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Star and Linear Imide Oligomers Containing Reactive End Caps: Preparation 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 monomers 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and 4,4′-diaminodiphenyl ether and the end-capping monomers (3- or 4-aminophenyl)acetylene or 2-aminobiphenylene. Star imide oligomers having biphenylene or acetylene end groups were made by utilizing 1,3,5-tris(4-aminophenoxy)benzene as the star point. Melt processing these prepolymers in the presence or absence of a catalyst, $Ni(PPh_3)_2(CO)_2$, was carried out to give high-quality dark films, having increased T_g's and improved mechanical properties, especially above the T_g, as compared with the uncured resins. The melt processing of a blend of biphenylene and acetylene end-capped prepolymers also was carried out to form high-quality films. Films of melt-processed star prepolymers showed better mechanical properties than films of the analogous linear polymers. The mechanical properties above T_g for the melt-processed films increased in the following order, according to the end groups: acetylene > blend (acetylene and biphenylene) > biphenylene.

Introduction

Polyimides are some of the most industrially important thermally stable polymers.[1] However, the processability of polyimides is problematic due to their poor solubility and infusibility. The inclusion of flexible linkages into the polymer chain generally improves the processability but lowers the use temperature as a consequence of lower phase transition temperatures.

One approach to processability is to cross-link a polymer after or during processing to give a material with improved properties.[2] Highly cross-linked polymers show desirable properties such as excellent dimensional stability with low creep rates, high resistance to solvents, increased softening temperatures, and improved thermal stability over the analogous linear polymers. The introduction of a cross-linking site as an end-cap for low molecular weight oligomers has received much attention because the oligomer usually has good melt-flow characteristics compared to higher molecular weight polymers.

A variety of cross-linking sites have been used to cure thermally stable polymers. Acetylene[3] and nadic (bicyclo[2.2.1]hept-4-ene-2,3-dicarboxylic anhydride)[4] end groups are currently being used in commercially available prepolymers. While these prepolymers give cross-linked resins that show impressive performance at high temperature, the retention of mechanical properties for extended times at high temperatures is less for these materials than for high molecular weight polyimides.[5]

When biphenylene is used as a cross-linking site, primarily a dimerization reaction to yield tetrabenzocyclooctatetraene occurs.[6] Biphenylene has been applied as a cross-linking cite for polyquinolines,[7] aromatic polyamides, polyquinoxalines, and poly(benzimidazoles),[8] as well as for polyimides and poly(ether keto sulfones)[9] to give resins higher T_g's and thermally improved properties after the cure. Biphenylene also is known to react with acetylene groups to give the phenanthrene structure,[6b] which should be highly thermally stable.

This paper reports the preparation of biphenylene or acetylene end-capped low molecular weight imide oligomers, the neat resin processing of these oligomers into films, and the properties of the resultant films. Blends of acetylene and biphenylene end-capped oligomers also were melt processed. Star oligomers end capped with acetylene or biphenylene units were prepared, since they were expected to give films of better thermal properties than the linear oligomers, as a result of a higher cross-link density.

Results and Discussion

Preparation of End-Capped Prepolymers. Biphenylene or acetylene end-capped imide oligomers **3** were prepared, along with phenyl end-capped oligomers, using 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (**1**) and 4,4′-diaminodiphenyl ether (**2**) as monomers (Scheme I). The degree of polymerization was controlled by the balance of two monomers, according to the equation[10] $\overline{DP} = (1 + r)/(1 + r - 2rp)$.

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Scheme I

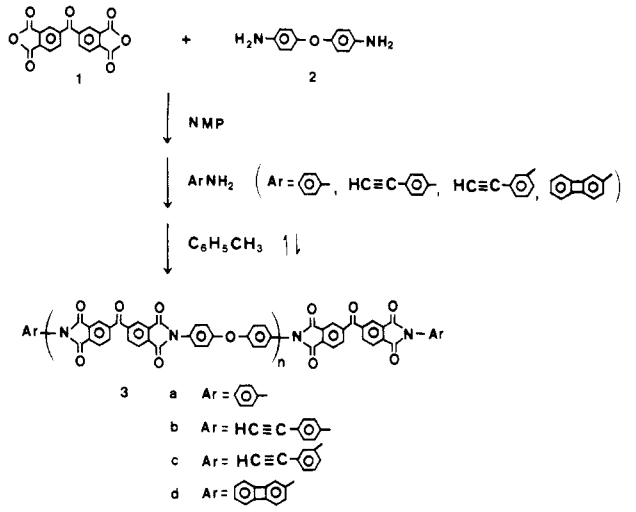


Table I
Model Study for the Hydrolysis of End-Capped Acetylene Units

dehydration conditions	8	9
reflux in *N,N*-dimethylacetamide[a]	22	78
reflux in *N*-methylpyrrolidone	52	48
reflux in toluene	89	11

[a] Reference 11.

An *N*-methylpyrrolidone (NMP) solution of **2** was added dropwise to the NMP solution of a calculated amount of excess **1** to give anhydride-terminated oligoamic acid solution, into which was added an NMP solution of the end-capping reagent. The end-capped amic acid solution was poured into toluene and cyclodehydrated by refluxing in toluene.

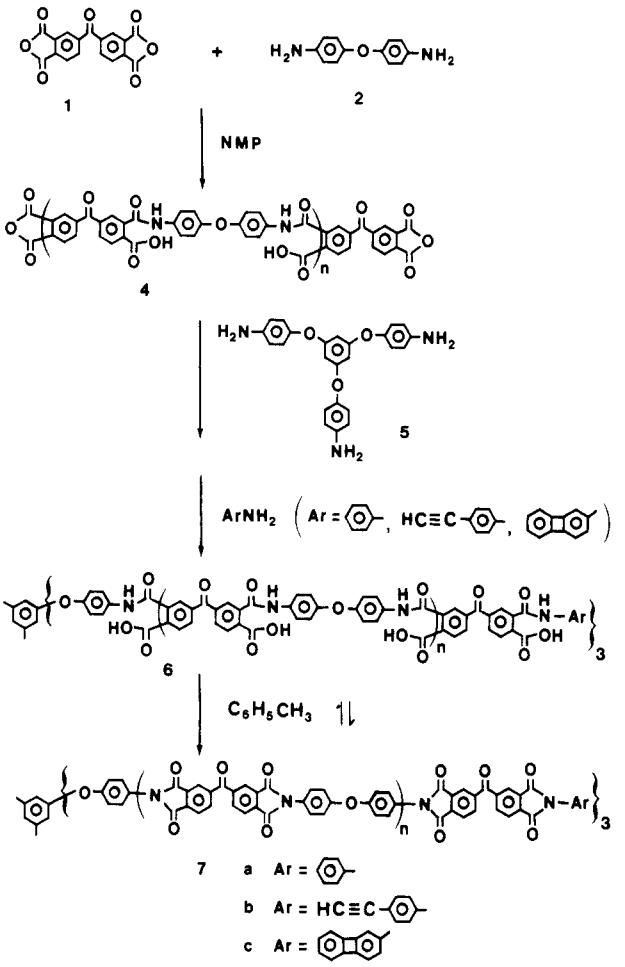
Star imide oligomers end capped with biphenylene (**7c**, $\overline{DP}_{arm}$ = 1, 3, 11), acetylene (**7b**, $\overline{DP}_{arm}$ = 1, 3, 11) and phenyl (**7a**, $\overline{DP}_{arm}$ = 1, 3, 11) also were prepared (Scheme II). As a star point, 1,3,5-tris(4-aminophenoxy)benzene (**5**) was synthesized by the reaction of phloroglucinol with *p*-fluoronitrobenzene. Anhydride-ended oligoamic acid **4** of controlled $\overline{DP}$, prepared from **1** and **2** as arms of the star prepolymer, was allowed to react with star triamine **5** and then with the various end-capping reagents to give star oligomeric amic acid **6**, which was cyclodehydrated by refluxing toluene to give star imide oligomers **7**.

The imide oligomers were yellow (for phenyl or acetylene end capped) or light brown (for biphenylene end capped) and insoluble in common organic solvents. The infrared spectra of the oligoimides indicated that complete imidization had occurred as evidenced by the absence of an OH absorption (broad at 3300–2500 cm^{-1}, characteristic of H-bonded COOH) after cyclization of the intermediate amide acid in toluene. The characteristic imide C=O stretch (1770–1780, 1710–1720 cm^{-1}) also was observed.

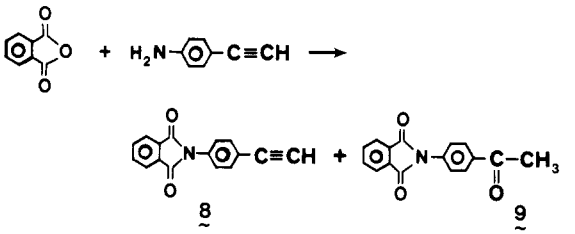
It had been reported[11] that 4-ethynylaniline could not be utilized as an effective end cap for imide prepolymers because the terminal acetylene groups were susceptible to hydration during the cyclodehydration in *N,N*-dimethylacetamide (DMAC), only 22% of the acetylene groups surviving.

Model reactions using phthalic anhydride and 4-ethynylaniline were carried out (Table I). When the condensation reaction was carried out in NMP and also dehydration in the same solvent at 150 °C, the ^1H NMR showed that 48% of the acetylene was hydrated to acetyl

Scheme II



groups (**9**), with only 52% of the acetylene groups remaining (**8**). The infrared spectra of the products showed



C=O stretching at 1680 and 1650 cm^{-1} with the ≡C—H stretch at 3260 cm^{-1} and a weak C≡C stretch at 2110 cm^{-1}. When the amide acid was dehydrated by refluxing toluene, only 10.8% of the acetylene groups had hydrolyzed to acetyl groups (^1H NMR) and 89.2% of acetylene groups were unchanged. The infrared spectrum also showed a strong, sharp ≡C—H stretch at 3260 cm^{-1}, a clear C≡C stretch at 2110 cm^{-1}, and a very small C=O stretch.

For the preparation of the acetylene end-capped imide oligomer of $\overline{DP}$ = 3, chemical cyclodehydration using acetic anhydride/pyridine also was applied along with the thermal cyclodehydration in toluene. 3-Ethynylaniline, whose acetylene group reportedly survive the cyclodehydration,[11] also was used for the preparation of **3c** $\overline{DP}$ = 3, which was thermally cyclized in toluene.

Thermal Properties of the Prepolymers. The DSC of phenyl end-capped imide oligomers **3a** ($\overline{DP}$ = 3, 11, 22) showed that these oligoimides have a T_g at 160–165 °C and a number of sharp endotherms characteristic of T_m between 280 and 420 °C (Table II). The DSC's of **3b–d** showed T_g's near 150–170 °C and T_m's between 275–375

Table II
Thermal Transitions of Prepolymers by DSC

	unannealed				annealed				
prepolymer	T_g, °C	T_c, °C	T_m, °C	$T_{exo,max}$, °C	annealed[c] temp, °C	T_g, °C	T_c, °C	T_m, °C	$T_{exo,max}$, °C
3a ($\overline{DP}$ = 3)	165	330	305, 355, 372		325	165	330, 371	320, 345, 374	
					400	164, 229	330, 375	310, 340, 380	
3a ($\overline{DP}$ = 11)	160	335	300, 345, 392, 419		325	162, 224	335, 375	322, 350, 392, 419	
					450	227	325, 377	392, 416	
					440 (20 min)	234			
3a ($\overline{DP}$ = 22)	160	330	288, 330, 377		420	240			
3b ($\overline{DP}$ = 1)				310					
3b ($\overline{DP}$ = 3)	170		335	320	250	165		333	315
3b ($\overline{DP}$ = 11)	165		320	*a*	275	237		341	311
3b ($\overline{DP}$ = 22)	152		343	*a*	275	268		350	342
3b[b] ($\overline{DP}$ = 3)	170			314					
3c ($\overline{DP}$ = 3)	151			254					
3d ($\overline{DP}$ = 3)	160		273	430	375	175		295, 375	450
3d ($\overline{DP}$ = 11)	154		375	500	420	244		359	500
					420 (5 min)	252			535
3d ($\overline{DP}$ = 22)	167		338	480	420	254			*a*
					400	252		407	*a*

[a] Unable to determine due to overlap with T_m or decomposition. [b] Chemically cyclized. [c] Carried out by heating in a DSC cap at a rate of 20 °C/min and then cooling upon reaching the indicated temperature, except in those cases held at the temperature as indicated in parentheses.

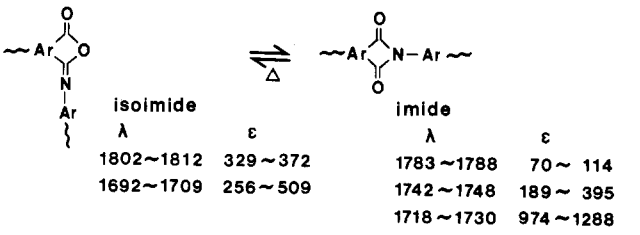
°C. The DSC's of **3b–d** also showed exotherms due to the thermal reaction of the end-capping groups at 430–500 °C for the biphenylene end-capped oligoimides **3d** and at 310–340 °C for the acetylene end-capped oligoimides **3b**. In some cases, the exotherms characteristic of the acetylene group (310–340 °C) and endotherms for T_m (320–343 °C) were so close that it was difficult to identify the exothermic maxima. The three acetylene end-capped imide oligomers **3b** (thermally cyclized, $\overline{DP}$ = 3), **3b** (chemically cyclized, $\overline{DP}$ = 3), and **3c** (3-ethynyl end capped, $\overline{DP}$ = 3), showed basically the same DSC pattern, although **3c** had a much lower temperature of exothermic maximum, 254 °C. Star imide oligomers had T_g's near 153–163 °C and T_m's between 270 and 350 °C, almost the same as the linear oligomers. The exotherm observed for the acetylene groups was 314–350 °C and for the biphenylene groups 422–450 °C (Table III).

When phenyl end-capped imide oligomers were heated in a DSC cap to 400–450 °C and then quenched, the T_g increased 60–80 °C and the exotherm due to crystallization (T_c) became more apparent (at 330 and 371 °C for $\overline{DP}$ = 3 and at 325 and 377 °C for $\overline{DP}$ = 11). When these oligomers were heated at high temperatures for longer times, both T_c and T_m disappeared and only the endotherm due to T_g appeared at 236 °C for $\overline{DP}$ = 11 and 240 °C for $\overline{DP}$ = 22. When linear and star acetylene and biphenylene end-capped oligoimides were annealed by heating to a temperature below the onset of the exotherm, an increase in the T_g was observed, while the T_m remained nearly the same. During annealing, a very small amount of amic acid undetectable by IR could be present and undergoing dehydration to the imide or a small amount of isoimide could be rearranging to imide, thereby resulting in an increased T_g as a result of different amorphous states. Imide and isoimide structures reportedly can be assigned in the IR spectrum. Although both absorb in the carbonyl region, the value of the molecular extinction coefficient, E, of the longest wavelength band is on the order of 200–400 for isoimide and 850–1300 for imides.[12] The difference is so large that it enables assignment of structure. In the present case, the absorption at 1720–1730 cm^{-1} was much larger than the absorption at 1770–1790 cm^{-1}, which strongly suggests that almost all units were present as the imide, although the presence of a small amount of isoimide cannot be dismissed.

Table III
Thermal Transitions of Star Prepolymers by DSC

prepolymer	T_g, °C	T_m, °C	$T_{exo,max}$, °C
7a ($\overline{DP}$ = 1)	153	333, 359	
7a ($\overline{DP}$ = 3)	147	328	
7a ($\overline{DP}$ = 11)	165	286	
7b ($\overline{DP}$ = 1)	156		314
7b ($\overline{DP}$ = 3)	159	307	350
7b ($\overline{DP}$ = 11)	162	272	340
7c ($\overline{DP}$ = 1)	156	351	422
7c ($\overline{DP}$ = 1)[a]	233	348	422
7c ($\overline{DP}$ = 3)	155	304	438
7c ($\overline{DP}$ = 3)[a]	242	357	455
7c ($\overline{DP}$ = 11)	163	351	450
7c ($\overline{DP}$ = 11)[b]	258	364	450

[a] Annealed in a DSC cap at 350 °C for 20 min. [b] Annealed in a DSC cap at 350 °C for 30 min.



Films of the imide oligomers were prepared by casting NMP solutions of the amic acid on a glass plate and then heating in a vacuum oven at 118 °C overnight. The quality of the film improved as the degree of polymerization increased. For the linear prepolymers (**3**), those of $\overline{DP}$ = 3 and 11 were too brittle and only those of $\overline{DP}$ = 22 were good enough for modulus measurements. For the star prepolymers (**7**), cast films that had an average degree of polymerization of 11 for each arm of the star were strong

Table IV
Properties of Prepolymer Cast Films by Rheovibron

prepolymer	T_g, °C	$10^{-10}E'_{25\,°C}$, dyn/cm^2	$10^{-7}E'_{lowest}$,[c] dyn/cm^2
3a ($\overline{DP}$ = 22)	153	2.4	2.1 (368 °C)
3a ($\overline{DP}$ = 22)[a]	234	2.3	2.2 (373 °C)
7a ($\overline{DP}$ = 11)	153	2.4	3.2 (313 °C)
7a ($\overline{DP}$ = 11)[b]	232	2.2	
7b ($\overline{DP}$ = 11)	146	3.1	5.7 (316 °C)
7c ($\overline{DP}$ = 11)	138	2.1	3.6 (343 °C)
7c ($\overline{DP}$ = 11)[b]	239	3.0	6.5 (344 °C)

[a] Annealed by heating in a DSC cap to 420 °C at 10 °C/min. [b] Annealed at 350 °C for 30 min. [c] This is the lowest storage module at the temperature indicated.

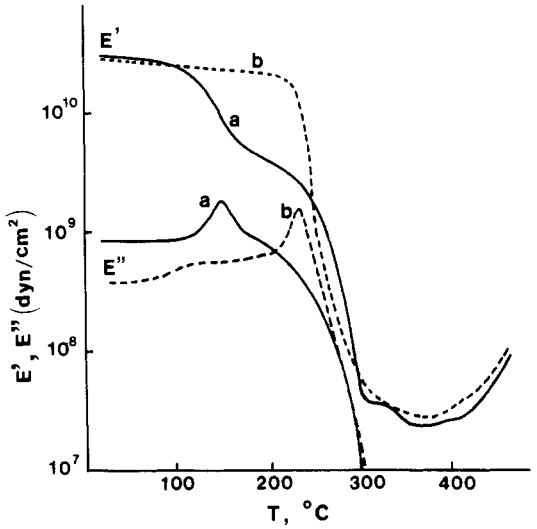


Figure 1. Young's modulus as a function of temperature for **3a** ($\overline{DP}$ = 22): (a) unannealed, (b) annealed at 420 °C.

enough for Rheovibron measurement; cast films of prepolymers having $\overline{DP}$ = 1 and 3 for each arm were too brittle. The thermomechanical properties of a cast film of **3a** ($\overline{DP}$ = 22) also was examined by Rheovibron (Table IV). The T_g obtained from Rheovibron for **3a** as the temperature at E''_{max} was 153 °C, which was in good agreement with T_g from DSC (160 °C as shown in Table II). When the cast film was annealed by heating to 420 °C (10 °C/min) and quenched in a DSC cap, T_g (E''_{max}) increased to 234 °C, in agreement with the T_g (240 °C) obtained from the DSC after annealing (Table II). The mechanical properties decrease rapidly above the T_g (Figure 1). The moduli vs. temperature for cast films of the star prepolymers (Table IV) also indicated that these uncured prepolymers show the loss of mechanical properties near 150 °C. When the cast films of **7c** ($\overline{DP}$ = 11) were annealed at 350 °C for 30 min, T_g increased to 239 °C (ΔT = 101 °C).

Attempts to make uncured films by casting the imide oligomers were hindered by the poor solubility of the imidized oligomers. Melt pressing of **3d** ($\overline{DP}$ = 11) without catalyst under the following conditions did not produce good films due to the poor melt-flow characteristics: T = 340 °C, P = 5000 psi, t = 15 min and T = 350 °C, P = 10 000 psi, t = 50 min.

The thermal gravimetric analyses of the prepolymers were measured under nitrogen or under air at a program rate of 5 °C/min (Table V). These prepolymers were thermally stable enough to keep their weight loss to about 5% at 500 °C. In air, these prepolymers begin to lose

Table V
TGA of Prepolymers

	temp (°C) of % wt loss (air)		temp (°C) of % wt loss (nitrogen)	
prepolymer	5%	20%	5%	20%
3a ($\overline{DP}$ = 3)	422	498		
3a ($\overline{DP}$ = 11)	496	570	515	575
3a ($\overline{DP}$ = 22)	514	560	520	578
3b ($\overline{DP}$ = 3)[a]	497	565	510	582
3b ($\overline{DP}$ = 11)	506	554	534	590
3b ($\overline{DP}$ = 22)	518	557	537	586
3c ($\overline{DP}$ = 3)	490	565	518	584
3d ($\overline{DP}$ = 3)	498	566	535	595
3d ($\overline{DP}$ = 11)	495	559	515	572
3d ($\overline{DP}$ = 22)	507	566		
7a ($\overline{DP}$ = 1)	412	471	420	501
7a ($\overline{DP}$ = 3)	437	506	465	562
7a ($\overline{DP}$ = 11)	490	542	543	590
7b ($\overline{DP}$ = 1)	443	498	497	579
7b ($\overline{DP}$ = 3)	469	526	526	598
7b ($\overline{DP}$ = 11)	513	554	557	613
7c ($\overline{DP}$ = 1)	508	557	560	613
7c ($\overline{DP}$ = 3)	519	560	546	602
7c ($\overline{DP}$ = 11)	506	556	550	603

[a] Chemically cyclized.

weight around 500 °C and lose almost all their weight (>95%) at 650 °C. Under nitrogen, these polymers were more stable and began to lose weight 10–20 °C higher. The tendency for prepolymers of higher $\overline{DP}$ to exhibit better thermal stability than those of lower $\overline{DP}$ was observed. There also was a tendency for the biphenylene end-capped prepolymers to be the most thermally stable, followed by the acetylene end-capped prepolymers, and then phenyl end-capped prepolymers.

Prepolymer Processing and Properties of the Cured Polymers. The prepolymers having acetylene and/or biphenylene end groups, **3b** ($\overline{DP}$ = 3, 11, 22), **3d** ($\overline{DP}$ = 3, 11, 22), **7b** ($\overline{DP}$ = 1, 3, 11), and **7c** ($\overline{DP}$ = 1, 3, 11), were melt processed with $Ni(PPh_3)_2(CO)_2$ catalyst. For the linear prepolymers, 20 mol % of Ni catalyst based on the incorporated biphenylene or acetylene was used for $\overline{DP}$ = 11 and $\overline{DP}$ = 22 (8.4 wt % for $\overline{DP}$ = 11 and 4.5 wt % for $\overline{DP}$ = 22) and 8 mol % for $\overline{DP}$ = 3 (10 wt %). For the star prepolymers, 10 mol % of Ni was used for $\overline{DP}$ = 1 (12 wt % for **7b** and 11 wt % for **7c**), 20 mol % (12.5 wt %) of Ni for $\overline{DP}$ = 3, and 20 mol % (4.3 wt %) of Ni for $\overline{DP}$ = 11. Curing conditions were as follows. For the linear prepolymers, T = 325 °C, P = 5000 psi, t = 20 min for $\overline{DP}$ = 3; T = 350 °C, P = 5000 psi, t = 60 min for $\overline{DP}$ = 11 and 22. For the star prepolymers, T = 350 °C, P = 5000 psi, t = 30 min for $\overline{DP}$ = 1; t = 90 min for $\overline{DP}$ = 3 and 11. The melt-pressed films were dark and opaque, but tough.

The thermal properties of the cured films were examined by DSC and by Rheovibron (Table VI). The DSC of the films show that all the acetylene groups were consumed and almost all the biphenylene reacted during melt processing, with the exception of **7c** ($\overline{DP}$ = 1), in which case a small exotherm at 425 °C was observed. By melt processing, the T_g increased to 223–326 °C. Some of the melt-processed films also had an endotherm due to T_m. Young's modulus measured as a function of temperature showed that the cured films maintained their mechanical

Table VI
Properties of Films Melt Processed with Catalyst

prepolymer	DSC T_g, °C	DSC T_m, °C	Rheovibron E''_{max}, °C	Rheovibron $10^{-10}E'_{25\,°C}$, dyn/cm²	Rheovibron E'_{lowest}, dyn/cm²
3b ($\overline{DP}$ = 1)[a]	233				
3b ($\overline{DP}$ = 3)	245	370	270	2.7	1.8×10^9 (365 °C)
3b ($\overline{DP}$ = 11)	240	370	266, 295	2.8	3.4×10^8 (373 °C)
3b ($\overline{DP}$ = 11)[a]	238	387	293	2.8	1.3×10^8 (383 °C)
3b ($\overline{DP}$ = 22)	263	384	272	2.7	2.1×10^8 (388 °C)
3b ($\overline{DP}$ = 3)[b]	236	380	275	2.5	2.1×10^9 (358 °C)
3c ($\overline{DP}$ = 3)	244	340	246	2.9	4.8×10^8 (357 °C)
3d ($\overline{DP}$ = 3)	244	344	258	2.8	1.0×10^8 (340 °C)
3d ($\overline{DP}$ = 11)	248	376	245	1.8	1.1×10^8 (370 °C)
3d ($\overline{DP}$ = 22)	251	370	254	2.6	1.0×10^8 (369 °C)
7b ($\overline{DP}$ = 1)	326		326	2.2	3.0×10^9 (380 °C)
7b ($\overline{DP}$ = 3)	253		280	2.5	9.5×10^8 (371 °C)
7b ($\overline{DP}$ = 11)	275		261	3.0	2.4×10^8 (360 °C)
7c ($\overline{DP}$ = 1)	253	370	248	2.3	3.0×10^8 (368 °C)
7c ($\overline{DP}$ = 3)	223	335	220	3.1	1.4×10^8 (350 °C)
7c ($\overline{DP}$ = 11)	262	342	261	2.6	1.4×10^8 (363 °C)

[a] Without Ni. [b] Chemically cyclized.

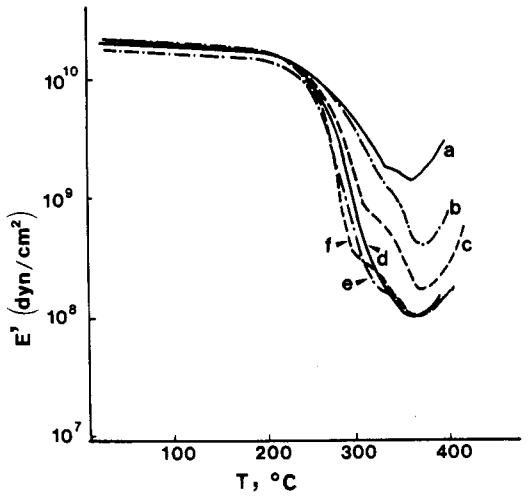


Figure 2. Young's modulus of melt-processed polyimides as a function of temperature: (a) **3b** ($\overline{DP}$ = 3); (b) **3b** ($\overline{DP}$ = 11); (c) **3b** ($\overline{DP}$ = 22); (d) **3d** ($\overline{DP}$ = 3); (e) **3d** ($\overline{DP}$ = 11); (f) **3d** ($\overline{DP}$ = 22).

properties above T_g. The polymers of lower $\overline{DP}$ had higher T_g's and better mechanical properties, especially in the case of acetylene end-capped star series. In the case of linear acetylene end-capped polyimides and the star biphenylene end-capped polymers, those of lower $\overline{DP}$ also showed better mechanical properties above T_g. The thermal properties of these films from the acetylene end-capped polyimides were better than those of the biphenylene end-capped polyimides and the order of the thermomechanical strength above T_g was as follows (Figure 2): **3b** ($\overline{DP}$ = 3) > **3b** ($\overline{DP}$ = 11) > **3b** ($\overline{DP}$ = 22) > **3d** ($\overline{DP}$ = 3) ~ **3d** ($\overline{DP}$ = 11) ~ **3d** ($\overline{DP}$ = 22); **7b** ($\overline{DP}$ = 1) > **7b** ($\overline{DP}$ = 3) > **7c** ($\overline{DP}$ = 1) > **7b** ($\overline{DP}$ = 11) > **7c** ($\overline{DP}$ = 3) ~ **7c** ($\overline{DP}$ = 11). Comparison of the lowest value of E' for melt-processed films of star and linear prepolymers showed that star polyimides had better thermomechanical property than the linear polyimides (Figure 3, thermomechanical strength vs. $\bar{M}_n$ of the prepolymer). Thus a highly effective network structure was achieved in the star polyimides. The prepolymers of lower $\overline{DP}$, having a higher density of end groups than those of higher $\overline{DP}$, made cross-linking

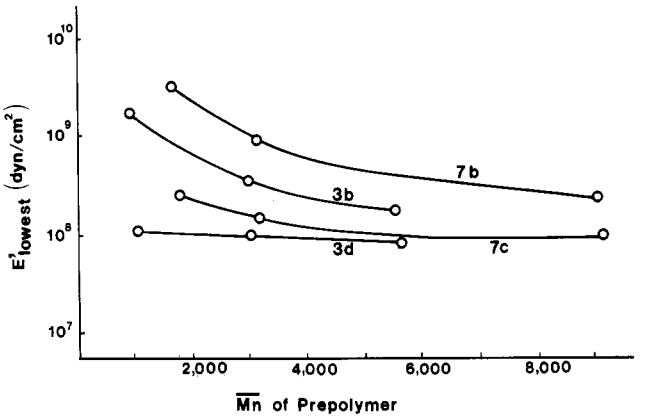


Figure 3. Comparison of E'_{lowest} vs. $\bar{M}_n$ of prepolymer.

more effective, resulting in better thermomechanical properties. The higher mechanical strength of the acetylene end-capped over the biphenylene end-capped polyimides also was attributable to the better cross-linking ability of the acetylenic groups. One biphenylene end group can react with another end group to form a linear polymer by a chain-extension reaction,[7,13] but an acetylene end group can react with two other end groups to form a true cross-link.[14]

Prepolymer **3b** ($\overline{DP}$ = 1) also was melt pressed, but very brittle film was obtained, which hindered the determination of its modulus. Prepolymers **3b** ($\overline{DP}$ = 3) that had been thermally and chemically cyclized showed about the same thermal properties, suggesting that the 10% of the acetyl groups present in the thermally cyclized polymer had little effect on the thermal properties of the cured resin. Prepolymer **3c** ($\overline{DP}$ = 3) had no better thermal properties than its para isomeric analogues.

The reactions of biphenylene end groups occurred at a rather high temperature as shown from the DSC, and rhodium or nickel catalysts were used to lower the reaction temperature. The effect of the $Ni(CO)_2(PPh_3)_2$ catalyst, as determined by DSC for biphenylene and acetylene end-capped polyimides, showed that small amounts of nickel catalyst (4.5 wt % for **3d** ($\overline{DP}$ = 22) and 8.7 wt % for **3b** ($\overline{DP}$ = 11)) plasticized these polymers very little, the difference in T_g with and without nickel being negli-

Table VII
TGA's of Melt-Processed Films

prepolymer	Ni	temp (°C) of % wt loss (air) 5%	20%	temp (°C) of % wt loss (N_2) 5%	20%
3a ($\overline{DP}$ = 3)[a]	W	417	508	430	545
3a ($\overline{DP}$ = 11)	W	438	512	465	554
3a ($\overline{DP}$ = 22)	W	500	568	520	587
3c ($\overline{DP}$ = 3)	W			425	558
3d ($\overline{DP}$ = 3)	W	394	533	405	566
3d ($\overline{DP}$ = 11)	W	444	492	484	576
3d ($\overline{DP}$ = 22)	W	482	550	485	579
3b/3d ($\overline{DP}$ = 11)	W	453	545	445	573
3b/3d ($\overline{DP}$ = 22)	W	490	562	515	586
7b ($\overline{DP}$ = 1)	W	450	513	460	571
7b ($\overline{DP}$ = 3)	W	480	545	485	587
7b ($\overline{DP}$ = 11)	W	507	558	538	600
7c ($\overline{DP}$ = 1)	W	457	544	481	594
7c ($\overline{DP}$ = 3)	W	518	557	504	589
7c ($\overline{DP}$ = 11)	W	503	560	531	595
7b/7c ($\overline{DP}$ = 1)	W	472	545	445	571
7b/7c ($\overline{DP}$ = 1)	W/O	484	535	511	578
7b/7c ($\overline{DP}$ = 3)	W	473	555	483	581
7b/7c ($\overline{DP}$ = 3)	W/O	497	544	519	585
7b/7c ($\overline{DP}$ = 11)	W	508	552	527	589
7b/7c ($\overline{DP}$ = 11)	W/O	511	556	534	593

[a] Chemically cyclized.

gible, while the temperature of the exothermic maximum was lowered in some cases. The formation of a good film from **3d** ($\overline{DP}$ = 11), for example, could be obtained with the nickel catalyst, while a film could not be made without the nickel catalyst.

The effect of the nickel catalyst on the cross-linking was examined for **3b** ($\overline{DP}$ = 11) by melt pressing it with and without the catalyst. The mechanical strength of the film melt pressed with the catalyst was slightly better than that melt pressed without catalyst (Table VI). It is possible that the nickel catalyst is more effective in cross-linking via generation of benzene rings.

TGA analyses of the melt-processed film (Table VII) showed that films from prepolymers of lower $\overline{DP}$ were less thermally stable than those from higher $\overline{DP}$. The melt-processed films of lower $\overline{DP}$ were much more susceptible to lose weight than the corresponding prepolymers, while, for the films of higher $\overline{DP}$, there was little difference between melt-processed films and their corresponding prepolymers, which might indicate the formation of thermally unstable cross-links. The prepolymers of lower $\overline{DP}$ would contain more end groups than the prepolymers of higher $\overline{DP}$ and therefore result in many more thermally unstable cross-links, which would accelerate degradation.

As a result of the generation of tetrabenzocyclooctatetraene from the biphenylene end-capped polyimides, and a chain extension rather than a true cross-linking, the thermooxidative stability of these resins were, in some cases, not as high as expected. The two most probable sources of degradation are unreacted biphenylene end caps and tetrabenzocyclooctatetraene, the product of the biphenylene chain extension reaction. Acetylene end-capped polyimides, on the other hand, form cross-linked resins by partial cyclotrimerization of three end groups to afford benzene links. The efficiency of the reaction, however, is very low, and the ratio of benzene ring formation, estimated by solid-state ^{13}C CP/MAS NMR,[15] is as low as 30%. Vinyl and other functionalities are generated, leading to points of degradation. For the benzene formation, the assembly of three acetylene groups are necessary, and this becomes even more difficult as the cross-linking reaction proceeds and the mobility of the neat resins diminishes. Biphenylenes react with acetylenes to give phenanthrenes,[6b] and it was expected that a phenanthrene structure, formed during curing of blend prepolymers, would give high thermooxidative stability to the blend resin. Blend curing of acetylene and biphenylene end-capped polyimides, therefore, was examined.

The acetylene and biphenylene end-capped polyimides of the same degree of polymerization were mixed so that they would contain the equivalent amount of acetylene and biphenylene end groups, and melt pressed with and without the nickel catalyst. The thermal properties of the melt-pressed film were examined by DSC and Rheovibron (Table VIII). After the films were cured, exotherms were hardly detectable by DSC, which indicated both the acetylene and biphenylene units were consumed. Both the T_g and T_m were almost the same as those for the individual cured acetylene and biphenylene end-capped polyimides. The thermomechanical properties showed that these films maintained their mechanical properties above T_g and that these blend polymers had mechanical properties intermediate between pure acetylene and biphenylene end-capped polyimides. This is reasonable, since the phenanthrene-forming reaction between two end groups is only a chain-extension and not a cross-linking reaction. The effect of the nickel catalyst was very small, as can be seen in the case of star blend. This is rather surprising, since biphenylene groups could be expected to remain unchanged without the nickel catalyst. The high pressure and longer cure times or the presence of acetylene groups might have induced the reaction of biphenylene groups.

The TGA of the blended films (Table VII) showed clearly that cured polymers from the lower $\overline{DP}$ pre-

Table VIII
Properties of Blend Melt-Processed Films

prepolymer	Ni	DSC T_g, °C	DSC T_m, °C	Rheovibron E''_{max}, °C	Rheovibron $10^{-10}E'_{25\,°C}$, dyn/cm²	Rheovibron E'_{lowest}, dyn/cm²
3b/3d ($\overline{DP}$ = 3)	W	237	348	248	2.2	2.5×10^8 (352 °C)
3b/3d ($\overline{DP}$ = 11)	W	238	385	259	2.1	6.5×10^8 (384 °C)
3b/3d ($\overline{DP}$ = 22)	W	260	375	263	2.8	1.9×10^8 (378 °C)
7b/7c ($\overline{DP}$ = 1)	W	230		297	2.3	2.9×10^9 (415 °C)
7b/7c ($\overline{DP}$ = 1)	W/O	235	355	298	3.3	2.7×10^9 (396 °C)
7b/7c ($\overline{DP}$ = 3)	W	242		273	2.6	4.1×10^8 (364 °C)
7b/7c ($\overline{DP}$ = 3)	W/O	260		283	2.7	4.3×10^8 (367 °C)
7b/7c ($\overline{DP}$ = 11)	W	282		263	2.3	1.9×10^8 (354 °C)
7b/7c ($\overline{DP}$ = 11)	W/O	275	380	268	3.1	2.1×10^8 (377 °C)

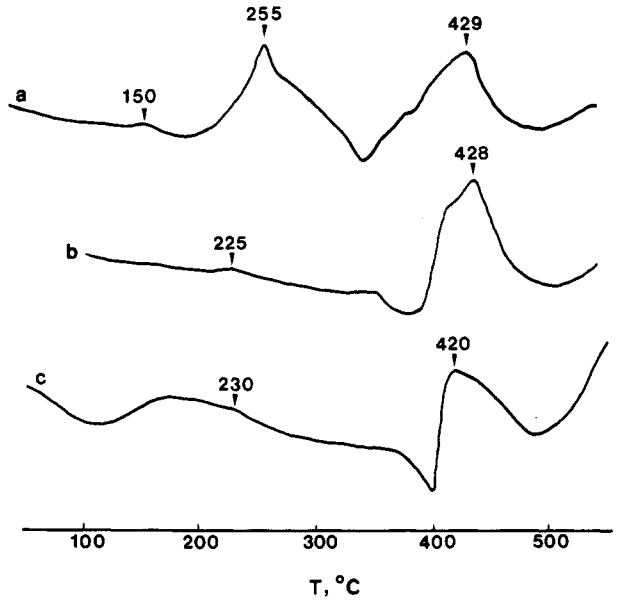


Figure 4. DSC of the blend prepolymers. **3c** ($\overline{DP}$ = 3)/**3d** ($\overline{DP}$ = 3): (a) uncured pellet of powder mixture; (b) cured in a DSC cap at 350 °C for 30 min; (c) melt pressed at 350 °C/5000 psi for 60 min.

Table IX
Thermal Analysis of Blended Prepolymers

prepolymer	Ni	DSC T_g, °C	DSC $T_{exo,max}$, °C
7b/**7c** ($\overline{DP}$ = 1)	W		330, 430
7b/**7c** ($\overline{DP}$ = 1)[a]	W	240	425
7b/**7c** ($\overline{DP}$ = 1)	W/O	158	325, 422
7b/**7c** ($\overline{DP}$ = 1)[a]	W/O	232	418
7b/**7c** ($\overline{DP}$ = 3)	W	152	348, 428
7b/**7c** ($\overline{DP}$ = 3)[a]	W	237	
7b/**7c** ($\overline{DP}$ = 3)	W/O	145	350, 450
7b/**7c** ($\overline{DP}$ = 3)[a]	W/O	234	455

[a] Cured in a DSC cap at 350 °C for 30 min.

polymers were less thermally stable. Cured films from blends also were thermally stable, but there was little difference between cured films of the blends and individual cured films of the same $\overline{DP}$. Films melt processed without nickel were more thermally stable than films melt processed with nickel.

How the acetylene and biphenylene end-groups react during melt processing was examined by observing the DSC exotherms. Linear oligoimides, **3c** ($\overline{DP}$ = 3) and **3d** ($\overline{DP}$ = 3), were mixed; the two exotherms (Figure 4) show that each group reacts separately. When the films were cured at 350 °C for 30 min in a DSC cap, only the acetylene groups reacted, the biphenylene groups remaining almost unchanged. The same examination for a star blend (Table IX), showed that the preferential reaction between acetylene groups occurred first with or without a nickel catalyst and almost all of the biphenylene groups remained unchanged. In the reaction of end-capped prepolymers, the mobility of the end groups becomes very low as the cross-linking reaction proceeds, thereby hindering the reaction and possibly leading to the formation of unstable products. Because melt-processed films were insoluble, ^{13}C/MAS solid-state NMR study was carried out with blend-cured films and a blend of uncured powder (**3b** ($\overline{DP}$ = 3)/**3d** ($\overline{DP}$ = 3)). The loss of acetylene groups (at about 80 ppm) and biphenylene groups (at 151 ppm) was observed by subtracting the uncured powder's spectrum from the cured film's spectrum. However, the signal overlapping the vinyl carbons and aromatic carbons prevented the evaluation of the kind of reaction occurring during the cure (Figure 5).

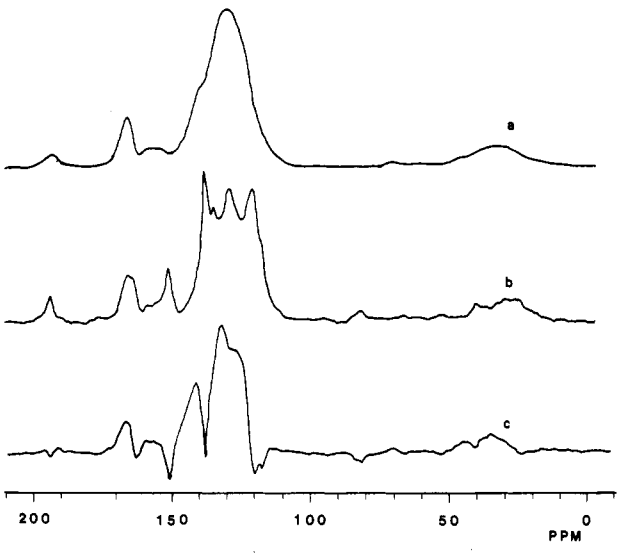


Figure 5. ^{13}C CP/MAS solid-state NMR of blend (**3b** ($\overline{DP}$ = 3)/**3d** ($\overline{DP}$ = 3)): (a) cured film; (b) uncured powder; (c) difference (a)–(b).

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 and 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).

The ^{13}C NMR spectra of solid, insoluble polymer samples were obtained on a Nicolet NT-150 spectrometer at a carbon frequency of 37.735 MHz with a cross-polarization magic-angle spinning (CP/MAS) unit built by the Regional NMR Center. The decoupling field was 55 KHz, and the samples were spun at 100 rpm. The CP contact time was 1 ms, and the repetition time was 1 s. A total of 2K points was collected with a spectrum width of 20 kHz. Chemical shifts are relative to external tetramethylsilane, with hexamethylbenzene as a secondary standard (methyl signal at 17.35 ppm).

The purification of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (**1**)[9] and 4,4′-diaminodiphenyl ether (**2**)[9] and the preparation of 2-aminobiphenylene[9] were carried out by known procedures.

(Tributylstannyl)acetylene. To 15.2 g (0.165 mol) of lithium acetylide EDA (Columbia Organic Chemicals Co.) suspended in 300 mL of dry THF and cooled to 0 °C under Ar with stirring was added 48.8 g (0.150 mol, 40.7 ml) of tributyltin chloride, dropwise over 30 min, and the mixture was kept at 0 °C for 4 h. The mixture was warmed to room temperature and stirred for 12 h, 50 mL of water was added, and the mixture was suction filtered through a Celite pad. The THF was removed and the organics were extracted with ether. The ether solution was washed with water and brine and then dried over sodium sulfate. The product was obtained by vacuum distillation; bp 69–74 °C (0.03 mmHg) to yield 7.8 g (20%) of the acetylide. ^1H NMR ($CDCl_3$) δ 2.1 (s, 1 H, C≡CH), 0.7–1.7 (m, 27 H, Bu_3). A large amount (45%) of high boiling product, $Bu_3SnC{\equiv}CSnBu_3$, was obtained, bp 140–143 °C (0.03 mmHg). The low yield of the desired product

was attributed to the decomposed lithium acetylide (black instead of yellow). The yield was improved to 44% by using a large excess of lithium acetylide.

4-Ethynylaniline. To a solution of 3.06 g (14.0 mmol) of 4-iodoaniline (Aldrich) and 0.324 g (0.280 mmol) of tetrakis(triphenylphosphine)palladium[16] in 150 mL of dry THF under Ar was added 5.29 g (16.8 mmol) of (tributylstannyl)acetylene. The mixture was heated to 60 °C for 43 h. The THF was removed and 200 mL of ether was added. The mixture was washed with half-saturated potassium fluoride 3 times, and the precipitate formed was filtered with the aid of a Celite pad. The ether layer was washed with water and then dried over sodium sulfate. Crude 4-ethynylaniline, obtained by removing the ether, was purified by column chromatography on silica gel (1:1 benzene/hexane) followed by sublimation (50–60 °C at 0.05 mmHg) to give 1.10 g (67%) of product, mp 99–102 °C, (lit.[17] 104–105 °C). ^{1}H NMR ($CDCl_3$) δ 2.87 (s, 1 H, C≡CH), 3.63 (b, 2 H, NH_2), 6.3–7.2 (m, 4 H, aromatic).

4-Ethynylaniline. 4-Ethynylaniline also was made from (trimethylsilyl)acetylene as follows.[17] To a solution of 6.57 g (30.0 mmol) of 4-iodoaniline and 5.09 mL (3.54 g, 36.0 mmol) of (trimethylsilyl)acetylene in 120 mL of distilled triethylamine under Ar were added 0.420 g (0.600 mmol) of dichlorobis(triphenylphosphine)palladium[18] and 0.0300 g (0.300 mmol) of cuprous iodide and stirred at 40 °C for 4 h. The triethylamine was removed by a rotary evaporator and the residue was extracted into benzene. The benzene was removed under reduced pressure to give a black solid, which was dissolved in methanol and 30 mL of 1 N aqueous KOH was added. The mixture was stirred at 25 °C for 1 h. After removal of the methanol, the product was extracted with ether (100 mL × 3). The ether layer was dried over sodium sulfate. After the removal of ether, the residue was purified by chromatography on silica gel (1:1 benzene/hexane) to afford 2.11 g (60.0%) of a crude yellow solid. The crude product was further purified by sublimation (50–60 °C (0.05 mmHg)) to yield 1.93 g (54.9%): mp 101.5–103 °C (lit.[17] 104–105 °C); ^{1}H NMR ($CDCl_3$) δ 2.90 (s, 1 H, C≡CH), 3.55 (b, 2 H, NH_2), 6.3–7.1 (m, 4 H, aromatic).

3-Ethynylaniline.[19] To a solution of 0.186 g (0.161 mmol) of tetrakis(triphenylphosphine)palladium[16] in 150 mL of dry THF were added 3.06 g (14.0 mmol, 1.74 ml) of 3-iodoaniline and 5.29 g (16.8 mmol) of (tributylstannyl)acetylene. The mixture was heated to 60 °C and stirred for 42 h, after which time THF was removed and 150 mL of ether was added. The ether solution was washed with 100 mL of half-saturated potassium fluoride 4 times, washed with water and then with brine, and dried over sodium sulfate. The crude black oil, obtained after the removal of ether, was purified by column chromatography on silica gel (1:1 hexane/benzene) to give 1.28 g (78%) of a yellow oil. The oil was further purified by chromatography on silica gel to give 0.92 g (56%) of a light-yellow oil. ^{1}H NMR ($CDCl_3$) δ 2.93 (s, 1 H, C≡CH), 3.55 (b, 2 H, NH_2), 6.3–7.1 (m, 4 H, aromatic).

***N*-(4-Ethynylphenyl)phthalimide (Dehydrated in Toluene).** To a solution of 0.296 g (2.00 mmol) of phthalic anhydride in 2 mL of NMP at 75 °C under Ar was added dropwise 0.234 g (2.00 mmol) of 4-ethynylaniline in 0.6 mL of NMP. An additional 0.2 mL × 2 of NMP was used to transfer the 4-ethynylaniline completely. The reaction was continued for 1 h, after which time it was poured into toluene and heated to the reflux temperature for 15 h. The solution was poured into 130 mL of ethanol, but a precipitate did not form. The readily volatile solvents were removed under reduced pressure and the resulting yellow solution was poured into 200 mL of water. The precipitate formed was filtered and dried at 75 °C (0.05 mmHg) for 20 h to yield 0.303 g (61.3%) of product as a 89.2/10.8 mixture of *N*-(4-ethynylphenyl)phthalimide and *N*-(4-acetylphenyl)phthalimide, mp 152–154 °C [lit.[11] 164–165 °C for pure *N*-(4-ethynylphenyl)phthalimide]. IR (KBr) 3260 (C≡C-H), 2100 cm^{-1} (C≡C). ^{1}H NMR ($CDCl_3$) δ 3.13 (s, C≡CH), 2.65 (s, C(O)CH_3).

***N*-(4-Ethynylphenyl)phthalimide (Dehydrated in *N*-Methylpyrrolidone).** To a solution of 0.296 g (2.00 mmol) of phthalic anhydride in 2 mL of NMP under Ar at 75 °C was added dropwise 0.234 g (2.00 mmol) of 4-ethynylaniline in 0.6 mL of NMP. Any residual 4-ethynylaniline was washed in with 0.2 mL × 2 of NMP. The reaction was continued for 1 h at 75 °C and then the solution was heated up to 150 °C for 1 h. The cooled solution was poured into 200 mL of water. The precipitate was filtered and dried at 75 °C (0.05 mmHg) for 39 h to yield 0.399 g of product as a 52/48 mixture of *N*-(4-ethynylphenyl)phthalimide and *N*-(4-acetylphenyl)phthalimide, mp 165–180 °C. [lit.[11] 164–165 °C for *N*-(4-ethynylphenyl)phthalimide; lit.[11] 239–240.5 °C for *N*-(4-acetylphenyl)phthalimide.] IR (KBr) 3260 (C≡CH), 1680 and 1650 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$), δ 2.65 (s, C(O)CH_3), 3.13 (s, C≡CH).

Phenyl End-Capped Polyimide 3a ($\overline{DP}$ = 3). To 2 mL of distilled NMP was added 0.7025 g (2.180 mmol) of **1**, and the mixture was heated to 90 °C with mechanical stirring under Ar to effect solution. The solution was kept at 50 °C, and 0.2183 g (1.090 mmol) of **2** in 0.6 mL of NMP was added dropwise over 30 min. An additional 0.4 mL of NMP was used to ensure complete transfer of the monomer. The solution was heated at 50 °C for 30 min, at which time 0.244 g (2.62 mmol) of aniline was added dropwise. Heating was continued for 1 h. The yellow solution was added to 50 mL of stirred toluene, and the solution was heated to the reflux temperature in a Dean–Stark apparatus for 10 h. The toluene solution containing the precipitate was added to 150 mL of ethanol, and the mixture was stirred for 1 h and then suction filtered to give a yellow powder. The powder was dried at 110 °C (0.05 mmHg) for 40 h to afford 0.93 g (89%) of **3a** ($\overline{DP}$ = 3). IR (KBr) 1780 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{58}H_{30}N_4O_{11}$: C, 72.65; H, 3.15; N, 5.84. Found: C, 72.51; H, 3.25; N, 6.03.

Phenyl End-Capped Polyimide 3a ($\overline{DP}$ = 11). The above procedure was followed, except 1.1387 g (3.534 mmol) of **1**, 0.6007 g (3.000 mmol) of **2**, and 0.121 g (1.34 mmol) of aniline were used to yield 1.61 g (93%) of **3a** ($\overline{DP}$ = 11). IR (KBr) 1780 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{174}H_{86}N_{12}O_{35}$: C, 71.95; H, 2.98; N, 5.79. Found: C, 70.39; H, 3.28; N, 6.10.

Phenyl End-Capped Polyimide 3a ($\overline{DP}$ = 22). The above procedure was followed, except 1.0385 g (3.223 mmol) of **1**, 0.6007 g (3.000 mmol) of **2**, and 0.096 g (1.03 mmol) of aniline were used to yield 1.61 g (100%) of **3a** ($\overline{DP}$ = 22). IR (KBr) 1775 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{334}H_{163}N_{23}O_{68}$: C, 71.79; H, 2.94; N, 5.77. Found: C, 71.20; H, 3.22; N, 6.07.

Acetylene End-Capped Polyimide 3b ($\overline{DP}$ = 3). The above procedure was followed, except 0.7025 g (2.180 mmol) of **1**, 0.2183 g (1.090 mmol) of **2**, and 0.2809 g (2.398 mmol, 10% excess) of 4-ethynylaniline, as the end-cap, were used to yield 0.89 g (81%) of **3b** ($\overline{DP}$ = 3). IR (KBr) 1780 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{62}H_{30}N_4O_{11}$: C, 73.96; H, 3.00; N, 5.56. Found: C, 70.93; H, 3.29; N, 5.68.

Acetylene End-Capped Polyimide 3b ($\overline{DP}$ = 11). The above procedure was followed, except 1.0155 g (3.151 mmol) of **1**, 0.5357 g (2.675 mmol) of **2**, and 0.1393 g (1.191 mmol) of 4-ethynylaniline (12% excess) were used to yield 1.56 g (99%) of **3b** ($\overline{DP}$ = 11). IR (KBr) 1785 and 1725 cm^{-1} (C=O, imide). Anal. Calcd for $C_{178}H_{86}N_{12}O_{35}$: C, 72.41; H, 2.94; N, 5.69. Found: C, 70.50; H, 3.22; N, 6.07.

Acetylene End-Capped Polyimide 3b ($\overline{DP}$ = 22). The above procedure was followed, except 1.0385 g (3.223 mmol) of **1**, 0.6007 g (3.000 mmol) of **2**, and 0.0804 g (0.686 mmol) of 4-ethynylaniline (20% excess) were used to yield 1.63 g (99%) of **3b** ($\overline{DP}$ = 22). IR (KBr) 1770 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{338}H_{163}N_{23}O_{68}$: C, 72.03; H, 2.92; N, 5.72. Found: C, 69.94; H, 3.44; N, 6.39.

Chemically Cyclodehydrated Acetylene End-Capped Polyimide 3b ($\overline{DP}$ = 3, Chemically Cyclized). To a solution of 0.7025 g (2.180 mmol) of **1** in 2 mL of *N*-methylpyrrolidone at 75 °C under Ar was added dropwise 0.2183 g (1.090 mmol) of **2** in 0.6 mL of NMP. An additional 0.2 mL × 2 of NMP was used to transfer the monomer and the mixture was stirred for 30 min at 75 °C. A solution of 0.2809 g (2.398 mmol, 10% excess) of 4-ethynylaniline in 0.6 mL of NMP was added dropwise over 30 min and an additional 0.2 mL × 3 of NMP was used to rinse the end-capping agent. The solution was stirred for 1 h at 75 °C. The mixture was added dropwise to the boiling solution of acetic anhydride (30 mL)/pyridine (2 mL) and heated at the reflux temperature for 1 h. The cooled solution was poured into 350 mL of water and stirred for 30 min. The precipitate was filtered

and dried at 75 °C (0.05 mmHg) for 43 h to yield 1.08 g (98%) of **3b** ($\overline{DP}$ = 3). IR (KBr) 1780 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{62}H_{30}N_4O_{11}$: C, 73.96; H, 3.00; N, 5.56. Found: C, 72.97; H, 3.13; N, 5.49.

Acetylene End-Capped Polyimide 3c ($\overline{DP}$ = 3). The procedure for the preparation of **3b** ($\overline{DP}$ = 3) was followed, except a 10% excess of 3-ethynylaniline (0.2809 g, 2.398 mmol) was used as the end-capping agent to yield 0.90 g (82%) of **3c** ($\overline{DP}$ = 3). IR (KBr) 1780 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{62}H_{30}N_4O_{11}$: C, 73.96; H, 3.00; N, 5.56. Found: C, 71.24; H, 3.17; N, 5.70.

Acetylene End-Capped Polyimide 3b ($\overline{DP}$ = 1). To a solution of 0.7025 g (2.180 mmol) of 1 dissolved in 2 mL of NMP at 75 °C under Ar was added dropwise 0.5101 g (4.360 mmol) of 4-ethynylaniline in 0.6 mL of NMP and an additional 0.2 mL × 2 of NMP was used to transfer the end-capping agent completely. The reaction was continued for 1 h at 75 °C. The solution was added to 20 mL of vigorously stirred toluene, and the mixture was heated to reflux temperature for 14 h with a Dean–Stark apparatus. (A yellow precipitate formed after a few hours.) The precipitate was filtered and dried at 75 °C (0.05 mmHg) for 45 h to yield 0.874 g (78.5%) of **3b** ($\overline{DP}$ = 1). IR (KBr) 3260 (C≡CH), 2110 cm^{-1} (C≡C). Anal. Calcd for $C_{33}H_{16}N_2O_5$: C, 76.15; H, 3.10; N, 5.38. Found: C, 74.52; H, 3.39; N, 5.30.

Biphenylene End-Capped Polyimide 3d ($\overline{DP}$ = 3).[9] To 2 mL of distilled NMP was added 0.7025 g (2.180 mmol) of 1. The solution of 1 was effected by heating the mixture to 75 °C with mechanical stirring under an Ar atmosphere. The solution was kept at 50 °C, and 0.2183 g (1.090 mmol) of **2** in 0.6 mL of NMP was added dropwise over 30 min to the solution. An additional 0.4 mL of NMP was used to ensure complete transfer of the monomer. The solution was heated at 50 °C for 30 min, after which time 0.4010 g (2.398 mmol) of 2-aminobiphenylene[9] in 0.6 mL of NMP was added dropwise over 30 min. An additional 0.2 mL × 5 of NMP was used to rinse any residual 2-aminobiphenylene into the polymerization flask. Heating was continued for 1 h. The light brown solution was poured into 50 mL of vigorously stirred toluene, and the solution was heated to the reflux temperature in a Dean–Stark apparatus for 10 h (a precipitate appeared after 2 h). The mixture was poured into 130 mL of ethanol, stirred for 1 h, and suction filtered to give a fine, orange powder. The solid was dried at 110 °C (0.03 mmHg) for 40 h to afford 1.00 g (83%) of **3d** ($\overline{DP}$ = 3). IR (Nujol) 1770 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{70}H_{34}N_4O_{11}$: C, 75.95; H, 3.10; N, 5.06. Found: C, 73.20; H, 3.44; N, 5.29.

Biphenylene End-Capped Polyimide 3d ($\overline{DP}$ = 11). The above procedure was followed, except 1.1387 g (3.534 mmol) of 1, 0.6007 g (3.000 mmol) of **2**, and 0.2232 g (1.335 mmol) of 2-aminobiphenylene (12% excess) were used to yield 1.78 g (98%) of **3d** ($\overline{DP}$ = 11). IR (KBr) 1785 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{186}H_{90}N_{12}O_{35}$: C, 73.18; H, 2.97; N, 5.51. Found: C, 70.78; H, 3.35; N, 5.90.

Biphenylene End-Capped Polyimide 3d ($\overline{DP}$ = 22). The above procedure was followed, except 1.0385 g (3.223 mmol) of 1, 0.6007 g (3.000 mmol) of **2**, and 0.0938 g (0.561 mmol) of 2-aminobiphenylene were used to yield 1.53 g (88%) of **3d** ($\overline{DP}$ = 22). IR (Nujol) 1775 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{346}H_{167}N_{23}O_{68}$: C, 72.44; H, 2.94; N, 5.62. Found: C, 70.48; H, 3.26; N, 6.01.

1,3,5-Tris(4-nitrophenoxy)benzene. A mixture of 24.8 g (0.153 mol) of 1,3,5-trihydroxybenzene dihydrate, 64.9 g (48.8 mL, 0.460 mol) of 4-fluoronitrobenzene, 53.3 g (0.918 mol) of potassium fluoride and 500 mL of dimethyl sulfoxide was heated to reflux temperature for 30 min. The reaction mixture was allowed to cool to room temperature, and the precipitated solid was filtered, washed with 1.6 L of water, and allowed to dry to yield 44.5 g of a tan, flaky solid. Into the supernatant of the initial filtration was added 500 mL of water, and the solid was filtered, washed with 1 L of water, and allowed to dry to yield an additional 20.0 g of product. (Total crude yield was 64.5 g, 86%). The crude solid was recrystallized from ethyl acetate/charcoal to yield 40.0 g (54%) of an off-white solid product; mp 203.5–205.5 °C; ^1H NMR ($CDCl_3$) δ 8.26 (d, 2 H, J = 9.2 Hz), 7.14 (d, 2 H, J = 6.94 Hz), 6.67 (s, 1 H); IR (mull) 1610 (s, Ar), 1345 (s, C–NO_2), 1225 (s, C–O–C), 850 cm^{-1} (s, C–N); ^{13}C NMR ($CDCl_3$) δ 161.38, 158.12, 126.11, 118.38, 107.56, 95.55. Anal. Calcd for $C_{24}H_{15}N_3O_9$: C, 58.90; H, 3.09; N, 8.59. Found: C, 59.04; H, 3.20; N, 8.64.

1,3,5-Tris(4-aminophenoxy)benzene. A suspension of 40.0 g (81.7 mmol) of 1,3,5-tris(4-nitrophenoxy)benzene in 1.6 L of 50% dioxane/methanol was warmed to 65 °C, and a solution of 147.9 g (612.8 mmol) of sodium sulfide nonahydrate and 51.8 g (612.8 mmol) of sodium bicarbonate in 245 mL of water was added in three equal portions over 15 min. The addition caused the reaction mixture to turn deep red and a fine precipitate appeared. The reaction mixture was heated to reflux temperature overnight and allowed to sit at room temperature for a day. The mixture was diluted with 1.5 L of water and extracted with methylene chloride. The organic phases were collected, combined, washed with water and brine, and dried over magnesium sulfate. Removal of the solvent under reduced pressure yielded a golden viscous oil, which was converted immediately to the hydrochloride salt by dissolving the oil in 500 mL of methylene chloride and treated with hydrogen chloride (gas) until a pink precipitate formed. The solid was filtered and dried at 50 °C under reduced pressure to yield 22.6 g (54%) of pale yellow solid. Treatment of the solid with 10% sodium hydroxide gave the free amine, which was filtered and dried under reduced pressure: mp 88–89 °C; IR (KBr) 3380 and 3320 (m, NH_2), 1620 and 1610 (Ar), 1229 (C–O), 835 cm^{-1} (C–N); ^1H NMR ($CDCl_3$) δ 6.83 (d, 2 H, aromatic), 6.64 (d, 2 H, aromatic), 6.15 (s, 1 H, aromatic), 3.60 (b, 2 H, NH_2); ^{13}C NMR ($CDCl_3$) δ 160.8, 148.1, 142.9, 121.2, 116.2, 100.3. Anal. Calcd for $C_{24}H_{21}N_3O_3$: C, 72.16; H, 5.30; N, 10.52. Found: C, 71.95; H, 5.25; N, 10.55.

Phenyl End-Capped Star Polyimide 7a ($\overline{DP}$ = 1). To 2 mL of NMP was dissolved 0.5800 g (1.800 mmol) of 1 by heating the mixture to 90 °C under Ar with mechanical stirring. The solution was kept at 50 °C and 0.2397 g (0.600 mmol) of **5** in 0.6 mL of NMP was added dropwise. The solution was heated for 1 h, after which time 0.2514 g (2.700 mmol) of aniline was added and the mixture was stirred for 1 h. The yellow solution was added to 50 mL of toluene and heated to reflux temperature in a Dean–Stark apparatus for 10 h. The precipitate formed was filtered and dried at 110 °C (0.05 mmHg) for 40 h to yield 0.816 g (88.5%) of **7a** ($\overline{DP}$ = 1). IR (KBr) 1785 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{93}H_{48}N_6O_{18}$: C, 72.66; H, 3.15; N, 5.47. Found: C, 71.06; H, 3.33; N, 5.74.

Acetylene End-Capped Star Polyimide 7b ($\overline{DP}$ = 1). The above procedure was followed, except 0.4833 g (1.500 mmol) of 1, 0.1997 g (0.500 mmol) of **5**, and 0.2109 g (1.800 mmol) of 4-ethynylaniline in a NMP solution were used to yield 0.734 g (91.2%) of **7b** ($\overline{DP}$ = 1). IR (KBr) 1785 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{99}H_{48}N_6O_{18}$: C, 73.88; H, 3.01; N, 5.22. Found: C, 71.46; H, 3.35; N, 5.32.

Biphenylene End-Capped Star Polyimide 7c ($\overline{DP}$ = 1). The above procedure was followed, except 0.4833 g (1.500 mmol) of 1, 0.1997 g (0.500 mmol) of **5**, and 0.2759 g (1.650 mmol) of 2-aminobiphenylene were used to yield 0.521 g (59.2%) of **7c** ($\overline{DP}$ = 1). IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{111}H_{54}N_6O_{18}$: C, 75.77; H, 3.09; N, 4.78. Found: C, 74.08; H, 3.25; N, 4.79.

Phenyl End-Capped Star Polyimide 7a ($\overline{DP}$ = 3). To 2 mL of NMP was dissolved 0.5800 g (1.800 mmol) of 1 by heating the mixture to 90 °C under Ar with mechanical stirring. The solution was kept at 50 °C and 0.1802 g (0.900 mmol) of **2** in 0.6 mL of NMP was added dropwise. The solution was heated at 50 °C for 30 min, after which time 0.1198 g (0.300 mmol) of **5** in NMP was added dropwise and the mixture was stirred for 30 min. Then 0.1257 g (1.350 mmol) of aniline was added and the mixture was stirred for 1 h. The solution was added to 50 mL of toluene and heated in a Dean–Stark apparatus for 10 h. The precipitate was filtered and dried at 110 °C (0.05 mmHg) for 40 h to yield 0.879 g (97.8%) of **7a** ($\overline{DP}$ = 3). IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{180}H_{90}N_{12}O_{36}$: C, 72.14; H, 3.03; N, 5.61. Found: C, 70.74; H, 3.25; N, 6.06.

Phenyl End-Capped Star Polyimide 7a ($\overline{DP}$ = 11). The above procedure was followed, except 0.5694 g (1.767 mmol) of 1, 0.3004 g (1.500 mmol) of **2**, 0.0399 g (0.100 mmol) of **5**, and 0.042 g (0.45 mmol) of aniline were used to yield 0.890 g (100%) of **7a**

($\overline{DP}$ = 11). IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{528}H_{258}N_{36}O_{108}$: C, 71.79; H, 2.94; N, 5.71. Found: C, 69.72; H, 3.16; N, 5.66.

Acetylene End-Capped Star Polyimide 7b ($\overline{DP}$ = 3). The above procedure was followed, except 0.5800 g (1.800 mmol) of **1**, 0.1802 g (0.900 mmol) of **2**, 0.1198 g (0.300 mmol) of **5**, and 0.1265 g (1.080 mmol) of 4-ethynylaniline were used to yield 0.900 g (97.8%) of **7b** ($\overline{DP}$ = 3). IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{186}H_{90}N_{12}O_{36}$: C, 72.80; H, 2.96; N, 5.48. Found: C, 69.29; H, 3.18; N, 5.53.

Acetylene End-Capped Star Polyimide 7b ($\overline{DP}$ = 11). The above procedure was followed, except 0.5694 g (1.767 mmol) of **1**, 0.3004 g (1.500 mmol) of **2**, 0.0399 g (0.100 mmol) of **5**, and 0.0439 g (0.375 mmol) of 4-ethynylaniline were used to yield 0.888 g (99.7%) of **7b** ($\overline{DP}$ = 11). IR (KBr) 1780 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{534}H_{258}N_{36}O_{108}$: C, 72.02; H, 2.92; N, 5.66. Found: C, 70.22; H, 3.15; N, 5.80.

Biphenylene End-Capped Star Polyimide 7c ($\overline{DP}$ = 3). The above procedure was followed, except 0.5800 g (1.800 mmol) of **1**, 0.1802 g (0.900 mmol) of **2**, 0.1198 g (0.300 mmol) of **5**, and 0.1655 g (0.990 mmol) of 2-aminobiphenylene were used to yield 0.873 g (90.4%) of **7c** ($\overline{DP}$ = 3). IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{198}H_{96}N_{12}O_{36}$: C, 73.88; H, 3.01; N, 5.22. Found: C, 72.90; H, 3.16; N, 5.18.

Biphenylene End-Capped Star Polyimide 7c ($\overline{DP}$ = 11). The above procedure was followed, except 0.5694 g (1.767 mmol) of **1**, 0.3004 g (1.500 mmol) of **2**, 0.0399 g (0.100 mmol) of **5**, and 0.0627 g (0.375 mmol) of 2-aminobiphenylene were used to yield 0.871 g (96.2%) of **7c** ($\overline{DP}$ = 11). IR (KBr) 1775 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{546}H_{264}N_{36}O_{108}$: C, 72.41; H, 2.94; N, 5.57. Found: C, 70.30; H, 3.10; N, 5.65.

Preparation of Prepolymer Films by Casting onto a Glass Plate. The amic acid solution in NMP was cast on a glass plate and heated in a vacuum oven at 118 °C for 12 h. If necessary, the glass plate with film was dipped in cold water for a day to remove the film.

Melt Processing of the Prepolymer (Neat Resin Processing). Appropriate amounts of dicarbonylbis(triphenylphosphine)nickel (Aldrich) was added to 200 mg of the prepolymer swelled in 50 mL of benzene under Ar. The mixture was stirred for 1 h. 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 treated in this way 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. 3a, 102920-44-5; **3b**, 102920-45-6; **3c**, 102920-46-7; **3d**, 87829-09-2; **5**, 102852-92-6; **5** (nitro derivative), 102852-91-5; **8**, 73819-75-7; **9**, 24980-39-0; $Bu_3SnC{\equiv}CH$, 994-89-8; $LiC{\equiv}CH$, 1111-64-4; Bu_3SnCl, 1461-22-9; $4\text{-}IC_6H_4NH_2$, 540-37-4; $4\text{-}HC{\equiv}CC_6H_4NH_2$, 14235-81-5; $(CH_3)_3SiC{\equiv}CH$, 1066-54-2; $3\text{-}IC_6H_4NH_2$, 626-01-7; $3\text{-}HC{\equiv}CC_6H_4NH_2$, 54060-30-9.

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