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Biphenylene End-Capped Imide Oligomers Having Internal Acetylene Groups in the Backbone: Preparation and Thermal Properties

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ABSTRACT: Biphenylene end-capped imide oligomers having internal acetylene groups in the backbone were prepared from bis(3-aminophenyl)acetylene as the internal acetylene source and 2-aminobiphenylene as the end cap. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride and 4,4′-diaminodiphenyl ether were used as comonomers. Phenyl end-capped imide oligomers having internal acetylene groups also were prepared in order to evaluate the effect of the biphenylene groups. The DSC of the biphenylene end-capped prepolymers containing internal acetylene units showed only one exotherm, about 60 °C lower than that of the corresponding phenyl end-capped prepolymers containing internal acetylene units and about 150 °C lower than that of a prepolymer containing only biphenylene end groups, indicative of a clean and quantitative reaction between the internal acetylene and biphenylene end-cap units to yield the phenanthrene structure. Melt processing of the prepolymers was carried out both with and without the $Ni(PPh_3)_2(CO)_2$ catalyst. Films melt processed without the Ni catalyst were tough, flexible, and transparent, while those with Ni catalyst were black, opaque, and somewhat brittle. The melt-processed films made from biphenylene end-capped prepolymers showed excellent thermal properties; T_g's above 400 °C were observed and the films maintained their mechanical properties above T_g, in some cases without showing any loss of mechanical strength near T_g. TGA analyses for the prepolymers and for the melt-processed films showed excellent thermal stability, exhibiting only 5% weight loss well above 500 °C in air and above 550 °C under nitrogen.

Introduction

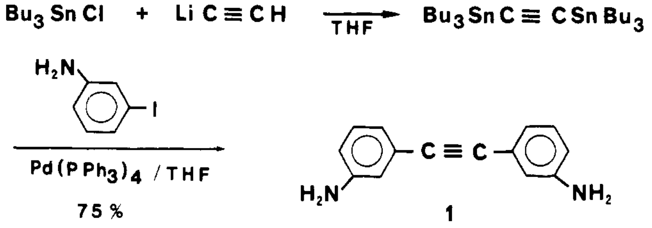
In the preparation of thermally stable polyimide resins, cross-linking a processable prepolymer after or during processing has received considerable attention.[1] A variety of cross-links have been used to improve the properties of readily processable thermally stable polymers, but the retention of mechanical properties for extended times at high temperatures has not been as good as might have been expected considering the fact that polyimides are some of the most thermally stable polymers. The lower thermal stability can be attributed to the generation of a cross-link that is not as thermally stable as the polymer main chain. For example, acetylene end-caps, which are currently used in commercially available prepolymers, cyclotrimerize to benzene.[2] However, the efficiency in this reaction is as low as 30%,[3] and vinyl and other thermally unstable cross-links are formed.

In our previous paper, we succeeded in generating thermally stable polyimides. These polyimides maintained their mechanical properties above their T_g's by introducing branch points (three-armed star) in the prepolymer.[4] However, the cross-linking reaction between the acetylene end-capped polymer and a biphenylene end-capped polymer to form phenanthrene links did not give materials as thermally stable as should have been realized. Here we report the syntheses of biphenylene end-capped imide oligomers having acetylene groups in the prepolymer main chain and their melt processing to form high-quality thermally stable films by the selective reaction between the biphenylene and acetylene groups.

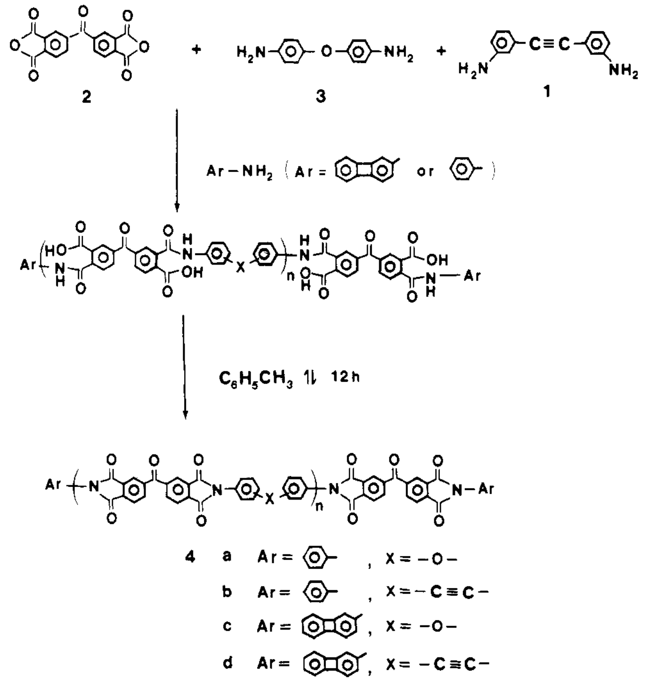
Results and Discussion

Preparation and Properties of Prepolymers. A polyimide synthesis utilizing the diamino monomer bis(3-aminophenyl)acetylene allows the incorporation of acetylene linkages in the backbone of the biphenylene end-capped oligomeric imides. The diamino monomer having an internal acetylene was prepared by a palladium-catalyzed carbon–carbon coupling reaction (Scheme I).

Scheme I



Scheme II



Prepolymers having internal acetylene were prepared from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (**2**), 4,4′-diaminodiphenyl ether (**3**) and **1** (Scheme II). As

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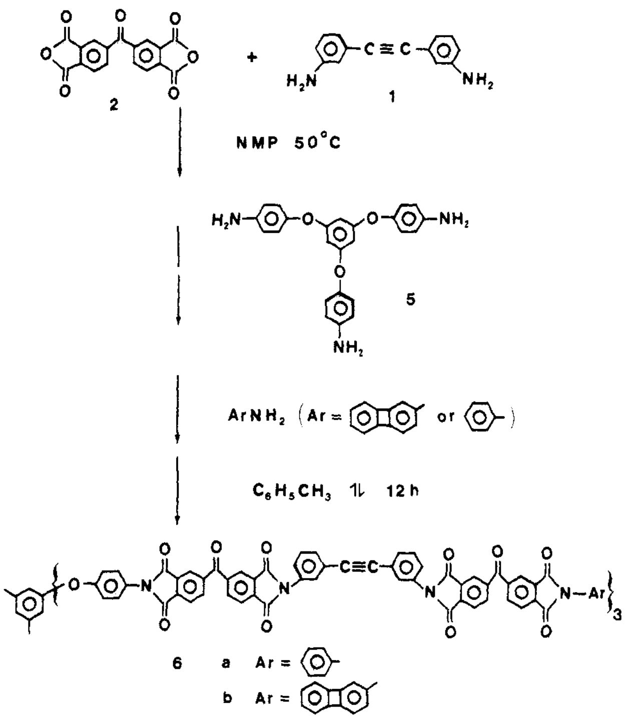
Table I
Properties of Prepolymers

run	prepolymer	$\overline{DP}$	% acetylene[a]	A/B[b]	DSC T_g, °C	DSC T_m, °C	DSC $T_{exo,max}$, °C
1	**4a**	3	0	0/0	165	305, 355, 372	
2	**4c**	3	0	0/2	150	275	430
3	**4b**	3	100	1/0	175	265, 288, 325	408
4	**4d**	3	100	1/2	183		360
5	**4d**	5	100	2/2	200		395
6	**4a**	11	0	0/0	160	300, 345, 392, 419	
7	**4b**	11	10	0.5/0	196	257	425
8	**4b**	11	40	2/0	226	278, 318	415
9	**4b**	11	60	3/0	229		410
10	**4c**	11	0	0/2	154	375	500
11	**4d**	11	10	0.5/2	215		395
12	**4d**	11	40	2/2	158, 228		348
13	**4d**	11	60	3/2	224		348
14	**6a**	3	100	3/0	176, 237		408
15	**6b**	3	100	3/3	180, 267		362

[a] Percent of acetylene groups as calculated from the incorporate of 1 vs. 3 by [1 (mol)/1 (mol) + 3 (mol)] × 100. [b] The average ratio of acetylene group to biphenylene group.

Scheme III



end-capping reagents, 2-aminobiphenylene and aniline were used to provide biphenylene and phenyl end caps. The degree of polymerization was controlled by the imbalance[5] of the two monomers, dianhydride and diamine, as demonstrated in the preceding paper. To 2 dissolved in NMP was added a calculated amount of 3 and/or 1 dissolved in NMP. The ratio of 3 and 1 was selected to control the ratio of internal acetylene to end-capped biphenylene. Phenyl or biphenylene end-capped star prepolymers, whose three arms each had $\overline{DP}$ = 3, also were prepared (Scheme III). The prepolymers were brown (for biphenylene end capped) or yellow (for phenyl end capped) and insoluble in common organic solvents.

Casting films from the amic acid solution onto a glass plate was attempted, but the films obtained were too brittle, in every case, for determination of the mechanical properties. The brittleness probably was due to a combination of the low molecular weight and the more rigid structure of acetylene groups compared to the ether groups.

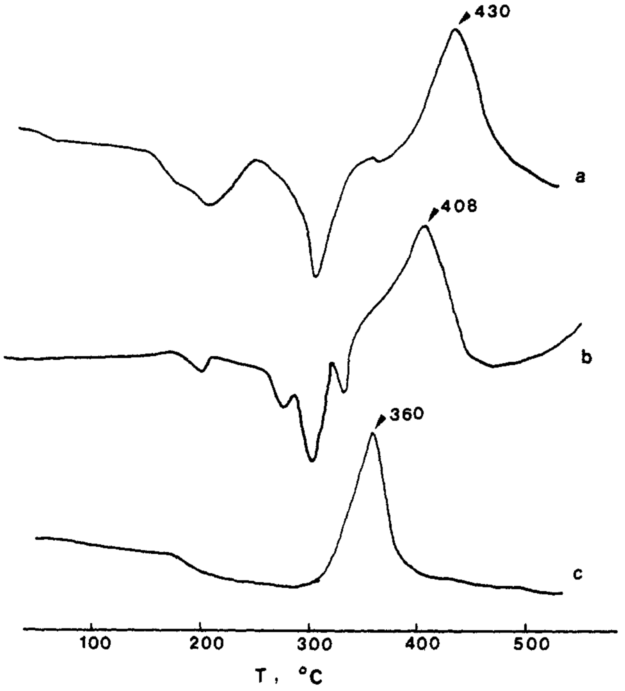


Figure 1. DSC's of the prepolymers 4: (a) **4c** ($\overline{DP}$ = 3); (b) **4b** ($\overline{DP}$ = 3); (c) **4d** ($\overline{DP}$ = 3).

As reported in the previous paper, cast films that were flexible and tough enough for Rheovibron analysis were prepared from ether-linked diamino monomers.

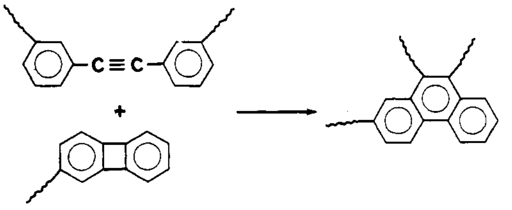
The thermal properties of the prepolymers were measured by DSC (Table I). The T_g's increased as the acetylene group content increased; for the phenyl end-capped prepolymers, T_g's were 160, 196, 226, and 229 °C for polyimides containing 0, 10, 40, and 60 mol % internal acetylene (runs 6–9, Table I). The same was true for the biphenylene end-capped prepolymers (runs 10–13). The exotherm for the ring opening of biphenylene itself appeared above 430 °C (runs 2 and 10) and those of polyimides containing internal acetylenes alone at 408–425 °C, much higher than those polyimides containing terminal acetylenes. When the prepolymer contained both the internal acetylene and the biphenylene end cap, however, the exotherm appeared well below 400 °C as a single peak (Figure 1). This indicates that internal acetylene and biphenylene react with each other to generate phenanthrene links instead of reacting separately.[6] This is

Table II
TGA of Prepolymers

prepolymer	$\overline{DP}$	% acetylene[a]	temp (°C) at % wt loss (air flow)		temp (°C) at % wt loss (N_2 flow)	
			5%	20%	5%	20%
4a	3	0	422	498		
4c	3	0	498	566	535	595
4b	3	100	416	503	423	500
4d	3	100	554	584	564	627
4d	5	100	527	564	549	611
4a	11	0	496	570	515	575
4b	11	10	504	578	514	572
4b	11	40	520	577	510	584
4b	11	60	510	576	508	592
4c	11	0	495	559	515	572
4d	11	10	548	576	545	595
4d	11	40	546	576	555	610
4d	11	60	530	561	561	614
6a	3	100	448	556	460	580
6b	3	100	532	567	562	621

[a] Percent of acetylene groups as calculated from the incorporation of **1** vs. **3**, by [**1** (mol)/**1** (mol) + **3** (mol)] × 100.

noteworthy, considering that a blend of polyimide prepolymers, one containing biphenylene end caps and the other containing terminal acetylenes, showed two exotherms at about 300–350 and 420–450 °C due to the reactions of acetylene and biphenylene, respectively. Terminal acetylenic groups can react with themselves to crosslink the polymers, which undoubtedly is a lower energy pathway than the self-reaction of internal acetylenic units. Thus, in polymers such as **4**, containing internal acetylenes and biphenylene end caps, the cross-linking reaction to form phenanthrene links apparently is the preferred pathway; the lower temperature for this reaction precludes the self-reactions of biphenylene to yield tetrabenzocyclooctatetraene units (eq 1).



(1)

In determining the thermal stability, the oligomers containing acetylene and/or biphenylene units undergo the curing reaction, resulting in a thermally stable resin. The TGA analyses of the prepolymers (Table II) emphasize the high thermal stability of the series of polymers (**4d**, containing both internal acetylenic units and biphenylene end caps), compared to those of polyimide **4b** or **4c**. The temperature at 5% weight loss for the **4d** series was 545–564 °C, while lower stabilities 423–514 °C for **4b** and 515–535 °C for **4c**, were observed under nitrogen. Under air the temperatures for 5% weight loss were about 10–30 °C lower.

Prepolymer Processing and the Properties of the Cured Films. A series of phenyl or biphenylene end-capped polyimide prepolymers having internal acetylenic units in the main chain, **4b** ($\overline{DP}$ = 3, 11) and **4d** ($\overline{DP}$ = 3, 11), were melt processed with a nickel catalyst (10 mol % or 20 mol % of Ni based on the end groups present). The nickel catalyst is known to lower the temperature of the self-reaction of biphenylene[7] and acetylene.[4] Biphenylene end-capped prepolymers **4d**, some of which had exotherms as low as 348 °C, also were melt processed without the nickel catalyst. The polymers were melt processed at 350 °C for 60–90 min under 5000 psi.

Prepolymers were melt processed with a 0.0127-cm-thick spacer between copper foils, and the thickness of the films was 0.021 ± 0.004 cm for those melt processed with nickel and 0.012 ± 0.003 cm for those without nickel. Thus prepolymers without nickel underwent melt flow much better than those containing nickel. Films melt processed with nickel were black, opaque, and hard, but somewhat brittle in some cases. Films melt processed without nickel were brown, transparent, flexible, and tough.

The melt-processed films, measured by DSC and dynamic mechanical analysis (Rheovibron, Table III) showed good thermal properties. Films of cured phenyl end-capped prepolymers (runs 7–9, Table III), containing a higher content of internal acetylenes, gave materials with higher cross-link densities, resulting in higher T_g's and better mechanical strength, particularly above the apparent glass transition temperature. As the content of acetylene groups increases from 10% to 40% and 60%, the T_g's increased from 205 to 259 and 275 °C, E' being from 1.5×10^8 to 3.6×10^8 and 8.3×10^8 dyn/cm² above the T_g. The temperatures at which the storage modulus reached the lowest

Table III
Properties of Melt-Processed Films

run	prepolymer	$\overline{DP}$	% acetylene[a]	A/B[b]	Ni	DSC		Rheovibron		
						T_g, °C	T_m, °C	E''_{max}, °C	$10^{-10}E'_{25°C}$, dyn/cm²	E'_{lowest}, dyn/cm²
1	AECPI[c]	3		2/0	W	245	370	270	2.7	1.8×10^9 (365 °C)
2	**4c**	3	0	0/2	W	244	344	258	2.8	1.0×10^8 (340 °C)
3	**4b**	3	100	1/0	W	164	308			
4	**4d**	3	100	1/2	W	342		330	3.0	2.4×10^9 (394 °C)
5	**4d**	3	100	1/2	W/O	343		355	2.1	6.8×10^9 (380 °C)
6	**4d**	5	100	2/2	W/O	354		367	2.5	1.1×10^{10} (404 °C)
7	**4b**	11	10	0.5/0	W	198	323, 388	205	2.2	1.5×10^8 (300 °C)
8	**4b**	11	40	2/0	W	242		259	3.0	3.6×10^8 (369 °C)
9	**4b**	11	60	3/0	W	233		275	2.5	8.3×10^8 (380 °C)
10	AECPI[c]	11		2/0	W	240	370	266	2.8	3.4×10^8 (373 °C)
11	**4c**	11	0	0/2	W	248	376	245	1.8	1.1×10^8 (370 °C)
12	**4d**	11	10	0.5/2	W	276	366	276	2.9	2.1×10^8 (374 °C)
13	**4d**	11	40	2/2	W	310		298	2.5	5.5×10^8 (368 °C)
14	**4d**	11	40	2/2	W/O	347		361	2.7	2.2×10^9 (428 °C)
15	**4d**	11	60	3/2	W/O	332		420	3.0	6.0×10^9 (441 °C)
16	**6a**	3	100	3/0	W	230		250	3.3	1.0×10^9 (371 °C)
17	**6b**	3	100	3/3	W/O	353		414	3.1	7.2×10^9 (437 °C)

[a] Percent of acetylene groups as calculated from the incorporation of **1** vs. **3**, by [**1** (mol)/**1** (mol) + **3** (mol)] × 100. [b] Ratio of acetylene to biphenylene. [c] Acetylene end-capped polyimide of preceding paper, ref 4.

Table IV
TGA of the Melt-Processed Films

run	prepolymer	$\overline{DP}$	% acetylene[a]	Ni	temp (°C) of % wt loss (air flow)		temp (°C) of % wt loss (N_2 flow)	
					5%	20%	5%	20%
1	**4b**	3	100	W	373	470	373	465
2	**4d**	3	100	W	478	557	500	610
3	**4d**	3	100	W/O	524	559	565	632
4	**4d**	5	100	W/O	519	558	552	620
5	**4b**	11	10	W	425	543	388	557
6	**4b**	11	40	W	470	566	450	580
7	**4b**	11	60	W	465	573	472	593
8	**4d**	11	10	W	464	551	490	586
9	**4d**	11	40	W	514	572	504	596
10	**4d**	11	40	W/O	539	570	558	617
11	**4d**	11	60	W/O	538	570	560	626
12	**6a**	3	100	W	448	562	425	588
13	**6b**	3	100	W/O	518	552	546	612

[a] Percent of acetylene groups as calculated from the incorporation of **1** vs. **3**, by [**1** (mol)/**1** (mol) + **3** (mol)] × 100.

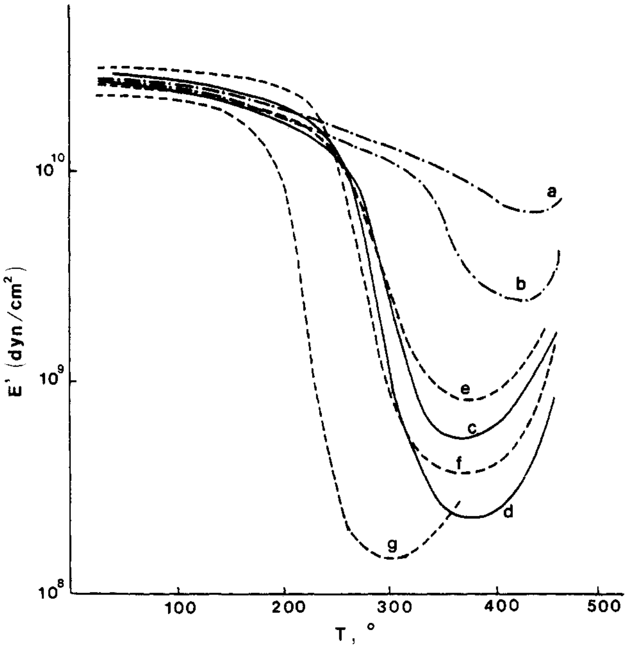


Figure 2. Thermomechanical properties of melt processed films of $\overline{DP}$ = 11: (a) **4d** (60% acetylene groups); (b) **4d** (40% acetylene groups); (c) **4d** (40% acetylene groups) (Ni cat); (d) **4d** (10% acetylene groups) (Ni cat); (e) **4b** (60% acetylene groups) (Ni cat); (f) **4b** (40% acetylene groups) (Ni cat); (g) **4b** (10% acetylene groups) (Ni cat).

value were 300, 369, and 380 °C. Thus, the use temperature increased as the ratio of internal acetylene increased. When biphenylene was used as an end cap, the thermal properties of the polyimide were much improved compared to the corresponding phenyl end-capped polyimides (Figure 2). Melt-processed films of the prepolymers, containing both acetylene and biphenylene groups (runs 4 and 13), showed T_g's above 300 °C and maintained their mechanical strength above T_g.

When polyimides **4d** were melt processed without a nickel catalyst, the transparent and tough films showed much more improved properties than those melt processed with nickel. Films processed without nickel (runs 13 and 14, Table III) showed higher T_g's (361 vs. 298 °C) and higher mechanical strength above T_g (lowest E' of 2.2 × 10^9 dyn/cm^2 at 428 °C vs. 5.5 × 10^8 dyn/cm^2 at 368 °C). The same was true with **4d** ($\overline{DP}$ = 3, runs 4 and 5). For all polyimides melt processed without nickel, the T_g's were well above 300 °C and some were higher than 400 °C. The mechanical properties above 400 °C were maintained with little loss of mechanical strength near T_g. For example, the storage modulus for **4d** ($\overline{DP}$ = 5) at room temperature, 2.5 × 10^{10} dyn/cm^2, drops to 1.1 × 10^{10} dyn/cm^2 at 404 °C (Figure 3).

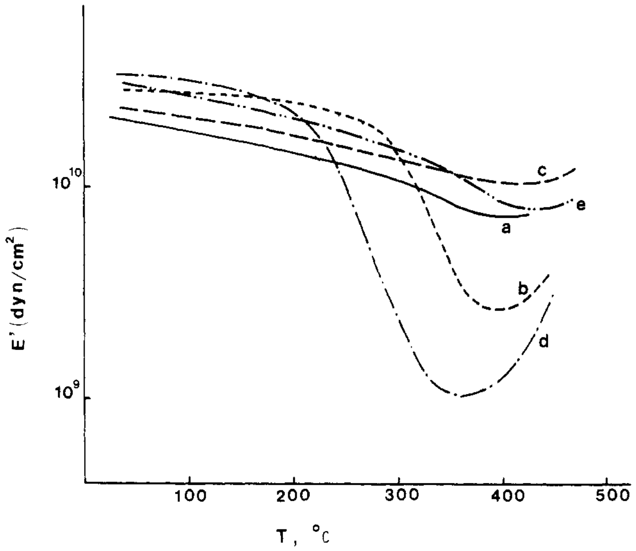


Figure 3. Thermomechanical properties of melt-processed films: (a) **4d** ($\overline{DP}$ = 3); (b) **4d** ($\overline{DP}$ = 3) (Ni cat); (c) **4d** ($\overline{DP}$ = 5); (d) **6a** ($\overline{DP}$ = 3) (Ni cat); (e) **6b** ($\overline{DP}$ = 3).

The melt processed films showed good thermal stability by TGA analyses, particularly those films melt processed without the nickel catalyst (Table IV). It is also interesting that films melt processed without nickel showed equal or better thermal stability as compared with corresponding prepolymers. This suggests that a desirable curing reaction, the selective formation of phenanthrene links without the formation of an appreciable amount of thermally unstable byproducts, took place. On the other hand, films melt processed with nickel showed lower thermal stability as compared to their prepolymers.

Conclusions

Biphenylene end-capped imide oligomers having internal acetylene units showed excellent thermal properties. As indicated by DSC, the internal acetylene groups react selectively with the biphenylene end groups. Melt-processed films showed good thermal properties, especially when the melt processing was carried out without nickel. The T_g's of cured films were above 400 °C and the resins maintained thermomechanical strength well above 400 °C, losing very little strength near the T_g. High thermal stability was also shown by TGA analyses. Both the prepolymers and films, melt processed without nickel, lost 5% of their weight at 545–565 °C under nitrogen and 5 wt % at 519–554 °C in air. These results also suggest that a selective reaction between biphenylene and the internal acetylene takes place during the cure in the absence of nickel while films cured with a nickel catalyst showed a lower thermal stability. Nickel has a deleterious effect, either because of a nonselective reaction between acetylene and biphenylene or possibly because it catalyzes the oxidative decomposition of the polyimide.

Experimental Section

All melting points are uncorrected. Infrared spectra were determined with a Beckman 4240 spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc. Proton NMR spectra were measured with a Varian EM-360 spectrometer or an IBM WP-270 spectrometer. All chemical shifts are expressed in ppm downfield from internal tetramethylsilane.

Thermal analyses were performed with a Du Pont 990 thermal analyzer equipped with a differential scanning calorimeter (DSC) cell base (heating rate, 10 °C/min). A Du Pont 951 thermogravimetric analyzer (TGA) was used for thermal stability tests (heating rate, 5 °C/min). Dynamic thermomechanical analyses were obtained on a Rheovibron DDV-II-C dynamic viscoelastometer (frequency, 35 Hz).

Preparation of Bis(3-aminophenyl)acetylene (1). To a solution of 2.41 g (11.0 mmol) of 3-iodoaniline and 0.173 g (0.150 mmol) of tetrakis(triphenylphosphine)palladium(0)[8] in 100 mL of THF under Ar was added dropwise 3.02 g (5.00 mmol) of bis(tributylstannyl)acetylene,[6] obtained from the reaction of lithium acetylide–ethylenediamine complex and tributyltin chloride. The solution was heated to 60 °C and stirred for 40 h, at which time the THF was removed and 200 mL of ether was added. The ether solution was washed with half-saturated potassium fluoride, water, and brine and dried over sodium sulfate. Removal of ether afforded the crude product as a yellow oil, which crystallized on standing overnight. The crude product was purified by column chromatography on silica gel (ether) to afford yellow crystals. The product can be further purified by recrystallization from hexane/toluene (2:1) to yield 0.78 g (75%) of product, mp 104.5–105.5 °C. ^{1}H NMR (CDCl$_3$) δ 6.3–7.5 (m, 8 H, aromatic), 3.6 (b, 4 H, NH$_2$). Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.66; H, 5.84; N, 13.36.

Preparation of Phenyl End-Capped Imide Oligomer Having Internal Acetylene 4b ($\overline{\mathrm{DP}}$ = 3). To 2 mL of NMP was added 0.6445 g (2.000 mmol) of 2, which was dissolved by heating to 75 °C with mechanical stirring under Ar. The solution was kept at 50 °C and 0.2083 g (1.000 mmol) of 1, dissolved in 0.6 mL of NMP, was added dropwise over 30 min. Any residual monomer was washed into the reaction flask using 0.2 mL × 2 of NMP. The reaction was allowed to continue for 30 min, after which time 0.3724 g (4.000 mmol) of aniline was added and the mixture was stirred at 50 °C for 1 h. The amic acid solution was added to 50 mL of toluene and the mixture was heated to reflux for 12 h. The precipitate was filtered and dried at 110 °C (0.05 mmHg) for 40 h to give 0.84 g (85%) of a yellow powder. IR (KBr) 3060 (aromatic C–H), 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{60}H_{30}N_4O_{10}$: C, 74.53; H, 3.13; N, 5.79. Found: C, 74.40; H, 3.19; N, 5.91.

Preparation of Biphenylene End-Capped Imide Oligomer Having Internal Acetylene 4d ($\overline{\mathrm{DP}}$ = 3). The above procedure was followed, except 0.3679 g (2.200 mmol) of 2-aminobiphenylene[9] was used as an end cap instead of aniline to obtain 0.89 g (80%) of a brown powder. IR (KBr) 1780 and 1710 cm^{-1} (C=O, imide). Anal. Calcd for $C_{72}H_{34}N_4O_{10}$: C, 77.55; H, 3.07; N, 5.02. Found: C, 75.96; H, 3.14; N; 5.10.

Preparation of Biphenylene End-Capped Imide Oligomer Having Internal Acetylene 4d ($\overline{\mathrm{DP}}$ = 5). The above procedure was followed, except 0.5800 g (1.800 mmol) of 2, 0.2499 g (1.200 mmol) of 1, and 0.2207 g (1.320 mmol) of 2-aminobiphenylene were used to yield 0.79 g (82%) of a brown powder. IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{103}H_{48}N_6O_{15}$: C, 76.86; H, 3.01; N, 5.22. Found: C, 75.54; H, 3.10; N, 5.25.

Preparation of Phenyl End-Capped Imide Oligomer Having 10% Internal Acetylene 4b ($\overline{\mathrm{DP}}$ = 11). To 2 mL of NMP was added 0.7592 g (2.356 mmol) of 2, which was dissolved by heating to 75 °C with mechanical stirring under Ar. The solution was kept at 50 °C and a solution of 0.3604 g (1.800 mmol) of 3,3′-diaminodiphenyl ether[9] and 0.0417 g (0.200 mmol) of 1 in NMP was added dropwise over 30 min. Any residual monomers were rinsed into the flask with 0.2 mL × 2 of NMP, and the mixture was allowed to react at 50 °C for 30 min, after which time 0.11 g (1.2 mmol) of aniline was added and the mixture was allowed to react for 1 h. The amic acid solution was added to 50 mL of toluene and heated to reflux for 12 h. The precipitate was filtered and dried at 110 °C (0.05 mmHg) for 40 h to yield 1.12 g (97%) of a yellow powder. IR (KBr) 1775 and 1710 cm^{-1} (C=O, imide). Anal. Calcd for $C_{175}H_{86}N_{12}O_{34.5}$: C, 72.26; H, 2.98; N, 5.78. Found: C, 71.64; H, 3.12; N, 6.01.

Preparation of Phenyl End-Capped Imide Oligomer Having 40% Internal Acetylene 4b ($\overline{\mathrm{DP}}$ = 11). The above procedure was followed, except 0.7592 g (2.356 mmol) of 2, 0.2403 g (1.200 mmol) of 3,3′-diaminodiphenyl ether, 0.1666 g (0.8000 mmol) of 1, and 0.11 g (1.2 mmol) of aniline were used to yield 1.10 g (95%) of product. IR (KBr) 1780 and 1710 cm^{-1} (C=O, imide). Anal. Calcd for $C_{178}H_{86}N_{12}O_{33}$: C, 73.20; H, 2.97; N, 5.75. Found: C, 72.64; H, 3.06; N, 5.90.

Preparation of Phenyl End-Capped Imide Oligomer Having 60% Internal Acetylene 4b ($\overline{\mathrm{DP}}$ = 11). The above procedure was followed, except 0.7592 g (2.356 mmol) of 2, 0.1602 g (0.800 mmol) of 4,4′-diaminodiphenyl ether, 0.2499 g (1.200 mmol) of 1, and 0.11 g (1.2 mmol) of aniline were used to yield 1.04 g (90%) of polyimide. IR (KBr) 1780 and 1710 cm^{-1} (C=O, imide). Anal. Calcd for $C_{180}H_{86}N_{12}O_{32}$: C, 73.82; H, 2.96; N, 5.74. Found: C, 72.59; H, 3.03; N, 5.84.

Preparation of Biphenylene End-Capped Imide Oligomer Having 10% Internal Acetylene 4d ($\overline{\mathrm{DP}}$ = 11). The above procedure was followed, except 0.7592 g (2.356 mmol) of 2, 0.3604 g (1.800 mmol) of 4,4′-diaminodiphenyl ether, 0.0417 g (0.200 mmol) of 1, and 0.1605 g (0.960 mmol) of 2-aminobiphenylene, instead of aniline, were used and 0.2 mL × 3 of NMP was used to rinse the 2-aminobiphenylene. The yield of the brown powder was 1.17 g (96%). IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{187}H_{90}N_{12}O_{34.5}$: C, 73.48; H, 2.97; N, 5.50. Found: C, 72.64; H, 3.07; N, 5.56.

Preparation of Biphenylene End-Capped Imide Oligomer Having 40% Internal Acetylenes 4d ($\overline{\mathrm{DP}}$ = 11). The above procedure was followed, except 0.7592 g (2.356 mmol) of 2, 0.2403 g (1.200 mmol) of 4,4′-diaminodiphenyl ether, 0.1666 g (0.800 mmol) of 1, and 0.1605 g (0.960 mmol) of 2-aminobiphenylene were used to yield 1.16 g (95%) of polyimide. IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{190}H_{90}N_{12}O_{33}$: C, 74.36; H, 2.96; N, 5.48. Found: C, 73.26; H, 3.13; N, 5.60.

Preparation of Biphenylene End-Capped Imide Oligomer Having 60% Internal Acetylenes 4d ($\overline{\mathrm{DP}}$ = 11). The above procedure was followed, except 0.7592 g (2.356 mmol) of 2, 0.1602 g (0.800 mmol) of 4,4′-diaminodiphenyl ether, 0.2499 g (1.200 mmol) of 1, and 0.1538 g (0.920 mmol) of 2-aminobiphenylene were used to yield 1.17 g (95%) of polyimide. IR (KBr) 1780 and 1710 cm^{-1} (C=O, imide). Anal. Calcd for $C_{192}H_{90}N_{12}O_{32}$: C, 74.95; H, 2.95; N, 5.46. Found: C, 73.74; H, 3.19; N, 5.51.

Preparation of Phenyl End-Capped Star Imide Oligomer Having Internal Acetylenes 6a ($\overline{\mathrm{DP}}$ = 3). To 2 mL of NMP was added 0.5800 g (1.800 mmol) of 2, which was dissolved by heating to 75 °C with mechanical stirring under Ar. The solution was kept at 50 °C and 0.1874 g (0.900 mmol) of 1, dissolved in 0.6 mL of NMP, was added dropwise over 30 min. Any residual monomer was washed into the flask by 0.2 mL × 2 of NMP. The mixture was allowed to react for 30 min, after which time 0.1198 g (0.300 mmol) of 5[4] in 0.6 mL of NMP was added dropwise. The star amine (5) was rinsed by 0.2 mL × 2 of NMP, and the mixture was allowed to react for an additional 30 min. To the reaction mixture, which became very viscous, was added 0.126 g (1.35 mmol) of aniline, and this mixture was allowed to react for 1 h. The amic acid solution was added into 50 mL of toluene and heated to reflux for 12 h. The resulting precipitate was filtered and dried at 110 °C (0.05 mmHg) for 40 h to yield 0.84 g (93%)

of star polyimides. IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{186}H_{90}N_{12}O_{33}$: C, 73.96; H, 3.00; N, 5.56. Found: C, 73.47; H, 3.25; N, 5.86.

Preparation of Biphenylene End-Capped Star Imide Oligomer Having Internal Acetylenes 6b ($\overline{DP}$ = 3). The above procedure was followed, except 0.1731 g (1.040 mmol) of 2-aminobiphenylene was used as an end cap instead of aniline and 0.2 mL × 3 of NMP was used to rinse the end cap. The yield was 0.86 g (88%). IR (KBr) 1775 and 1705 cm^{-1} (C=O, imide). Anal. Calcd for $C_{204}H_{96}N_{12}O_{33}$: C, 75.55; H, 2.98; N, 5.18. Found: C, 74.15; H, 3.20; N, 5.23.

Melt Processing of the Prepolymer (Neat Resin Processing). An appropriate amount of $Ni(CO)_2(PPh_3)_2$ (Aldrich) was added to 200 mg of prepolymer swelled in 50 mL of benzene under Ar. The mixture was stirred for 1 h. The benzene was removed under reduced pressure and the resulting powder was dried at 0.05 mmHg for 18 h.

A modified Wabash hydraulic press (Model 12 10) fitted with Carver heated platens (no. 2102) was used for the neat resin processing. The prepolymer powder (either with or without nickel) was placed in a small pile between 3 in. × 3 in. pieces of copper foil (0.005 in. thick, Baker no. 1-1714) with a 0.005-in. copper foil spacer. The copper foil was washed with 1 N HCl and then with water, prior to use. The assembly was placed in the hydraulic press and melt processed at 325–350 °C under 5000 psi for various times. Plunging the assembly into cold water immediately after processing facilitated removal of the film from the copper foil. Any residual copper that adhered to the surface of the film was removed by placing the film in concentrated ammonium hydroxide for 30 min, followed by a thorough rinsing with water and drying at 110 °C (0.05 mmHg) for 40 h.

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Registry No. 1, 102852-93-7; **4b**, 102920-43-4; **4d**, 102940-12-5; $(Ph_3P)_2Ni(CO)_2$, 13007-90-4; 3-$IC_6H_4NH_2$, 626-01-7; $Bu_3SnC\equiv CSnBu_3$, 994-71-8.

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Readily Processable Imide Oligomers Containing Perfluoroisopropylidene Connecting Units and Reactive Acetylenic and Biphenylene Groups: Synthesis, Curing, and Thermal Properties

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ABSTRACT: Biphenylene or acetylene end-capped imide oligomers of $\overline{DP}$ = 3, 11 and 22 were prepared by adjusting the stoichiometry of the fluorinated monomers 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and the end cap. Biphenylene end-capped imide oligomers having internal acetylene in the prepolymer backbone also were prepared similarly with bis(3-aminophenyl)acetylene as an internal acetylene source. Fluorinated star imide oligomers were prepared by utilizing 1,3,5-tris(4-aminophenoxy)benzene as the star point. The prepolymers were soluble in common organic solvents such as benzene, THF, CH_2Cl_2, $CHCl_3$, acetone, and ether and insoluble in hexane and ethanol, although the star prepolymers were less soluble than the linear ones. Melt processing of the prepolymers was carried out with and without the $Ni(PPh_3)_2(CO)_2$ catalyst. Blend melt processing between biphenylene and acetylene end-capped prepolymers also was performed. Prepolymers underwent melt flow to give good films. Films melt processed in the presence of the nickel catalyst were dark brown, while those without the catalyst were light brown and transparent. Melt-processed films showed higher T_g's than the uncured prepolymers and also showed good mechanical properties. Films obtained from prepolymers containing the biphenylene end cap and internal acetylene groups showed excellent thermal properties, considering they have flexible fluorinated groups. The T_g's were above 300 °C and the value for the storage modulus (above T_g) was as high as 2.9 × 10^9 dyn/cm^2 at 411 °C.

Introduction

Although polyimides are among the most thermally stable polymers,[1] their insolubility in the common organic solvents results in processing difficulties. One approach to the processable polyimides is the use of reactive groups placed on the ends of soluble oligomers, which could be thermally cured to yield cross-linked polyimides.[2] However, even the low molecular weight oligoimides do not have enough solubility and in most cases precursor amic acid solutions are used for processing. Amic acids are somewhat unstable,[1] especially to water, and the solubility of amic acid requires the use of N-methylpyrrolidone or similar high-boiling solvents for solution processing. Isoimide oligomers, which are more soluble than the analogous

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