Macromolecules **2002,** *35,* 5835−5839

Aryl Ethynyl Terminated Imide Oligomers and Their Cured Polymers

Craig M. Thompson[†] **and Paul M. Hergenrother***

NASA Langley Research Center, Hampton, Virginia 23681-2199

Received April 3, 2002

ABSTRACT: As part of a program to develop resins for high-performance/high-temperature aerospace structural applications, preliminary neat resin properties of naphthylethynyl terminated imide oligomers were determined and compared with the corresponding phenylethynyl terminated imide oligomers. Prior to oligomer work, four naphthylethynyl and phenylethynyl phthalimide and four naphthylethynyl and phenylethynyl naphthalimide model compounds were prepared and their thermal properties compared. The naphthylethynyl end-caps in *N*-phenyl- or *N*-naphthylphthalimide model compounds reacted at a lower temperature than the phenylethynyl end-cap in the same compounds, as previously reported. In contrast to these results, replacement of the phthalimide groups with naphthalimide groups showed that the phenylethynyl end-cap reacted at a lower temperature than the naphthylethynyl end-cap. Four aryl ethynyl terminated imide oligomers having the same imide backbone and molecular weight but different terminal units were prepared and the properties of the cured polymers compared. Phenylethynyl end-capped or naphthylethynyl end-capped oligomers, cured at 340 or 371 °C, exhibited similar tensile properties in thin films. The chemistry and properties of these materials are presented.

Introduction

In the development of polymers for high-performance/high-temperature applications, a major effort has focused over the past 25 years on oligomers and polymers containing phenylethynyl groups.[1] Phenylethynyl groups have been placed terminal on the ends of molecules, pendent along the backbone, and both pendent and terminal on the same molecules. More work has concentrated on imide oligomers and polymers than any other system with the emphasis on imide oligomers terminated with phenylethynyl groups. The initial work on phenylethynyl terminated imide oligomers (PETIs) and their cured polymers was performed in the early 1980s at The University of Akron.[2,3] This work was directed primarily toward the development of high-performance polymers for microelectronic applications. Since this early work, several organizations such as National Starch and Chemical Corporation,[4,5] NASA Langley Research Center,[6−8] Virginia Polytechnic Institute and State University,[9−11] General Electric Co.,[12] Dow Chemical Co.,[13] E. I. Du Pont de Nemours & Co., Inc.,[14] Mitsui Toatsu Chemicals, Inc.,[15] and Ube Industries, Ltd.[16] have been involved in the development of PETIs primarily as high-temperature structural resins (composite matrices and adhesives).

At NASA Langley, more than 100 different PETIs were prepared and evaluated. From this effort, a material designated PETI-5 from the reaction of 3,3′,4,4′-biphenyltetracarboxylic dianhydride, 85 mol % of 3,4′-oxydianiline, and 15 mol % of 1,3-bis(3-aminophenoxy)benzene and end-capped with 4-phenylethynylphthalic anhydride at a calculated molecular weight of 5000 g/mol evolved. After significant development, PETI-5 was selected as the adhesive and composite matrix for the United States Mach 2.4 high-speed civil transport (HSCT) technology development program. Large PETI-5, high-quality sandwich and skin stringer composite structures with excellent mechanical properties were fabricated without any major problems.[17] In addition, PETI-5 adhesive and composite structures demonstrated outstanding durability at 177 °C. Unfortunately, the HSCT program was canceled in 1999. Work on PETIs has continued at a lower effort with the emphasis on the development of low melt viscosity resins for use in high-temperature composite fabrication via resin transfer molding[18] and vacuum-assisted resin transfer molding.[19]

Recent work at Virginia Commonwealth University has involved terminating imide oligomers with naphthylethynyl and anthracenylethynyl groups.[20−22] Using the same imide segment as in PETI-5, these researchers made the corresponding naphthyl- and anthracenyl-terminated derivatives and claimed that these oligomers cured 30 and 80 °C lower, respectively, than PETI-5 (the phenyl analogue). The work reported herein was performed primarily to determine whether substituting a bulkier group (e.g., naphthyl) for the phenyl group offered any distinct advantages in the physical and/or mechanical properties and also to determine the properties of oligomers end-capped with aryl ethynyl naphthalic anhydride and their cured polymers.

Experimental Section[24]

Materials. The following chemicals were obtained from the indicated sources and used without further purification: 3,4′-oxydianiline (3,4′-ODA, Mitsui Petrochemical Ind., Ltd., mp 84 °C), 1,3-bis(3-aminophenoxy)benzene (APB, Mitsui Petrochemical Ind., Ltd., mp 108 °C), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA, Chriskev Co., Inc., mp 305 °C), 4-phenylethynylphthalic anhydride (PEPA, Daychem Laboratories, Inc., mp 152 °C), and *N*-methyl-2-pyrrolidinone (NMP, Aldrich Chemical Co.). 4-Bromo-1,8-naphthalic anhydride (Aldrich Chemical Co.) was recrystallized from xylenes to yield yellow crystals, mp 219 °C. *m*-Cresol (Fluka Chemical Co.) and phenylacetylene (Aldrich Chemical Co.) were distilled under reduced pressure before use. Other chemicals were used as-received.

Synthesis of Aryl Ethynyl Anhydrides. 4-(1-Naphthylethynyl)phthalic anhydride (NEPA) [mp 226 °C, lit.[21] mp 220−222 °C] was prepared following the literature procedure.[21]

Synthesis of 4-(1-Phenylethynyl)-1,8-naphthalic Anhydride. A 250 mL three-neck round-bottom flask containing

---

[†] National Research Council Research Associate.

* Corresponding author. E-mail: p.m.hergenrother@larc.nasa.gov.

10.1021/ma0205358

a magnetic stir bar, nitrogen inlet, and condenser was charged with 4-bromo-1,8-naphthalic anhydride (10.0 g, 0.0360 mol), phenylacetylene (6 mL, 5.5 g, 0.0540 mol), triphenylphosphine (0.1956 g, 0.75 mmol), copper(I) iodide (0.0657 g, 0.35 mmol), bis(triphenylphosphine)palladium dichloride (0.0322 g, 0.046 mmol), 50 mL of triethylamine, and 100 mL of toluene. The mixture was heated to reflux for 6.5 h. The reaction was cooled and filtered. The yellow solid was washed with water and dried for 1.5 h at 120 °C (8.6 g, 80% crude yield). The solid was recrystallized from toluene to give 7.5 g (69%) of yellow needles, which displayed a sharp crystalline melting peak at 225 °C by differential scanning calorimetry (DSC). Anal. Calcd for $C_{20}H_{10}O_3$: C, 80.53%; H, 3.38%. Found: C, 80.71%; H, 3.18%.

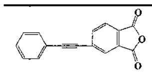
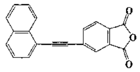
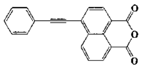
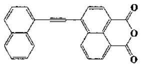
Synthesis of 4-(1-Naphthylethynyl)-1,8-naphthalic Anhydride. A 250 mL round-bottom flask containing a magnetic stir bar was charged with 4-bromo-1,8-naphthalic anhydride (2.5541 g, 0.0092 mol), triphenylphosphine (0.2860 g, 0.0011 mol), copper(I) iodide (0.0854 g, 0.45 mmol), bis(triphenylphosphine)palladium dichloride (0.0922 g, 0.13 mmol), and 50 mL of triethylamine. 1-Ethynylnaphthalene (2.5 mL, 2.6 g, 0.97 mol) was added to the flask with 100 mL of toluene. A condenser containing a nitrogen inlet was placed on the flask, and the reaction mixture was heated to reflux for 14 h. The reaction was cooled and filtered. The filtercake was washed with toluene and dried for 1.5 h at ~120 °C. The solid was stirred in 150 mL of water, collected, and dried for 1.5 h to give 2.93 g (92%) of yellow powder. The solid was recrystallized from xylenes to give yellow needles which had a crystalline melting peak at 224 °C by DSC. Anal. Calcd for $C_{24}H_{12}O_3$: C, 82.75%; H, 3.47%. Found: C, 82.53%; H, 3.36%.

Synthesis of Model Compounds. Phthalimide and naphthalimide model compounds were prepared by the reaction of the aryl ethynyl anhydrides with either aniline or 1-aminonaphthalene. The reactions were carried out in either acetic acid or *m*-cresol as warranted by reactivities of the anhydrides. A standard procedure follows for the preparation of model compounds in acetic acid: A 50 mL round-bottom flask containing a magnetic stir bar was charged with 4-(1-phenylethynyl)-1,8-naphthalic anhydride (1.0080 g, 0.0034 mol), 1-aminonaphthalene (0.4886 g, 0.0034 mol), and 25 mL of glacial acetic acid. A condenser was placed on the flask, and the reaction mixture was heated to reflux for 12 h under nitrogen. The reaction was cooled, and a yellow crystalline material precipitated. The solid was collected, washed with water, and dried at ~120 °C for 4 h (1.0559 g, 73% crude). The yellow solid was recrystallized from toluene to give yellow needles having a crystalline melting peak at 249 °C. Anal. Calcd for $C_{30}H_{17}NO_2$: C, 85.09%; H, 4.05%; N, 3.31%. Found: C, 84.81%; H, 3.89%; N, 3.33%.

Preparation of Model Compounds in m-Cresol. A 50 mL round-bottom flask fitted with a reflux condenser and containing a magnetic stirbar was charged with 4-(1-phenylethynyl)-1,8-naphthalic anhydride (0.4778 g, 0.0016 mol), aniline (1 mL, 1.022 g, 0.011 mol), and 10 mL of *m*-cresol. The reaction mixture was heated to reflux under nitrogen for 6 h. The reaction was cooled, and the dark solution was poured into stirred methanol. The resulting yellow precipitate was collected and dried in an oven overnight. The solid was recrystallized from ethyl acetate/hexanes and dried for 4 h at 150 °C in a vacuum oven to give 0.4432 g (74% yield) of yellow needles having a crystalline melting peak at 228 °C. Anal. Calcd for $C_{26}H_{155}NO_2$: C, 83.63%; H, 4.05%; N, 3.75%. Found: C, 83.70%; H, 4.00%; N, 3.72%.

Synthesis of Aryl Ethynyl Terminated Amide Acid and Imide Oligomers. Amide acid oligomers were prepared following a known procedure[7] where the BPDA and PEPA were added to the stirred diamine solution in NMP under nitrogen. After stirring overnight, a portion of the amide acid solution was removed and converted to the imide by heating in a nitrogen atmosphere with toluene to azeotrope the water from cyclodehydration. The cooled precipitated imide oligomer slurry was poured into water; the isolated solid washed in hot water and dried at 240 °C under vacuum for 4 h.

Table 1. Aryl Ethynyl Anhydrides

Structure	T_m Peak, °C (lit. m.p.) [ref.]	Formula		Elemental Analysis	
				%C	%H
	152 (152) [7]	-		-	-
	226 (220-222) [20]	-		-	-
	225	$C_{20}H_{10}O_3$	Theoretical	80.53	3.38
			Found	80.71	3.18
	224	$C_{24}H_{12}O_3$	Theoretical	82.75	3.47
			Found	82.53	3.36

One-Step Synthesis of Aryl Ethynyl Terminated Imide Oligomer. The following procedure was used to prepare an imide oligomer because the naphthylethynyl naphthalic anhydride failed to react at ambient temperature completely in NMP to form an amide acid. A 50 mL three-neck round-bottom flask fitted with a nitrogen gas inlet, mechanical stirrer, and reflux condenser was charged with 3,4′-ODA (5.4293 g, 0.0271 mol), 1,3,3-APB (1.3994 g, 0.0048 mol), and 15 mL of *m*-cresol. A slurry of BPDA (8.5398 g, 0.0290 mol) and 4-(1-naphthylethynyl)-1,8-naphthalic anhydride (2.0004 g, 0.0057 mol) in 15 mL of *m*-cresol was added to the flask. The solids were washed into the flask with an additional 19 mL of *m*-cresol (25% solids w/w). The mixture was stirred at room temperature under nitrogen for 12 h. Isoquinoline (15 drops) was added to the flask, and the reaction mixture was heated to ~200 °C for 8 h. The reaction was cooled, and a thin film was cast onto plate glass from a portion of the imide oligomer solution. Details on film curing is given below.

Films. Thin films (0.025−0.076 mm) were cast from either amide acid oligomer solutions in NMP or imide oligomer solutions in *m*-cresol generally at 25 or 30% solids (w/w) content. The solutions were generally centrifuged, and the decantate doctored onto clean, dry plate-glass and dried to a tack-free form in a low-humidity air chamber overnight at room temperature. The films were stage-cured in forced air ovens by heating for 1 h each at 100, 150, 200, 250, and 371 °C. In most cases, the thin films were removed from the glass by immersion in water. Specimens (15.2 cm long, 0.51 cm wide, 0.038−0.056 mm thick) were cut with a JDC precision sample cutter, Thwing-Albert Instrument Co. The tensile properties were determined following the general procedure in ASTM D882 using five specimens per test condition. The test specimen gauge length was 5.1 cm, and the crosshead speed for film testing was 0.51 cm/minute using a SinTech 2 instrument with an Eaton model 3397-139 11.4 kg load cell.

Other Characterization. Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-50 thermal analyzer with the sample sealed in an aluminum pan. Glass transition temperatures (T_g's) were determined by DSC at a heating rate of 20 °C/min with the T_g taken at the inflection point of the ΔT vs temperature curve. The crystalline melting points (T_m's) of the various compounds were taken at the endothermic peak in the DSC curve (heating rate of 10 °C/min). Dynamic thermogravimetric analyses (TGA) were determined on films using a TA Instruments Auto TGA 2950 at a heating rate of 2.5 °C/min in nitrogen and air atmospheres. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Results and Discussion

End Groups. Four aryl ethynyl anhydrides as shown in Table 1 were used in this study. 4-Phenylethynyl phthalic anhydride was obtained from a commercial source. 4-Naphthylethynyl-1,8-naphthalic anhydride was synthesized following a known procedure.[21] The

Table 2. Model Compound Characterization

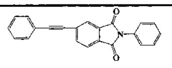
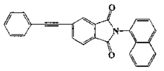
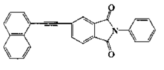
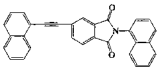
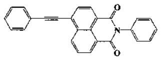
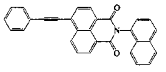
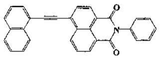
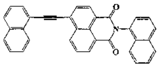
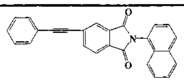
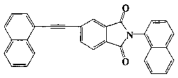
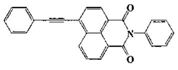
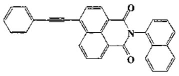
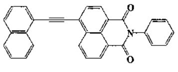
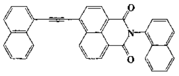
Compound Number	Structure	Reaction Solvent	DSC Data Endotherm, °C Peak (lit., m.p.) [ref.]	Exotherm, °C Onset	Peak	End
1a		Acetic Acid	202	346	387	423
1b		Acetic Acid	189	344	393	426
2a		Acetic Acid	159 (176-178) [20]	324	362	389
2b		Acetic Acid	191	327	361	385
3a		*m*-cresol	228	267	308	336
3b		Acetic Acid	249	297	323	351
4a		Acetic Acid	246	309	329	348
4b		*m*-cresol	265	321	338	364

Table 3. Model Compound Elemental Analysis

Compound Number	Structure		Elemental Analysis %C	%H	%N
1b		Theoretical	83.63	4.05	3.75
		Found	83.98	3.98	3.76
2b		Theoretical	85.09	4.05	3.31
		Found	85.08	3.82	3.35
3a		Theoretical	83.63	4.05	3.75
		Found	83.70	4.00	3.72
3b		Theoretical	85.09	4.05	3.31
		Found	84.81	3.89	3.33
4a		Theoretical	85.09	4.05	3.31
		Found	84.02	3.80	3.21
4b		Theoretical	86.24	4.04	2.96
		Found	86.26	3.96	2.92

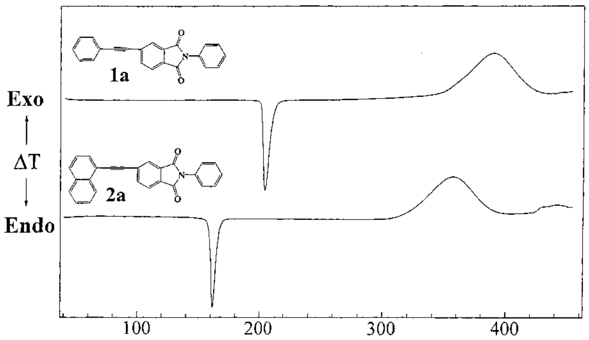


Figure 1. DSC traces of model compounds **1a** and **2a**.

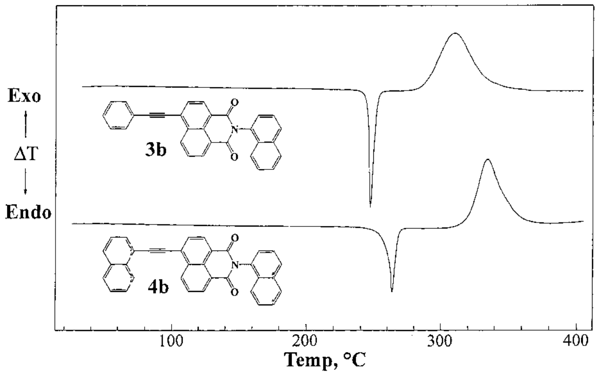


Figure 2. DSC traces of model compounds **3b** and **4b**.

other two compounds, 4-(1-phenylethynyl)-1,8-naphthalic anhydride and 4-(1-naphthylethynyl)-1,8-naphthalic anhydride, were synthesized in good yields from the palladium-catalyzed reaction of phenylacetylene or 1-ethynylnaphthalene with 4-bromo-1,8-naphthalic anhydride.

Model Compounds. Prior to oligomer and polymer work, a series of model compounds as shown in Table 2 were synthesized and characterized. Model compound work was performed primarily to obtain information on the curing reaction of these compounds as a function of chemical composition. A total of eight model compounds were made from the reaction of four aryl ethynyl anhydrides with aniline or 1-aminonaphthalene in boiling acetic acid or *m*-cresol (containing a catalytic amount of isoquinoline). Two model compounds were made in *m*-cresol because reasonably pure crude products in near-quantitative yield could not be obtained in acetic acid. The theoretical and found elemental analyses of the new model compounds agreed well as presented in Table 3.

Representative DSC curves are shown in Figure 1 for compounds **1a** and **2a** and in Figure 2 for compounds **3b** and **4b**. In comparing the DSC data in Table 2, the amine portion of the molecule, the phenyl or naphthyl group, had virtually no effect upon the exothermic reaction of the phthalimide model compounds **1a**, **1b**, **2a**, and **2b**. However, this trend did not continue with the naphthalimide model compounds **3a**, **3b**, **4a**, and **4b**. Compound **3b**, the naphthyl derivative, had higher onset, peak, and end temperatures than that of compound **3a**, the phenyl derivative. With compounds **4a** and **4b**, the naphthyl derivative again had higher onset, peak, and end temperatures than that of the phenyl derivative.

In comparing the effect from the other side of the compound, the phenylethynyl or naphthylethynyl group, the latter had lower onset, peak, and end temperatures than the corresponding phenylethynyl group for phthalimide model compound pairs **1a** and **2a** and **1b** and **2b**. This effect has been previously reported.[20−22] However, the reverse trend was observed for the other four model compounds derived from 4-aryl ethynyl-1,8-naphthalic anhydride. The naphthylethynyl compounds, **4a** and **4b**, had higher onset, peak, and end temperatures than the corresponding phenylethynyl compounds, **3a** and **3b**. The naphthalimide ring had a more pronounced effect on the reaction of the naphthyl ethynyl groups than the phenyl ethynyl groups. Besides electronic effects, the naphthalimide ring may have provided some steric hindrance to retard the reaction of the naphthylethynyl group more than that of the phenylethynyl group. In comparing the reaction exotherm data for groups of com-

Table 4. Oligomer and Film Properties

		thin film properties						
				TGA, temp (°C) 5 wt % loss		23 °C tensile properties		
oligomer designation	initial T_g (T_m), °C	cure temp, °C	T_g (T_m), °C	N_2	air	strength, MPa (COV, %)	modulus, GPa (COV, %)	elong, % (COV, %)
PEPTI-5	220 (290)	340	269 (366)			125.5 (5.5)	3.45 (2.3)	21.4 (86.0)
		371	285	493	488	135.8 (0.7)	3.54 (1.7)	19.7 (68.4)
NEPTI-5	220 (317)	340	266 (365)			115.8 (5.9)	3.27 (4.5)	15.5 (26.6)
		371	288	519	493	124.1 (4.6)	3.41 (4.4)	12.0 (32.2)
PENTI-5	225 (320)	371	279	532	499	129.6 (2.8)	3.37 (2.7)	34.4 (27.5)
NENTI-5	211	371	287	531	513	130.3 (2.4)	3.37 (2.9)	9.9 (14.9)

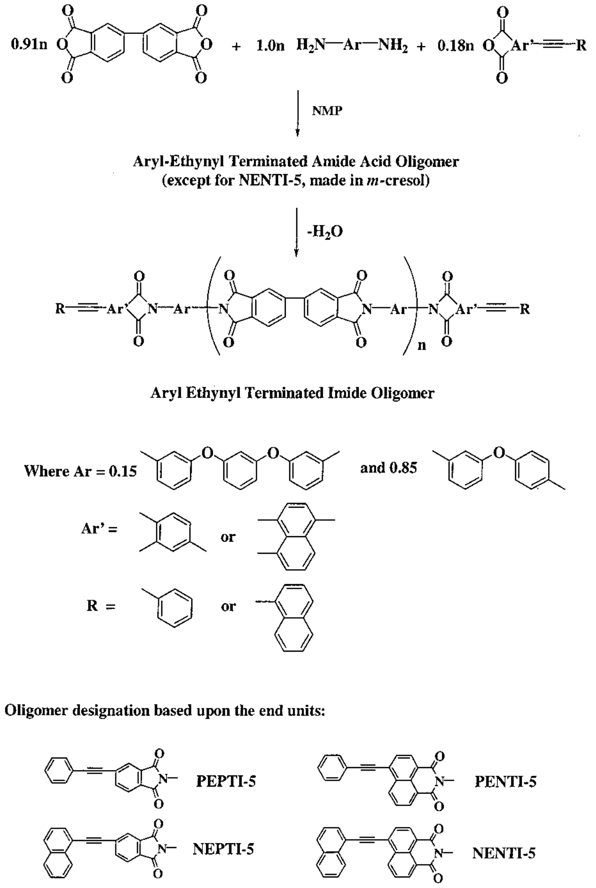


Figure 3. Oligomer chemistry.

pounds derived from aryl phenyl substituted phthalic and naphthalic anhydride, the naphthalimide compounds (**3a**, **3b**, **4a**, and **4b**) have lower onset, peak, and end temperature than those of the corresponding phthalimide compounds (**1a**, **1b**, **2a**, and **2b**).

Oligomers and Polymers. Four oligomers with the same imide backbone and similar calculated number-average molecular weights (~5000 g/mol) but different end units were prepared according to the synthetic scheme in Figure 3. Designations for the four oligomers are given in Figure 3. Three of the oligomers were made via the amide acid in NMP and subsequently cyclodehydrated to the imide by heating the NMP amide acid solutions containing toluene to azeotrope the water. The fourth oligomer (NENTI-5) was prepared in *m*-cresol since the naphthylethynyl naphthalic anhydride failed to react at ambient temperature completely in NMP to form an amide acid. Insoluble solid was isolated from the NMP solution and identified as unreacted naphthylethynyl naphthalic anhydride. The T_g's of the imide oligomers by DSC ranged from 211 to 225 °C as shown in Table 4. All of the imide oligomers made via the amide acid were semicrystalline. The T_m's were found to differ significantly and ranged from 290 to 320 °C. The T_m's are easily influenced by thermal history. The T_m of PEPTI-5 (same as PETI-5) as well as other phenylethynyl terminated imide oligomers (PETIs) has varied widely as a function of thermal history. For example, a crystalline melt temperature of 286 °C[7] and two crystalline melt temperatures of 251 and 352 °C and 290 and 353 °C[23] have been reported for PETI-5 that was exposed to different temperatures. No T_m was detected for the oligomer made in *m*-cresol (NENTI-5). In past work, PETIs made in *m*-cresol were amorphous.

By TGA at a heating rate of 2.5 °C/min, the temperature of 5% weight loss in nitrogen and air for films cured at 371 °C ranged from 493 to 532 °C and 488 to 513 °C, respectively. The NENTI-5 had the highest temperature of 5% weight loss in both nitrogen and air whereas PEPTI-5 has the lowest temperature of 5% weight loss. No definite trend was observed as a function of the reactive end group.

The NMP amide acid solutions and the *m*-cresol imide solution were doctored onto clean plate glass and stage-cured in air to 340 or 371 °C. Since the naphthylethynyl terminated oligomer has been reported to cure 30 °C lower than the corresponding phenylethynyl terminated oligomer,[21] the PEPTI-5 and the NEPTI-5 films were cured at 340 and 371 °C to determine whether the lower cure temperature offered any advantages. Past work however with PEPTI-5 films cured at 350 °C has provided good mechanical properties and a T_g of 270 °C.[7] Composites and adhesives of PETI-5 (same as PEPTI-5) are normally cured at 371 °C.[17] The curing of PETIs was proposed as a free radical process where curing in air is preferred over curing in an inert atmosphere or vacuum.[1] Films of PEPTI-5 and NEPTI-5 cured for 1 h at 340 °C in air were fingernail creaseable and opaque. The films showed T_g's by DSC at 269 and 266 °C and T_m's at 366 and 365 °C, respectively, for PEPTI-5 and NEPTI-5. Films cured at 371 °C were fingernail creaseable and transparent dark orange to dark red. The films cured at 371 °C had undergone further reaction as evidenced by the significant increase in T_g's to 285 and 288 °C for PEPTI-5 and NEPTI-5, respectively. The unoriented thin film average tensile properties are presented in Table 4 with the coefficient of variation (COV) for each set of films reported in parentheses. The tensile strengths and moduli are very similar, regardless of cure temperature or end unit. The noticeable difference is the elongation where films from the phenylethynyl terminated oligomers showed higher elongations than those from the naphthylethynyl terminated oligomers. This may be due more to film quality than to the difference in end group chemistry. Film elongation is more sensitive to flaws within the test specimens caused by foreign particles (e.g., gel particles and dust), wrinkles, and minor specimen misalignment during the test than strength or modulus. The five PEPTI-5 film specimens cured at 371 °C had an elongation at break that varied from 9 to 48%. The elongations of 19.7 and 34.4% for the films from the phenylethynyl terminated oligomers (PEPTI-5 and PENTI-5) cured at 371 °C suggest that these films have very low cross-link density.

Conclusions

Two new aryl substituted anhydrides, 4-(2-phenylethynyl)-1,8-naphthalic anhydride and 4-(1-naphthylethynyl)-1,8-naphthalic anhydride, were used to prepare model compounds and aryl ethynyl terminated imide oligomers. Other model compounds and oligomers were made using phenylethynyl and naphthylethynyl phthalic anhydride. Of the eight model compounds, naphthylethynyl phthalimide model compounds cured at lower temperature than the corresponding phenylethynyl phthalimide model compounds. However, the opposite was found for the naphthalimide model compounds. The phenylethynyl naphthalimide model compounds cured at lower temperature than the corresponding naphthylethynyl naphthalimide model compounds. Four imide oligomers with the same imide backbone and molecular weight end-capped with phenylethynyl and naphthylethynyl phthalimide units and phenylethynyl and naphthylethynyl naphthalimide units gave similar T_g's and thin film tensile properties after curing at 371 °C. Two of the oligomers terminated with phenylethynyl and naphthylethynyl phthalimide units gave very similar T_g's and thin film tensile properties after curing at 340 °C. The naphthylethynyl group did not afford any advantage over the phenylethynyl group.

References and Notes

(1) Connell, J. W.; Smith, J. G., Jr.; Hergenrother, P. M. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **2000**, *C40* (2&3), 207.

(2) Harris, F. W.; Pamidimukkala, A.; Gupta, R.; Das, S.; Wu, T.; Mock, G. *Polym. Prepr.* **1983**, *24* (2), 324.

(3) Harris, F. W.; Pamidimukkala, A.; Gupta, R.; Das, S.; Wu, T.; Mock, G. *J. Macromol. Sci., Chem.* **1984**, *A21* (8 and 9), 1117.

(4) Paul, C. W.; Schultz, R. A.; Fennelli, S. P. In *Advances in Polyimide Science and Technology*; Feger, C., Khoyasteh, M. M., Htoo, M. S., Eds.; Technomic: Lancaster, PA, 1993; p 220.

(5) Paul, C. W.; Schultz, R. A.; Fennelli, S. P. U.S. Pat. 5,138,28, 1992 (to National Starch and Chemical Corp.).

(6) Bryant, R. B.; Jensen, B. J.; Hergenrother, P. M. *Polym. Prepr.* **1993**, *34* (1), 566.

(7) Hergenrother, P. M.; Smith, J. G., Jr. *Polymer* **1994**, *35* (22), 4857.

(8) Hergenrother, P. M.; Smith, J. G., Jr. U.S. Pat. 5,567,800, 1996 (to NASA).

(9) Meyer, G. W.; Jayaraman, S.; McGrath, J. E. *Polym. Prepr.* **1993**, *34* (2), 540.

(10) (a) Meyer, G. W.; Glass, T. E.; Grubbs, H. J.; McGrath, J. E. *Polym. Prepr.* **1994**, *35* (1), 549. (b) Meyer, G. W.; Glass, T. E.; Grubbs, H. J.; McGrath, J. E. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33* (13), 2141.

(11) McGrath, J. E.; Meyer, G. W. U.S. Pat. 5,493,002, 1996 (to Virginia Polytechnic Institute and State University).

(12) Johnston, J. A.; Li, F. M.; Harris, F. W.; Takekoshi, T. *Polymer* **1994**, *35* (22), 4865.

(13) Earls, J. D.; Burton, B. L.; Colegrove, B. T. U.S. Patent 6,136,949, 1998 (to Dow Chemical Company).

(14) Boyce, R. J.; Gannett, T. P.; Sonnett, J. M.; Tanikella, M. S.; Auman, B. C. U.S. Pat. 5,478,913, 1995 (to E. I. Du Pont de Nemours and Company).

(15) Okawa, H.; Tamai, S.; Ohta, M.; Yamaguchi, A. U.S. Patent 5,708,128, 1998 (to Mitsui Toatsu Chemicals, Inc.).

(16) Yokota, R.; Hasegawa, M.; Yamaguchi, H. European Patent 1,018,507 A1, 2000 (to Ube Industries, Ltd.); U.S. Patent 6,281,323 B1, 2001 (to Ube Industries, Ltd.).

(17) Hergenrother, P. M. *SAMPE J.* **2000**, *36* (1), 30.

(18) Smith, J. G., Jr.; Connell, J. W.; Hergenrother, P. M.; Criss, J. M. *J. Compos. Mater.*, submitted.

(19) Criss, J. M.; Koon, R. W.; Hergenrother, P. M.; Connell, J. W.; Smith, J. G., Jr. *Int. SAMPE Technol. Conf. Ser.* **2001**, *33*, 1009.

(20) Wright, M. E.; Schorzman, D. E. *Macromolecules* **1999**, *32*, 8693.

(21) Wright, M. E.; Schorzman, D. E.; Pence, L. E. *Macromolecules* **2000**, *33*, 8611.

(22) Wright, M. E.; Schorzman, D. E. *Macromolecules* **2001**, *34*, 4768.

(23) Hou, T. H.; Jensen, B. J.; Hergenrother, P. M. *J. Compos. Mater.* **1996**, *30* (1), 109.

(24) The use of trade names of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautical and Space Administration.

MA0205358