High-temperature thermoset polyimides containing disubstituted acetylene end groups

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High-temperature thermoset polyimide resins were prepared using *p*-phenylenediamine and a 1:3 mixture of 1,1,1,3,3,3-hexafluoro-2,2-bis(3,4-dicarboxyphenyl)propane dianhydride (6FDA) and 3,3′,4,4′-tetracarboxybiphenyl dianhydride (BPDA) for the imide backbone, and diarylacetylene derivatives as reactive capping agents. The thermo-oxidative stability at 370°C of the cured resins was evaluated in comparison with control samples based on several known reactive capping agents. The polyimide resin end-capped with 4-(phenylethynyl)phthalic anhydride exhibited the best thermo-oxidative stability.

(Keywords: thermoset polyimide; disubstituted acetylene; thermal stability)

INTRODUCTION

The objective of this study is to determine the reactivity and performance of disubstituted acetylenes used as curing end groups in high temperature composite matrix resins. In particular, the study is aimed at developing an autoclavable high temperature matrix resin system capable of withstanding a 371°C environment. One of the main properties required for the composite matrix is a glass transition temperature (T_g) close to 400°C. Because high molecular weight polyimides with such a high T_g are not expected to flow readily, our effort was directed to the use of oligoimides with reactive end groups which were readily processed and capable of thermal crosslinking at the final process temperature. The crosslinking reactions of state-of-the-art thermoset matrix resins, such as bismaleimides[1], PMR-15 (nadimide)[2] and Thermid® series (terminal acetylene)[3], proceed at a relatively low temperature, 200–250°C. Because of its higher T_g, a 371°C matrix resin is expected to be processed at higher temperatures than the current state-of-the-art resins, thus, requiring a higher curing temperature. It has been reported[4,5] that disubstituted acetylenes undergo crosslinking reactions at temperatures between 300 and 350°C. Based on the higher cure temperature of disubstituted acetylene derivatives, 3-(phenylethynyl)aniline and 4-(phenylethynyl)phthalic anhydride were synthesized. These end groups were evaluated along with other curing systems in model reactions and also in imide oligomers. During this study, Paul *et al.*[6] reported a similar study on various (arylethynyl)aniline end groups. Our results are based on the oligomer chains composed of 75 mol% 3,3′,4,4′-tetracarboxybiphenyl dianhydride (BPDA), 25 mol% 1,1,1,3,3,3-hexafluoro-2,2-bis(3,4-dicarboxyphenyl)-propane dianhydride (6FDA) and 100% *p*-phenylenediamine (PPD). The resins were cured and subsequently characterized by a long-term isothermal oxidative test at 371°C in air, as well as by differential scanning calorimetry (d.s.c.), thermogravimetric analysis (t.g.a.) and thermal mechanical analysis (t.m.a.).

EXPERIMENTAL

Reagents

All dianhydrides were monomer grade materials obtained from either Hoechst-Celanese (6FDA), Chiskev (BPDA) or OxyChem (4,4′-oxybisphthalic anhydride (ODAN)). They were dried at 180°C under vacuum prior to use, and stored under a dry nitrogen atmosphere. PPD was obtained from DuPont and purified by vacuum sublimation. Nadic and phthalic anhydrides (Aldrich Chemicals), *p*-aminostyrene (Polyscience), 4-bromophthalic anhydride (Dead Sea Chemicals) and 3-aminoethynylbenzene (National Starch Co.) were used as received.

3-(Phenylethynyl)aniline[6]

A 100 ml flask was charged with 4.27 g (40 mmol) of 3-ethynylaniline, 9.42 g (60 mmol) of bromobenzene, 0.5 g (1.4 mmol) of tris(triphenylphosphine)copper(I) chloride, 0.52 g (0.73 mmol) of bis(triphenylphosphine)palladium(II) chloride and 40 ml of triethylamine under nitrogen atmosphere. The mixture was stirred and heated at 60–70°C for 24 h and then allowed to cool to room temperature. The reaction mixture was diluted with 125 ml of ether and filtered. The solid was washed with ether and the combined ether filtrate and washings were washed with 100 ml each of water and saturated ammonium chloride. The ethereal solution was filtered with the aid of Celite and the volatiles were removed on a rotary evaporator. The excess bromobenzene was distilled off and the residue was flash distilled under a

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high vacuum to afford 7.0 g (90.7%) of an amber oil. The product was recrystallized from cyclohexane, m.p. = 47–48°C (lit.[6] liquid); *FT*i.r.: 3375 (N–H) and 2231 ($C\equiv C$) cm^{-1}; ^1H n.m.r.: δ ($CDCl_3$) 7.5–6.5 (m, 9, ArH) and 3.5 ppm (s, 2, NH_2); ^{13}C n.m.r. ($CDCl_3$): 146.7, 124.2, 123.3, 131.8, 129.5, 128.6, 128.5, 122.0, 117.9, 115.6, 90.1, 89.1 ppm; mass spectrum (field desorption) m/e 193 M^+.

4-(Phenylethynyl)phthalic anhydride

In a 300 ml, three-necked flask were charged 4-bromophthalic anhydride (28.53 g, 0.1257 mol), tris(triphenylphosphine)copper(I) chloride (219 mg), bis(triphenylphosphine)palladium(II) chloride (143 mg) and 120 ml of triethylamine. The heterogeneous mixture was stirred under nitrogen at room temperature for 40 min. Phenylacetylene (13.27 g, 0.1299 mol) was added to the mixture together with an additional 20 ml of triethylamine. The resulting mixture was stirred and heated to reflux in an oil bath maintained at 100°C. After 10 min of heating, the flask was removed from the oil bath and the reaction mixture was allowed to cool and solidify. An aqueous sodium hydroxide (1 N, 300 ml) was added and the mixture was stirred overnight at room temperature under nitrogen. The insolubles were removed by filtration and the filtrate was extracted with toluene. The aqueous layer was acidified with 70 ml of a 1:1 mixture of conc. HCl and water. The resulting precipitate of 4-(phenylethynyl)phthalic acid was filtered, washed with water and dried, yield 33.13 g (99%). The diacid was ring closed to the anhydride by refluxing in acetic anhydride: m.p. 151–153°C; *FT*i.r. (nujol) 2207 ($C\equiv C$), 1869 ($C=O$), 1773 ($C=O$) cm^{-1}; ^1H n.m.r.: δ (DMSO-d_6) 7.4–8.3 (m, 8, ArH); ^{13}C n.m.r. (DMSO-d_6): 162.51, 162.49, 138.44, 132.26, 132.01, 131.77, 129.96, 129.77, 128.85, 127.55, 125.64, 121.14, 94.51, 87.44 ppm.

N-*[3-(Phenylethynyl)phenyl]phthalimide*

3-(Phenylethynyl)aniline (2.51 g, 13.0 mmol), phthalic anhydride (1.92 g, 13.0 mmol) and 15 ml of acetic acid were placed in a 50 ml, three-necked flask. The mixture was stirred under nitrogen and heated to reflux for 75 min. An acetic acid–water mixture was then allowed to distil. The solution temperature rose to 125°C, while 7.1 g of the distillate was collected. The reaction mixture was cooled and the precipitate was filtered, washed with water and then with hot isopropanol. The yield was 3.45 g (82.2%). The product was further purified by recrystallization from toluene: m.p. 165.5–166.5°C; *FT*i.r. (nujol) 2209 ($C\equiv C$), 1773 ($C=O$), 1717 ($C=O$) cm^{-1}; ^{13}C n.m.r. (DMSO-d_6): 166.83, 134.80, 132.36, 131.58, 131.48, 130.88, 130.07, 129.45, 129.08, 128.84, 127.87, 123.53, 122.83, 121.96, 90.12, 88.38 ppm.

N-*Phenyl-[4-(phenylethynyl)phthalimide]*

4-(Phenylethynyl)phthalic anhydride (2.09 g, 8.30 mmol), aniline (0.81 g, 8.70 mmol) and 15 ml of acetic acid were placed in a 50 ml, three-necked flask. The mixture was stirred under nitrogen and heated to reflux for 1.5 h. A total of approximately 5 ml of water and acetic acid mixture was distilled off during the following 0.5 h period. The reaction mixture was cooled and the crystalline solid was filtered. The product was washed with methanol and dried, the yield was 2.61 g (97.3%), m.p. 200.5–201.5°C; *FT*i.r. (nujol) 2216 ($C\equiv C$), 1780 ($C=O$), 1713 ($C=O$) cm^{-1}; ^{13}C n.m.r. (DMSO-d_6): 166.16, 166.07, 137.08, 132.08, 131.73, 131.58, 130.67, 129.42, 128.70(2), 128.40, 127.96, 127.09, 125.59, 123.64, 121.34, 93.31, 87.85 ppm.

Model crosslinking reaction

In order to assure a rapid rise of sample temperature to the reaction temperature, a small glass sealed tube (i.d. 3 mm, length 20 mm) was used as a reaction vessel. A portion (~30–40 mg) of the model compound was precisely weighed into a glass tube and the tube was sealed under vacuum. The sealed tube was heated in an aluminium heating block for a set time. After cooling, the contents of the tube were dissolved in 50 ml of acetonitrile with the aid of a sonicator. Approximately 40 mg of acetophenone was precisely weighed and added to the acetonitrile solution as an internal standard. The resulting solution was analysed by high performance liquid chromatography (h.p.l.c.) using a C18 reverse phase column, and an acetonitrile–water mixture as a mobile phase.

Preparation of oligo-amic acid solutions

Oligo-amic acid solutions were prepared using various end-capping agents. The following example represents the general procedure.

A mixture of PPD (3.091 g, 28.58 mmol) and 40 ml of NMP was stirred under nitrogen atmosphere at 60°C until a homogeneous solution resulted. The solution was cooled to room temperature and a powder mixture of 6FDA (2.722 g, 6.128 mmol) and BPDA (5.409 g, 18.383 mmol) was added in small portions over a period of 3 h. The residual dianhydride was washed in with an additional 35 ml of NMP. Upon complete dissolution of the dianhydrides, 4-(phenylethynyl)phthalic anhydride (2.021 g, 8.140 mmol) was added and the stirring was continued for 1 h.

Preparation of cured polyimide films

Approximately 5–6 ml of the amic acid solutions were cast onto a Pyrex glass disc of 76 mm diameter on a levelled stage which was placed in a modified Varian gas-chromatography oven continuously flushed with nitrogen ($50\,cm^3\,s^{-1}$). After initial drying overnight at 60°C, the films were heated at a rate of $2°C\,min^{-1}$ with a 120 min hold at 100°C, an 80 min hold at 200 and 300°C, and finally a 30 min hold at 400°C. The thicknesses of the cured films ranged from 0.05 to 0.20 mm.

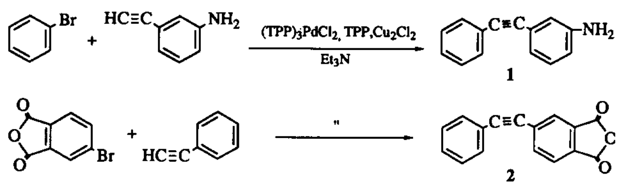
Thermo-oxidative test

Sections of each film (~0.6 g) were placed in a glass vial. The film was dried at 370°C under nitrogen for 2 h and cooled in a desiccator. The film was weighed precisely and placed in a forced air oven (General Signal Lindberg furnace) maintained at 370°C. After a given time of thermo-oxidative exposure, the film was cooled to room temperature in a desiccator over a period of 45 min and reweighed.

RESULTS AND DISCUSSION

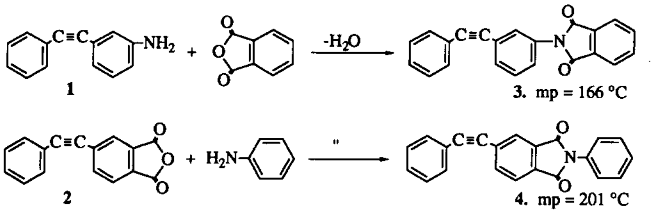
Studies on model curing systems

Preparation of capping agents. 3-(Phenylethynyl)aniline (**1**) and 4-(phenylethynyl)phthalic anhydride (**2**) were synthesized because they represent the simplest monofunctional amine and anhydride containing an internal acetylenic group. Both compounds were prepared by a transition metal catalysed acetylene coupling reaction according to the following one-step reaction scheme:



The reactions took place under mild conditions and afforded the diarylacetylenes in high yields. Both compounds were subsequently incorporated into the oligoimide resins and also converted to the model compounds.

Synthesis of model compounds. Each capping agent was converted, according to the following reaction scheme, to the corresponding phthalimide derivative (**3** and **4**), which were to serve as model compounds for the oligoimide resins:



Crosslinking reaction of model compounds. (i) Reaction kinetics. The thermal reactions of the model compounds were carried out in their neat form at temperatures of 320, 340 and 360°C. In order to minimize the time required to achieve temperature homogeneity, a small glass sealed tube (i.d. = 3 mm, length = 20 mm) was used as a reaction vessel. After the reaction, the total contents of the reaction mixture were dissolved in acetonitrile and analysed by h.p.l.c. using a C18 reverse phase column and a gradient elution technique based on water and acetonitrile. The thermal reaction of *N*-(3-phenylethynyl)phthalimide (**3**) was found to be extremely complex, as shown by the h.p.l.c. trace in *Figure 1*. Therefore, no particular effort was made to determine the structures of these products except for analysis by field-desorption mass spectrometry (f.d.-m.s.).

Despite the complexity of the reaction and the reaction products, the consumption of the starting material **3** followed a second-order kinetic scheme as shown in *Figure 2*. The rate was found to be slow. At 340°C the half-life of the model compound was approximately 80 min. It was reduced to only 30 min at 360°C. The rate seems to be too slow to be optimal for composite applications, considering the concentration of end groups in the actual oligomer resin. The Arrhenius plot of the kinetic results is shown in *Figure 3*. The apparent activation energy was 31.6 kcal mol^{-1}.

A similar kinetic study was performed for *N*-phenyl[4-(phenylethynyl)phthalimide] (**4**). Interestingly, the reaction of **4** more closely followed first-order kinetics, indicating that the rate controlling steps of the two model reactions may be different. In addition, the reaction of **4** was significantly faster than that of **3**, as seen in *Figure 4*. The half-lives of the model compound rates were approximately 50, 20 and 6 min at 320, 340 and 360°C, respectively. The rate profile seems to be adequate if not ideal for the expected processing window of the 371°C resin system. The Arrhenius plot of the kinetic results is also shown in *Figure 5*. The activation energy of the reaction was 36.5 kcal mol^{-1}.

(ii) F.d.-m.s. study of model compound reaction products. The products obtained by the thermal reaction of *N*-(phenylethynyl)phthalimide (**3**) at 360°C were analysed by f.d.-m.s. Unexpectedly, normal polymerization products, i.e. the dimer, trimer, tetramer, etc., did not appear as clearly dominant products, as shown in *Figure 6*. The spectrum showed several major products which were attributed to fragmentation products arising from certain primary products or intermediates rather than direct addition products themselves. Strong peaks at $m/e = 879$ and 1203 (1202) were attributed to the loss of C_6H_5–CH^+

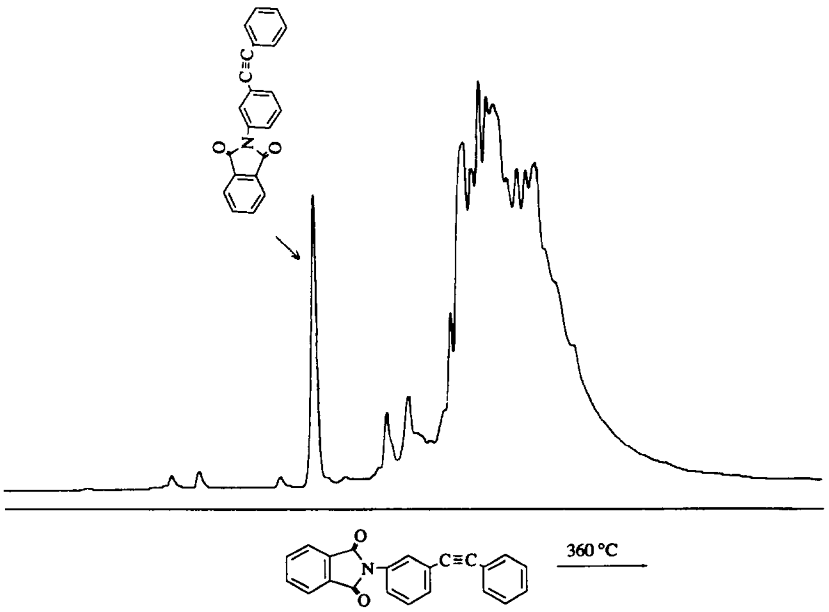


Figure 1 H.p.l.c. of the model thermal reaction products

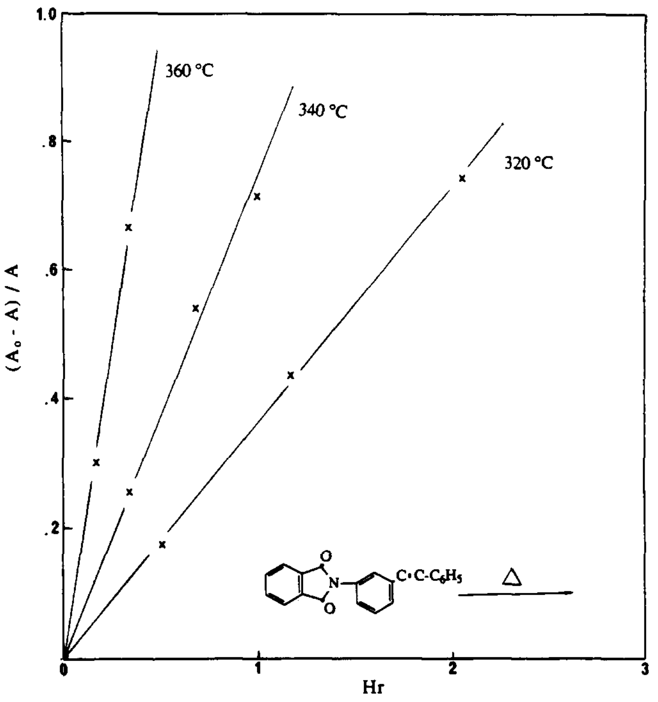


Figure 2 Reaction kinetic plot of the thermal reaction of model compound **3**

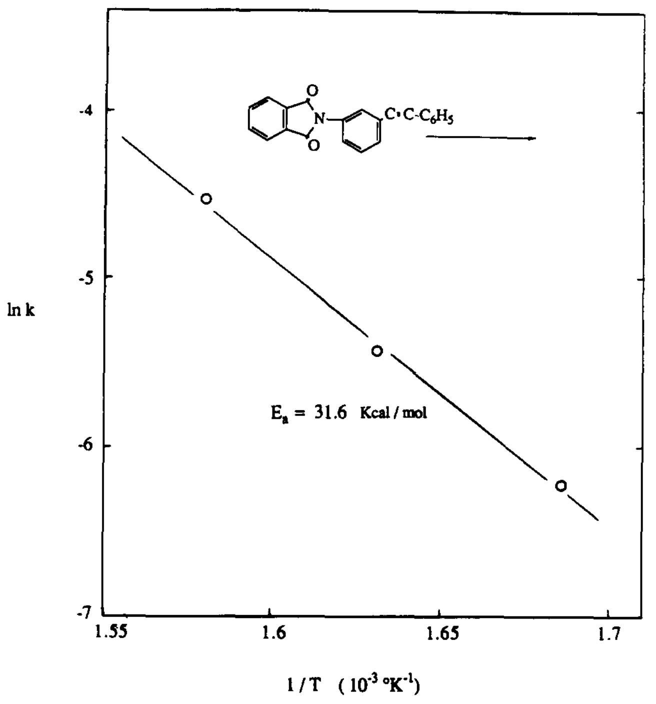
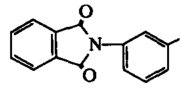


Figure 3 Arrhenius plot of the rate constants of the reaction of model compound **3**

($M_w=90$) or tropilium $C_7H_7^+$ ($M_w=91$) from the trimer ($m/e=969$) and tetramer ($m/e=1292$), respectively. Another series of fragmentation products with $m/e=734$ and 1055 (1057) were attributed to the loss of the fragment **5** or **5′** ($M_w=235$ or 236) from the trimer and tetramer, respectively.



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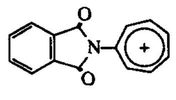


5'

It should be noted that the above fragments are not artifacts arising in the mass spectrometer but are the thermal degradation products formed at 360°C in the sealed tube reaction. Somewhat surprisingly, it indicates, at least formally, that the major mode of thermal degradation is the scission of acetylenic bonds. They are, however, more likely to be the secondary products expelled from the primary addition products, which are possibly unstable polycyclic compounds.

The f.d.-m.s. spectrum of the thermal reaction products of model compound **4** is shown in *Figure 7*. Model compound **4** is isomeric to **3** and, as expected, its

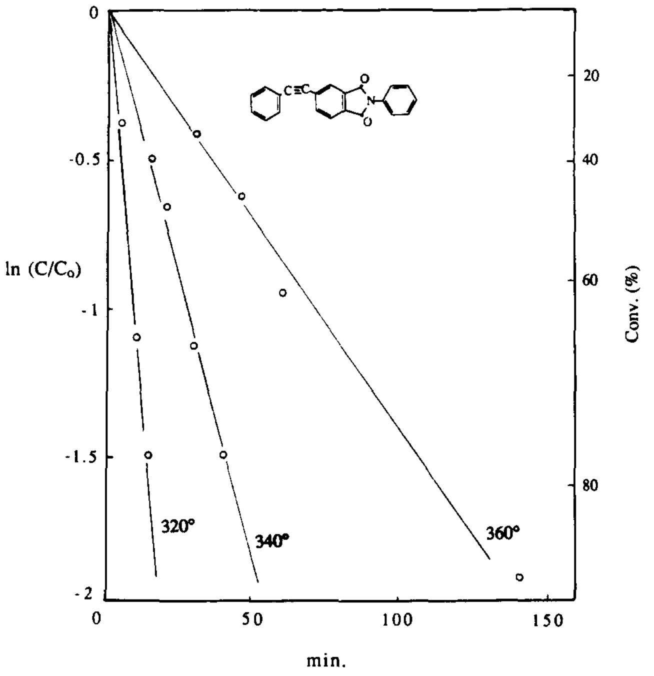


Figure 4 Reaction kinetic plot of the thermal reaction of model compound **4**

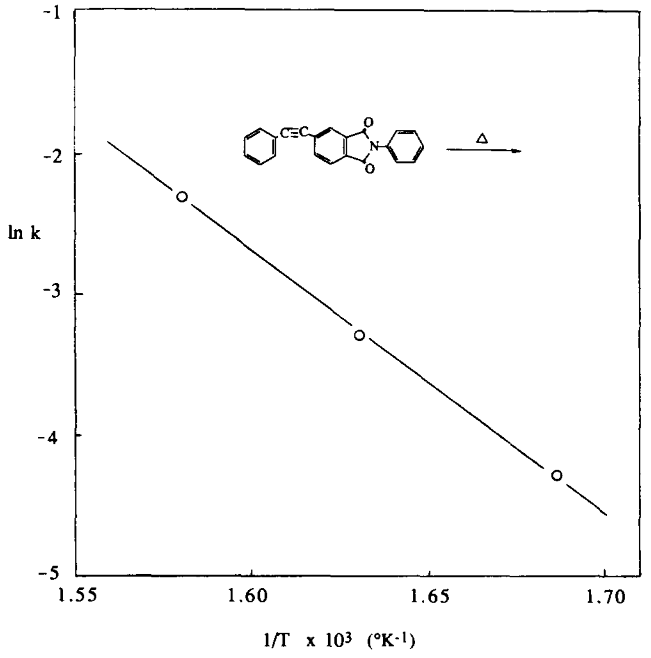


Figure 5 Arrhenius plot of the rate constants of the reaction of model compound **4**

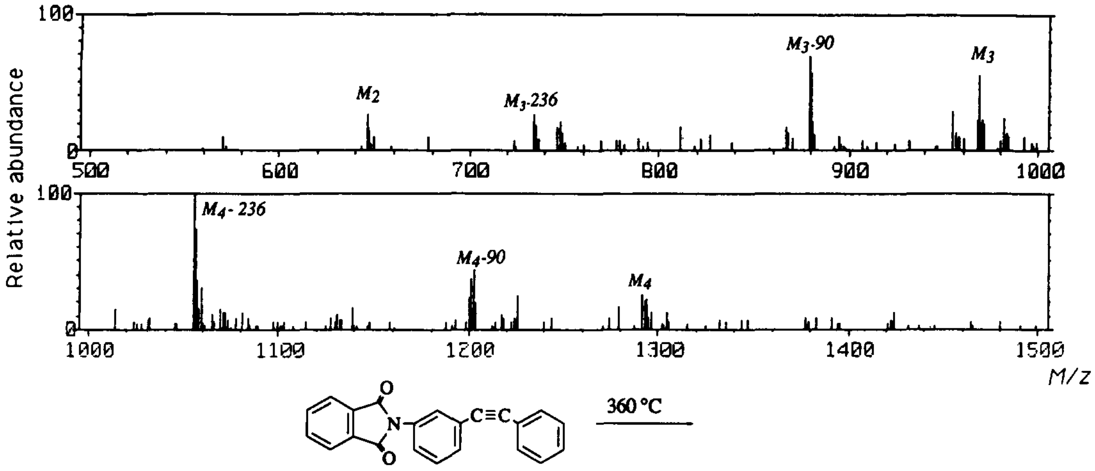


Figure 6 F.d.-m.s. spectrum of the thermal reaction products of model compound 3

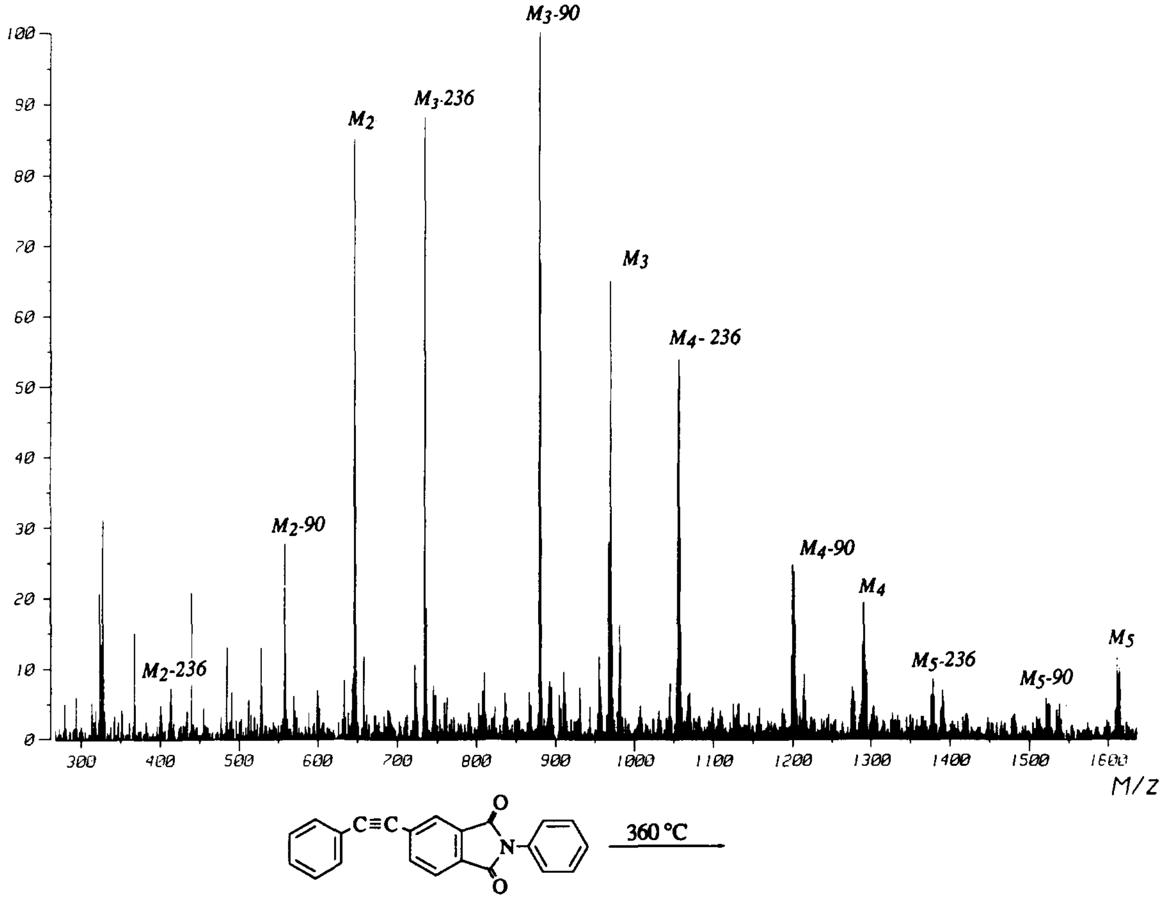
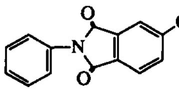
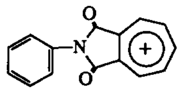


Figure 7 F.d.-m.s. spectrum of the thermal reaction products of model compound 4

degradation pattern is very similar. The major cleavage again occurred formally at the acetylenic C–C bond. One of the fragmentation products of model compound **4** should have the structure of **6** or **6′**, which are isomeric to **5** and **5′**.



6



6′

The formation of **6** or **6′** should be less favoured than **5** or **5′** because the positive charge is destabilized by the electron-withdrawing effect of the two carbonyl groups directly attached to the same benzene ring. The hypothesis is consistent with the results described in the following section, in which the resin system derived from the capping agent **2** showed substantially higher thermal stability than that derived from capping agent **1**.

Studies on end-capped oligoimides

Composition of oligoimides. Considering both the required high T_g and processability, the oligomer backbone used in all the formulations was prepared from a mixture of dianhydrides containing 75 mol% BPDA and 25 mol% 6FDA and PPD. The calculated molecular weight of the oligoimides with the various capping agents

Table 1 Thermo-oxidative test of cured resin at 371°C in atmospheric air

Capping agent	Final cure condition Temp. (°C)	Time (min)	Weight retention (%) 100 h	206 h	300 h	390 h	507 h
Phthalic anhydride	370	30	98.89	98.45	97.89	97.54	96.94
	400	30	99.11	98.56	98.08	97.56	96.98
	420	60	99.10	98.43	97.71	97.05[b]	95.40[c]
4-(Phenylethynyl)phthalic anhydride	370	30	95.67	91.83	86.41	79.74	65.47
	400	30	95.87	91.99	86.27	78.82	64.58
	420	60	96.48	90.82	80.93[a]	71.40[b]	44.71[c]
3-(Phenylethynyl)aniline	370	30	94.69	86.91	73.13[a]	62.65[b]	39.15[c]
	400	30	94.61	85.73	72.16[a]	61.26[b]	37.20[c]
	420	60	95.31	85.58	72.21[a]	61.73[b]	37.15[c]
Nadic anhydride	370	30	86.21	73.21	60.09	45.54	–
	400	30	85.36	71.68	56.68	41.64	–
	420	60	84.26	68.32	52.13	34.32	–
p-Aminostyrene	370	30	90.34	80.39	68.26	54.35	–
	400	30	89.89	77.99	64.85	50.88	–
	420	60	87.88	73.87	59.56	44.05	–

[a] 332 h
[b] 395 h
[c] 533 h

Table 2 Thermal and morphological properties of cured resins

Capping agent	Final cure condition (N_2) Temp. (°C)	Time (min)	T.m.a. T_g[a] (°C)	D.s.c. T_g[b] (°C)	T.g.a.[c] (°C)	X-ray diffraction[d]
Phthalic anhydride	370	30	381	372	500	
	400	30	408		500	+
	420	60	420			+ +
4-(Phenylethynyl)phthalic anhydride	370	30	394	394	500	
	400	30	415	414	500	+
	420	60	435			+
3-(Phenylethynyl)aniline	370	30	381	382		+
	400	30	410	409		
	420	60	429			
Nadic anhydride	370	30	385	382		–
	400	30	413	415		
	420	60	443	446	400	
p-Aminostyrene	370	30	388			
	400	30	418			
	420	60	443			

[a] The value is the mid-point of the transition at a heating rate of 10°C min^{-1}
[b] Heating rate 20°C min^{-1}
[c] Temperature at 2% weight loss. Heating rate was 2°C min^{-1}, N_2 atmosphere
[d] (+) Some ordered structure; (+ +) highly ordered; (–) no ordered structure

was fixed at 3000 g mol^{-1} based on the completely imidized but pre-crosslinked form. In order to evaluate the role of the crosslinking moiety, the present study focused on several reactive end-capping agents, including state-of-the-art capping agents as well as phthalic anhydride. The end-capping agents evaluated were: 4-(phenylethynyl)phthalic anhydride (**1**); 3-(phenylethynyl)-aniline (**2**); *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (nadic anhydride); *p*-aminostyrene (ASt); and phthalic anhydride (PA). PA was used to prepare a non-reactive end-capped control. Each end-capping agent was used at 14.24 mol% to afford a pre-crosslinked molecular weight of 3000 g mol^{-1}.

Preparation of cured films. Polyamic acid solutions were prepared at a concentration of 15 wt% solids in NMP. Each polyamic acid solution was cast on a 76 mm quartz disc placed on a levelling tripod stage in a Varian model 3700 g.c. oven, which was modified with a nitrogen inlet to provide an inert atmosphere. The cast solution was allowed to dry at 60°C overnight under nitrogen in the oven and then heated at a rate of 2°C min^{-1}. During the heating programme, the temperature was maintained for 120 min at 100°C, 80 min at 200°C, 80 min at 300°C, and then at the final temperature. For each polyamic acid solution, films were prepared under three different final cure conditions, i.e. 370 and 400°C with a 30 min hold, and at 420°C with a 60 min hold. After the final curing stage was complete, the films were cooled to room temperature under a nitrogen atmosphere.

Thermo-oxidative stability of cured oligoimide films

Cured films, each approximately 0.6 g, were placed in a glass vial and subjected to an isothermal thermo-oxidative test at 371°C in a forced air oven. Their weights were followed over a period of 400–500 h; the results are summarized in *Table 1*. Each weight retention value represents the mean of three determinations. Generally, the reactive end-capped systems showed substantially less stability compared to the unreactive PA-capped control. In each case the weight loss beyond 300 h exceeded the value expected if only the end groups underwent degradation (7–15 wt%). This suggests that once defects occurred in the structure, the main chains also become vulnerable to thermo-oxidative processes. Within each system, the final cure temperature did not significantly affect the thermo-oxidative stability result in short time exposure, but the sample cured at 420°C showed substantially lower stability at exposure time above 300 h. The overall order of thermo-oxidative resistance in terms of the difference in capping agents was phthalic anhydride > 4-(phenylethynyl)phthalic anhydride > 3-(phenylethynyl)aniline > *p*-aminostyrene > nadic anhydride. The disubstituted acetylene capping systems performed substantially better than the state-of-the-art capping systems. As discussed in the preceding section on the model system, the superiority of 4-(phenylethynyl)-phthalic anhydride as a capping agent can be attributed to the stabilization effect of the electron-withdrawing carbonyl groups.

Other properties of cured oligoimide films

Other thermal and morphological characterization results obtained from the cured polyimide films are shown in *Table 2*. The t.m.a. T_g represents the mid-point of the transition, and is reported as the mean of three determinations. Film samples were heated from 50 to 500°C at a heating rate of 10°C min^{-1}. In each case the t.m.a. T_g exceeded the final curing temperature by 8°C or more. Both an increase in crystallinity or an ordered state and an increase in crosslinking density will increase the T_g. The degree of crosslinking could not be assessed quantitatively at this stage. A qualitative assessment of degree of crystallinity (or other ordered state) was made by X-ray diffraction analysis. The analysis was performed using a transmission film technique with Cu Kα radiation with Ni filter. The linear polyimide based on BPDA and PPD is a highly crystalline polymer. The oligoimide end-capped with phthalic anhydride exhibited a moderate semicrystalline signature by X-ray analysis. Cured films based on the 4-(phenylethynyl)phthalic anhydride, and 3-(phenylethynyl)aniline systems appeared to have some type of weak ordering present, although it was not determined whether such structure was two-dimensional or three-dimensional.

The cured polyimide films were brittle, voidless, translucent, and had a thickness of 0.05–0.20 mm. The phthalic anhydride and disubstituted acetylene-capped films were amber coloured, while the nadic anhydride and *p*-aminostyrene-capped films were dark brown.

CONCLUSION

Disubstituted acetylenes, 4-(phenylethynyl)phthalic anhydride and 3-(phenylethynyl)aniline were evaluated as high temperature curing end groups in model compounds and in oligoimides with calculated molecular weights of 3000 g mol^{-1}. A crosslinking reaction took place at 340–360°C. The 371°C isothermal thermo-oxidative stabilities of the cured resins were compared with those of control samples prepared from other state-of-the-art resins formulated with nadic anhydride, phenylethynylaniline and aminostyrene. The disubstituted acetylene end-capped resins displayed the best thermo-oxidative stabilities. The resin end-capped with 4-(phenylethynyl)phthalic anhydride displayed the best stability.

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