. [b] Cured in DSC by heating in sealed aluminum pan. *T_g of the sample after being heated to 500 °C at a rate of 20 °C min^{-1} in the first DSC run.

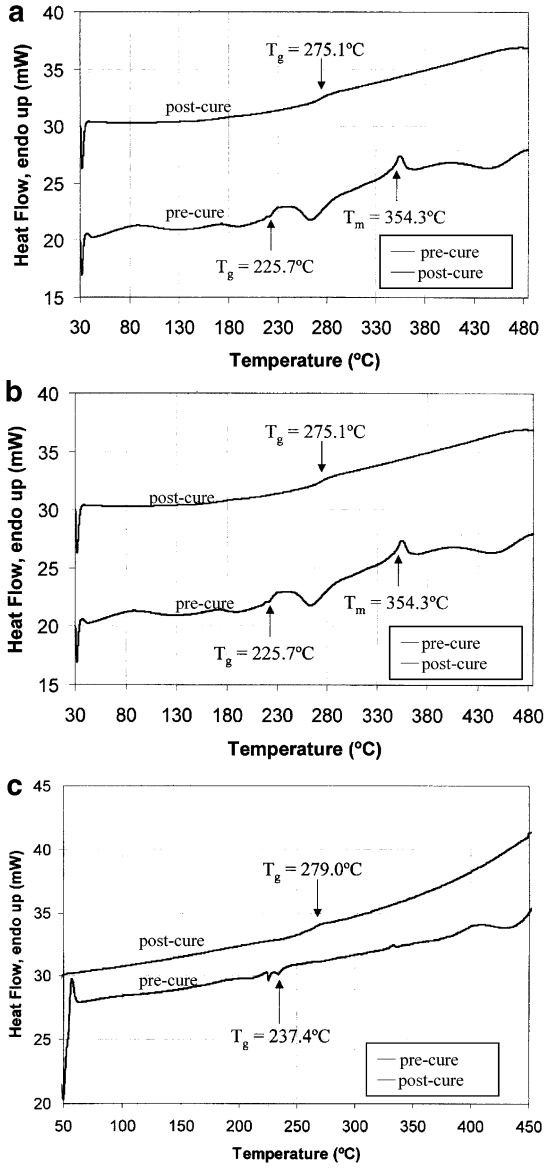

Figure 4. (a) DSC of PETI-5K. (b) DSC of PE-3F-PETI-5K. (c) DSC of PE-3F-BDAF-5K.

with slightly lower T_g's. These differences in molecular weight can also contribute to the small decrease in the uncured glass transition temperature.

In addition, none of the PE-6F or PE-3F oligomides exhibited a melt, clearly showing the amorphous nature of these materials. In contrast, PETI-2, -3, and -5K show melts at 320, 319, and 349 °C, respectively, all occurring before the exothermic cure, which is initiated at about 380 °C. The less ordered nature of the 3FDA- and 6FDA-containing oligomides suggests a greater degree of molecular freedom and less intermolecular interaction.

Table 3. PE-3F Oligomide TGA Characterization Data

sample	decomp onset (°C)	$T_d^{5\%}$ (°C)[a]	$T_d^{10\%}$ (°C)[b]	char yield at 800 °C (%)
PE-3F-PETI-3K	488	502	533	64.7
PE-3F-PETI-5K	515	534	554	62.6
PE-3F-4,4′-ODA-5K	505	522	534	62.2
PE-3F-3,4′-ODA-5K	475	497	524	61.7
PE-3F-APB-5K	477	507	537	63.3
PE-3F-TFMB-5K	493	509	528	61.7
PE-3F-BDAF-5K	508	526	544	63.8
PE-3F-*p*-PDA-5K	480	505	543	63.0
PE-6F-PETI-3K	493	508	526	58.6
PE-6F-PETI-5K	493	511	529	56.9
PETI-5K	510	532	548	62.9

[a] Temperature at 5 wt % loss. [b] Temperature at 10 wt % loss.

With the exception of the PE-3F-APB-5K oligomer, glass transition temperatures of the cured PE-3F polyimides ranged from 272 to 288 °C compared to 270 °C for PETI-5K. Therefore, replacement of the biphenylene dianhydride s-(BPDA) repeat unit in PETI-5K with 3FDA or 6FDA did not decrease the glass transition temperature of the cured polyimides, as might be expected for more bulky repeat units.

TGA Characterization. Thermogravimetric analysis (TGA) was performed to provide an insight into the thermal and thermooxidative stability of the (PE) fluorinated imide oligomers and to measure their decomposition temperatures. The samples were cured for 1 h at 371 °C prior to TGA measurements. The data are recorded in Figure 5 and Table 3. All of the fluorinated materials exhibited good thermal stability, relative to PETI-5K. The temperatures at which a weight loss of 5% ($T_d^{5\%}$) and 10% ($T_d^{5\%}$) occurred were recorded, along with the char yield at 800 °C (Table 3).

Dynamic Melt Rheology of Fluorinated Oligomers. The dynamic thermal melt complex viscosity curves are shown in Figures 6, and complex minimum melt viscosity data are tabulated in Table 4. Clearly, the minimum viscosity of the PE-3F-PETI-3K and -5K oligomides and PE-3F-BDAF-3K and -5K are much lower than the corresponding PETI-3K and PETI-5K oligomides. Replacement of the planar biphenylene dianhydride (s-BPDA) with the more bulky dianhydride

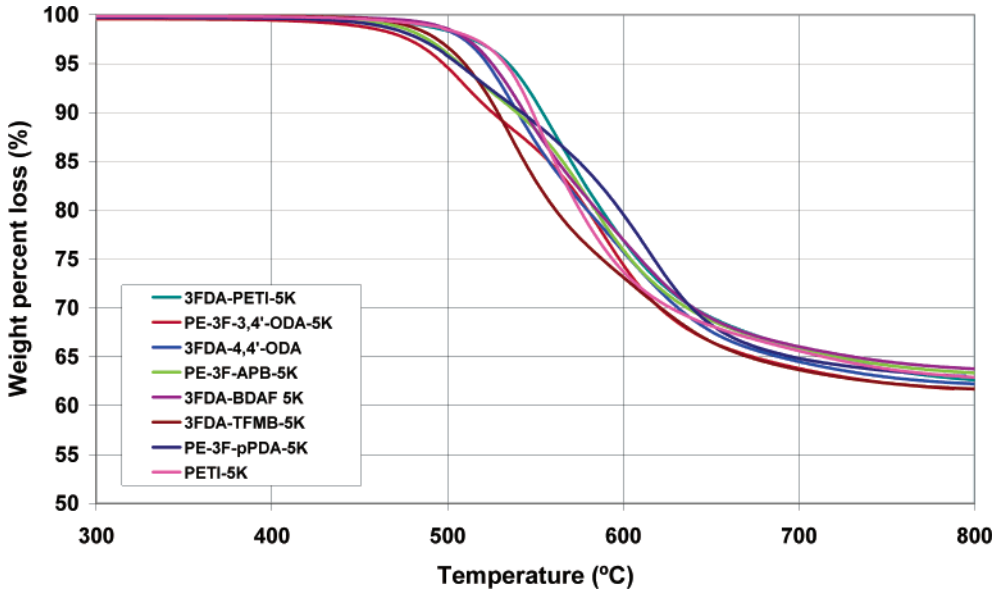

Figure 5. TGA curves of PE-3F PETI oligomers.

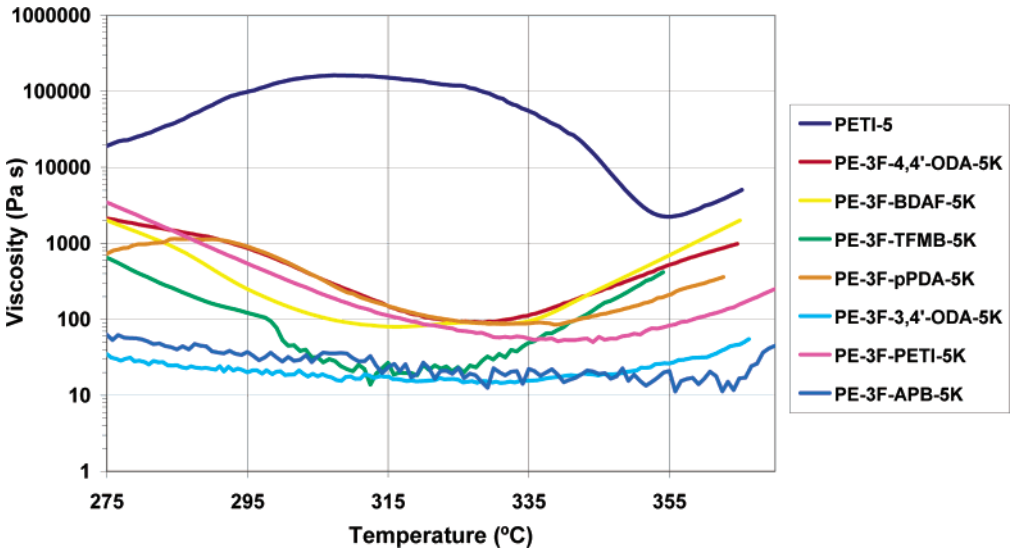

Figure 6. Complex viscosity curves of PE-3F oligomides.

Table 4. Complex Melt Viscosity Data of PE-3F Oligomides

material	complex melt viscosity (Pa s) at 290 °C	300 °C	310 °C	350 °C	min melt viscosity (Pa s, °C)
PETI-3K	1823	1170	302	14	9 at 353 °C
PETI-5K	71057	134770	161050	3353	2,237 at 354 °C
PE-3F-PETI-3K	27	17	7	29	6 at 314 °C
PE-3F-PETI-5K	860	350	154	65	51 at 339 °C
PE-3F-4,4′-ODA-5K	1192	576	230	347	91 at 328 °C
PE-3F-3,4′-ODA-5K	22	18	16	21	14 at 330 °C
PE-3F-APB-5K	38	32	31	19	11 at 355 °C
PE-3F-BDAF-3K			7		
PE-3F-BDAF-5K	367	165	99	312	68 at 325 °C
PE−3F-TFMB-5K	161	53	21	260	14 at 328 °C
PE−3F−p-PDA-5K	1135	602	218	149	87 at 329 °C

(3FDA) causes a sharp decrease in the minimum viscosity. This suggests that molecular interactions of the 3FDA containing polyimides are weaker than in the s-BPDA polyimide systems.

Isothermal Viscosity Studies on PE-3F Oligomides. Isothermal viscosity measurements at 310 °C were also conducted on several of the PE-3F imide oligomers (Figure 7). The isothermal viscosity data (Table 5) clearly demonstrate that, in addition to an initial lower viscosity, the viscosity increase after 30 and 60 min hold periods is much lower for the PE-3F oligomides than it is for the s-BPDA-containing PETI oligomides. The rates of viscosity increase after 30 and 60 min holds at 310 °C are listed in Table 5. The 3K M_n phenylethynyl imide oligomers containing the 3FDA repeat unit showed much lower viscosity increases (Pa s min^{-1}) than the PETI-3K oligomer, after 30 or 60 min holds.

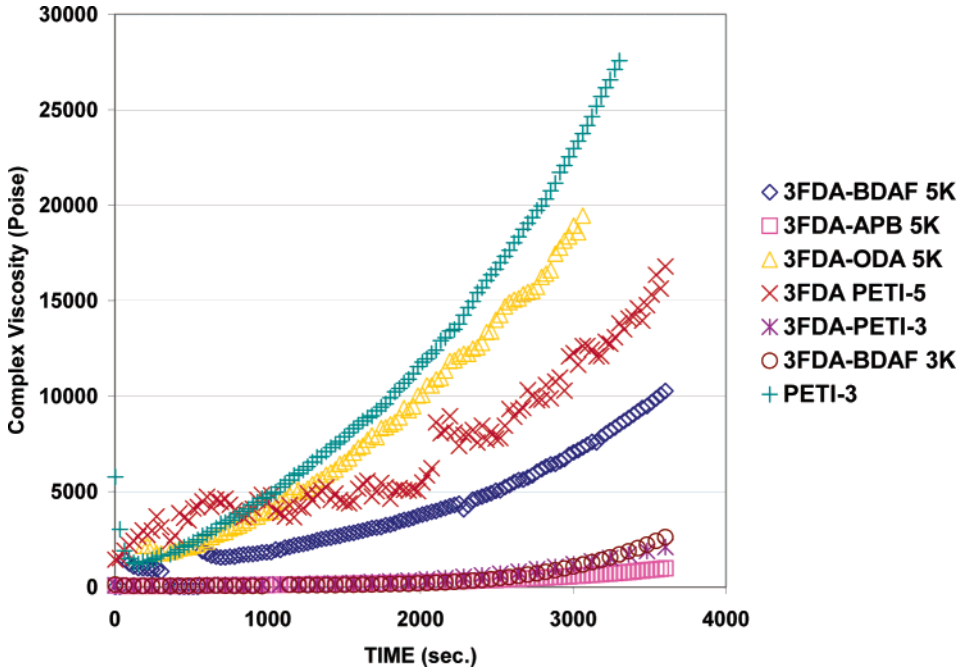

Figure 7. 310 °C Isothermal viscosity of PE-3F-PETI oligomides.

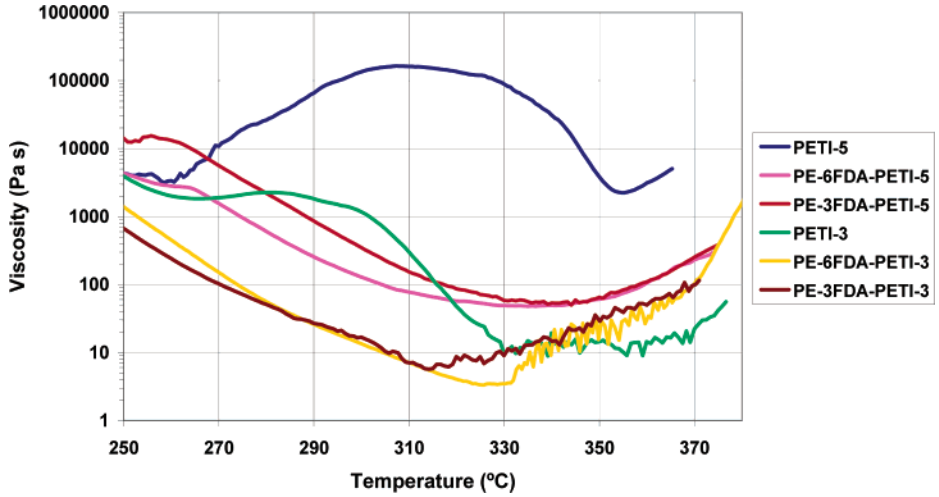

Figure 8. Complex melt viscosity curves of oligomers derived from s-BPDA, 3FDA, and 6FDA dianhydrides.

Table 5. PE-3F Oligomer Melt Stability

oligomer	initial viscosity at 310 °C (Pa s)	viscosity after 30 min (Pa s)	viscosity after 60 min (Pa s)	rate of viscosity increase (Pa s min^{-1}) after 30 min at 310 °C	rate of viscosity increase (Pa s min^{-1}) after 60 min at 310 °C
PETI-3K	1501	9913	>27500	280	>433
PE-3F-3,4′-ODA-5K	1781	8538	>14000	5.5	>286
PE-3F-APB-5K	53	207	978	5.1	15.4
PE-3F-PETI-3K	60	298	2098	7.9	33.9
PE-3F-PETI-5K	1433	4620	16791	106	256
PE-3F-BDAF-3K	821	3269	10266	81	255
PE-3F-BDAF-5K	72	147	2610	2.5	42.3

The reasons for the superior viscosity stability of the PE-3F oligomides over the s-BPDA-containing oligomides will be discussed under phenylethynyl reactivity vs melt stability.

Dynamic Complex Viscosities of PE-3FDA, PE-6FDA, and PE-BPDA Containing Oligomides. From a molecular structural prospective, it would be of interest to compare the influence of the dianhydrides 3FDA, 6FDA, and s-BPDA in oligomides with the same diamine repeat units. Therefore, rheology experiments were performed on oligomides derived from BPDA, 3FDA, and 6FDA dianhydrides and the same diamine comonomers (85% 3,4′-ODA; 15% APB). The complex melt viscosity data are shown in Figure 8 and Table 6. For oligomers with theoretical molecular weights of M_n = 5000 large minimum viscosity differences are noted between PETI-5K and the PE-3F and PE-6F oligomers. The minimum melt viscosities of the PE-3F-PETI-5K and PE-6F-PETI-5K oligomides are ∼50 Pa s at ∼340 °C, while the minimum melt viscosity of PETI-5 is 2237 Pa s at 354 °C. For the PE-3F-PETI-3K and PE-6F-PETI-3K oligomides the minimum melt viscosities are 3.5 Pa s at 324 °C and 6 at 314 °C, respectively, compared to 9 Pa s at 353 °C for PETI-3.

Table 6. Complex Viscosity Data for Oligomers from s-BPDA, 3FDA, and 6FDA

material	complex melt viscosity (Pa s) at 290 °C	300 °C	310 °C	350 °C	min melt viscosity (Pa s, °C)
PETI-3K	1823	1171	302	14	9 at 353 °C
PE-3F-PETI-3K	27	17	7	29	6 at 314 °C
PE-6F-PETI-3K	26	14	7	16	3.5 at 324 °C
PETI-5K	71057	134770	161050	3353	2237 at 354 °C
PE-3F-PETI-5K	860	350	154	65	59 at 344 °C
PE-6F-PETI-5K	255	129	77	61	48 at 337 °C

It is apparent that, at the higher molecular weights, structural influences on viscosity are much more significant than at the lower molecular weight levels. Another important aspect of the minimum viscosity data is the minimum viscosity temperature. As the minimum melt viscosity temperature approaches 350 °C, the stability of the melt decreases because it is within the cure temperature range of the phenylethynyl end-cap. This last point is to be discussed in more detail below under melt stability.

Isothermal Viscosity Studies and Influence of Dianhydride on Melt Stability. Isothermal complex viscosity measurements at 310 °C were also conducted on PE-3F-PETI, PE-6F-PETI, and PETI oligomides with M_n's of both 3000 and 5000 g mol^{-1}. The PETI oligomers used all have the same diamine comonomer compositions (85% 3,4′-ODA and 15% APB) but differ in the dianhydrides used. The isothermal viscosity curves and data for the 3000 and 5000 molecular weight systems are shown in Figures 9 and 10 and Tables 7 and 8, respectively. The isothermal viscosity data clearly demonstrate that for both molecular weight systems the viscosity increase after a 60 min hold period is much lower for the PE-3F and PE-6F fluorinated oligomides than it is for the s-BPDA-containing PETI oligomides. The PE imide oligomers containing 3FDA and 6FDA repeat unit showed much lower viscosity increases (Pa s) than the s-BPDA-based oligomers.

It should be noted that the molecular weights, M_n, as determined by GPC for PETI-5K was actually 8300 g/mol while the GPC M_n's for PE-3F-PETI-5K and PE-6F-PETI-5K (∼5300 g/mol) were close to the calculated values. While structural influences have a significant effect on the minimum melt viscosity, the higher M_n for PETI-5K could also be a contributing factor for the higher minimum melt viscosity over the PE-3F and PE-6F containing oligomides. The semicrystalline nature of the PETI-5K, however, is additional evidence for close intermolecular interactions, while the amorphous nature of the 3FDA- and 6FDA-containing oligomers suggest weaker intermolecular interactions.

Viscosity Influences Based on Molecular Modeling of Dianhydride Unit. The lower viscosities of the 3FDA-containing oligomides relative to the s-BPDA and 6FDA-containing oligomides may be explained by the calculated solvent accessible surface area, molecular surface area, and solvent excluded volume as determined by the Molecular Orbital Package (MOPAC) method.[32] The MOPAC energy minimization routine was performed on each molecular structure shown in Figure 11, and calculated data are listed in Table 9. The calculated dihedral angle of the bonds in the 1,1′ positions of each molecule are 42.6°, 47.9°, and 84.7° for s-BPDA, 6FDA, and 3FDA, respectively, indicating that the degree of out-of-plane twisting is much greater for 3FDA than it is for 6FDA and s-BPDA (Table 9). The calculated values for the solvent accessible surface area, molecular surface area, and solvent excluded free volume in all cases are considerably greater for 3FDA than they are for 6FDA and s-BPDA. This implies that there may be greater distances between adjacent molecules in PE-3F oligomers than in s-BPDA and PE-6F oligomers. The complex viscosity data support this contention.

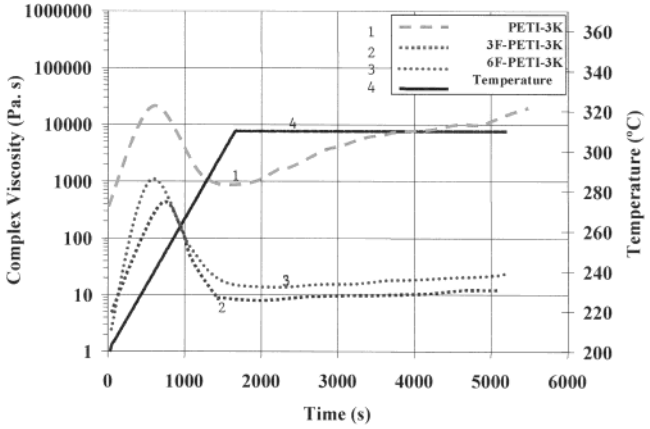

Figure 9. Isothermal viscosity profile for PE-3F-3K, PE-6F-3K, and PETI-3 oligomides.

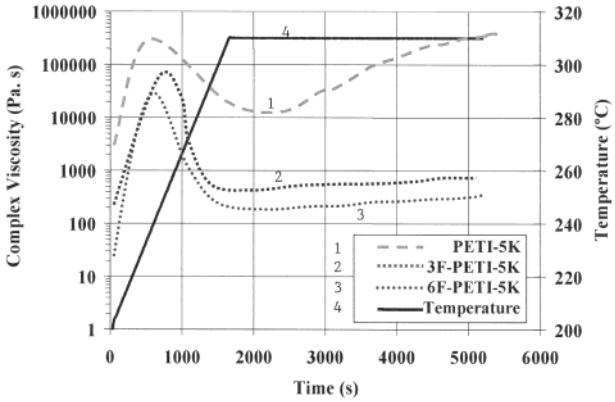

Figure 10. Isothermal viscosity profile for PE-3F-5K, PE-6F-5K, and PETI-5K oligomides.

Phenylethynyl Reactivity vs Melt Stability. It appears that, in addition to causing a viscosity decrease, the 3FDA and 6FDA repeat units stabilize the phenylethynyl end-caps, reducing the rate of cross-linking at the minimum viscosity temperature. It can be hypothesized that the presence of fluorine in the 3FDA and 6FDA unit decreases the reactivity of the ethynyl group, thereby allowing for greater stability at elevated temperatures, relative to the s-BPDA-containing PETI-imide oligomers.

To explain the variation in the reactivities of the fluorinated and nonfluorinated PETI oligomers, the electronic environment around the phenylethynyl end groups must be considered. Although several studies on the cure of phenylethynyl end-capped model compounds and oligomers have been reported,[33−35] the mechanism

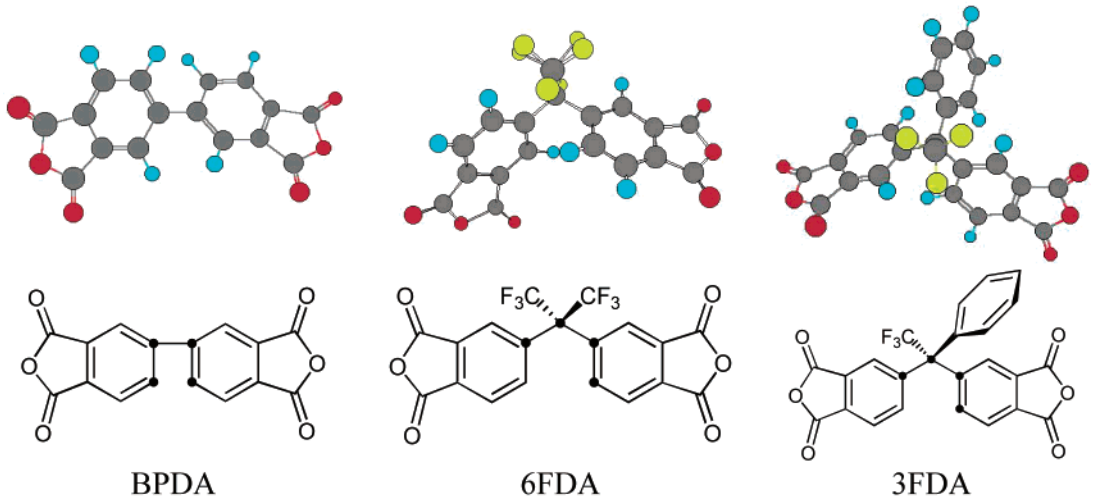

Figure 11. Molecular models of s-BPDA, 6FDA, and 3FDA.

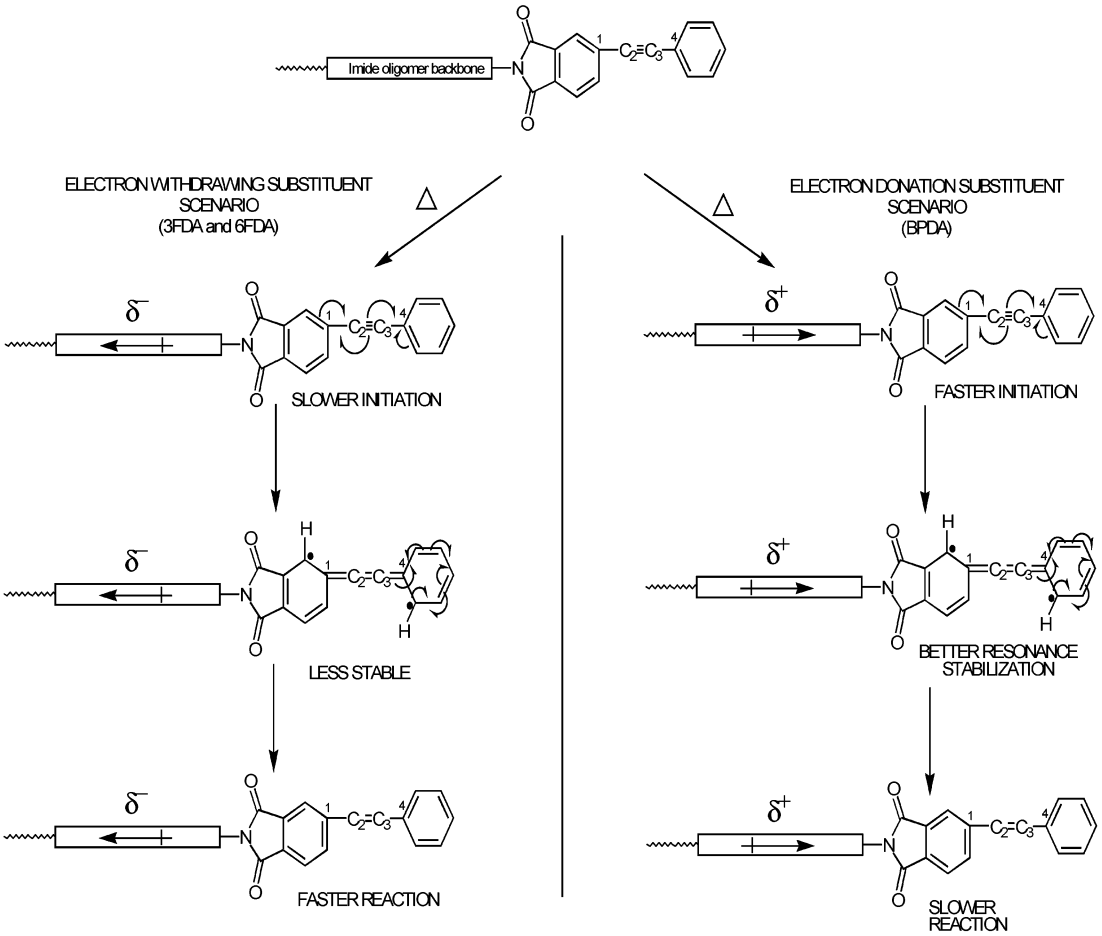

Figure 12. Electronic environment effects on phenylethynyl (PE) end group reactivity in PE-3F, PE-6F and s-BPDA PETI oligomides.

Table 7. Melt Stability of PE-3F-PETI-3K, PE-6F-PETI-3K, and PETI-3K Oligomers

oligomer	initial viscosity 310 °C (Pa s)	viscosity after 60 min isotherm at 310 °C (Pa s)
PETI-3K	899	22500
PE-3F-PETI-3K	9	15
PE-6F-PETI-3K	17	28

Table 8. Melt Stability of PE-3F-PETI-5K, PE-6F-PETI-5K, and PETI-5K Oligomers

oligomer	initial viscosity 310 °C (Pa s)	viscosity after 60 min isotherm at 310 °C (Pa s)
PETI-5K	20759	412205
PE-3F-PETI-5K	321	527
PE-6F-PETI-5K	199	348

of the thermal cure has not been fully elucidated. Studies by Amdur et al.[36] on the free radical polymerization of phenylacetylene and by Preston et al.[37] on the thermal and radiation curing of phenyethyl-terminated macromers suggest that the cure reaction occurs by a thermally induced free radical initiation and propagation. Whether the environment is electron donating or electron withdrawing may have a substantive impact

Table 9. Molecular Orbital Package (MOPAC) Calculation Data (Ref 32)

dianhydride monomer	indicated dihedral angle (deg)	solvent accessible surface area (Å^2)	molecular surface area (Å^2)	solvent-excluded volume (Å^3)
BPDA	42.6	457.34	237.35	194.6
6FDA	47.9	540.54	294.07	271.7
3FDA	84.7	602.2	333.08	309.5

in determining the rate at which this initiation reaction proceeds. The cure reaction mostly likely begins by the generation of radicals at high temperatures through cleavage of an ethynyl π-bond. It is well-known that radicals can be destabilized by the inductive effects of electron-withdrawing groups due to the electron-deficient nature of radicals, but they can also be stabilized through the resonance delocalization of the unpaired electron.[38,39] Therefore, this initial bond cleavage would be encouraged by the presence of nearby electron-donating substituents, causing increased electron density to the end group π-electrons and allowing for better resonance stabilization of the resulting vinyl radical. Resonance stabilization provided through the aromatic rings would require overlap of the p orbitals of the single electron occupied at C-2 and that of C-1, giving rise to an allene-like transition state species (Figure 12).

The identical process would also occur between C-3 and C-4 and would result in a species with three cumulative double bonds between the phenyl rings of the end-capper. Experimental evidence shows that aryl radicals stabilize adjacent acetylene bonds as well as form allenes from acetylenes at elevated temperatures.[40] An electron-donating substituent would likely increase the electron density across the C-1/C-2 bond and would therefore better stabilize a radical at C-2 of the ethynyl group. Furthermore, electron-donating substituents would facilitate the initiation step of the ethynyl bond cleavage, whereas electron-withdrawing substituents would hinder it. Still, the fact that the resulting new radical is stabilized by the electron-donating substituent would also hinder said radical from further reaction. On the other hand, while electron-withdrawing substituents suppress the generation of radicals on the ethynyl bond, once formed those radicals would react faster due to their comparatively reduced stability. In summary, for oligomers containing phenylethynyl end-cappers which undergo radical reaction at high temperature, it is proposed that electron-donating substituents will initiate faster but will propagate slower. Oligomers with electron-withdrawing substituents will initiate slower but will propagate faster. It would appear, on the basis of this rationale, that the phenylethynyl cross-linking reaction at 310 °C is greatly slowed due to the electron-withdrawing groups of the fluorinated dianhydrides, suppressing initial bond cleavage and radical formation.

Conclusions

Phenylethynyl end-capped 3FDA and 6FDA oligomides demonstrate lower minimum viscosities than BPDA oligomides. The PE-3F and PE-6F oligomers also show greater viscosity stability at elevated temperature 310 °C than s-BPDA oligomides. The lower viscosities can be explained by the presence of the bulky groups CF_3 and phenyl on 3FDA and two CF_3 groups on 6FDA relative to the planar configuration of the s-BPDA dianhydride. The greater viscosity stability of the PE-3F and PE-6F oligomers over the s-BPDA oligomers at 310 °C may be explained by the decreased electron density and hence lower reactivity of the ethynyl group in the PE-3F and PE-6F oligomers due to the influence of fluorine in the polymer chain.

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