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Gerber et al.

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[54] **CROSSLINKED POLYIMIDES PREPARED FROM N-(3-ETHYNYLPHENYL)MALEIMIDE**

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[22] Filed: **Dec. 3, 1991**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 528,666, May 18, 1990, abandoned.

[51] Int. Cl.⁵ **C08F 222/40**

[52] U.S. Cl. **526/262; 526/285; 528/322**

[58] Field of Search **526/262, 285; 528/322**

[56] References Cited

U.S. PATENT DOCUMENTS

4,861,882	8/1989	Hergenrother et al.	544/216
4,889,912	12/1989	Hergenrother et al.	528/125
4,937,356	6/1990	Hergenrother et al.	548/549

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[57] ABSTRACT

The compound N-(3-ethynylphenyl)maleimide (NEPMI) was used to prepare thermally stable, glassy polyimides which did not exhibit glass transition temperatures below 500° C. NEPMI was blended with the maleimide of methylene dianiline (BMI) and heated to form the polyimide. NEPMI was also mixed with Thermid 600® , a commercially available bisethynyl oligomeric material, and heated to form a thermally stable, glassy polyimide. Lastly, NEPMI was blended with both BMI and Thermid 600® to form thermally stable, glassy polyimides.

10 Claims, No Drawings

CROSSLINKED POLYIMIDES PREPARED FROM N-(3-ETHYNYLPHENYL)MALEIMIDE

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provision of Section 305 of the National Aeronautics and Space Act of 1958, as amended, Public Law 85-568 (72 Stat. 435; 42 USC 2457).

CROSS-REFERENCE

This application is a continuation-in-part of copending application Ser. No. 528,666, filed May 18, 1990, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to polyimides which are suitable for high temperature applications as a result of their high or nondetectable glass transition temperatures and their high thermooxidative stabilities. It relates particularly to three types of polyimides which are prepared from monomers containing carbon-carbon double and/or triple bonds, in particular N-(3-ethynylphenyl)maleimide (NEPMI).

2. Description of Related Art

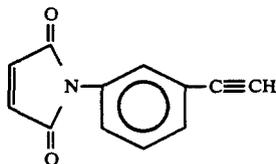
Polymers prepared from the reaction of organic compounds containing pendant ethynyl groups or organic oligomers containing pendant ethynyl groups are well known for their thermooxidative stability and exceptionally high glass transition temperatures. Likewise, organic compounds or oligomers containing activated carbon-carbon double bonds and imide moieties (i.e. maleimides) can be used to prepare thermally stable polymers.

Hergenrother et al. (U.S. Pat. No. 4,889,912 and U.S. Pat. No. 4,937,356) prepared acetylene terminated aspartimides by reacting an aromatic diamine with NEPMI. These acetylene terminated aspartimides were blended with acetylene terminated polyarylene ethers or sulfone oligomers to yield polymers with improved mechanical properties such as fracture toughness.

Hergenrother et al. (U.S. Pat. No. 4,861,882) also prepared ethynyl terminated imidothioethers by reacting a dimercaptan with NEPMI. These ethynyl terminated imidothioethers were then blended with other ethynyl terminated oligomers to produce resin blends which are useful as adhesives, coatings, and films. The glass transition temperatures of these blends ranged from 193°-245° C.

SUMMARY OF THE INVENTION

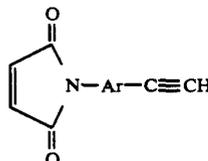
The compound N-(3-ethynylphenyl)maleimide (NEPMI) has the following structural formula:



This monomer is highly reactive due to its two types of unsaturation (double and triple bonded carbons). The ethynyl group allows for copolymerization with other ethynyl-containing monomers and oligomers and the

maleimide group allows for copolymerization with maleimide monomers and oligomers.

The highly reactive nature of NEPMI is demonstrated when it is heated past its melting point of 130° C. Depending on the heating rate, the liquid form of NEPMI exhibits an intense exotherm in the region of 155°-248° C. This exotherm is so strong that active cooling is necessary in order to dissipate the heat. The resulting polymers do not exhibit glass transitions below 500° C. These characteristics are also demonstrated by compounds having the following general structural formula:



where Ar is any aromatic moiety.

An object of the present invention is to provide high temperature polyimides by reacting NEPMI with bisethynyl-containing monomers and/or oligomers and heating them to a temperature where they react.

Another object is to provide high temperature polyimides by reacting NEPMI with bismaleimide monomers and/or oligomers and heating them to a temperature where they react.

Another object is to provide high temperature polyimides by reacting NEPMI with mixtures of bisethynyl and bismaleimide monomers and/or oligomers and heating them to a temperature where they react.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

EXAMPLE 1

High temperature polymers were prepared by heating 5-10 mg samples of NEPMI in an open pan at heating rates of 1° C./min., 10° C./min., 20° C./min., 50° C./min., and 100° C./min. using a DuPont 1090 Thermal Analyzer. Table 1 lists the melt onset, exotherm temperature and intensity, and temperature for 5% weight loss in air for each polymer prepared. For comparison, samples of the maleimide of methylene dianiline (BMI), and samples of Thermid 600®, a bisethynyl oligomeric compound available from National Starch, were heated at heating rates of 10° C./min. and 50° C./min. using the same thermal analyzer. These results are also recorded in Table 1.

TABLE 1

Sample	Heating Rate	Pure Reactants			Temp. 5% Wt. loss in air
		Melt Onset (°C.)	Exotherm Temp. (°C.)	Exotherm Intensity	
NEPMI	1° C./min	130.5	155	low	405° C.
NEPMI	10° C./min	131.2	200	low	412° C.
NEPMI	20° C./min	131.7	215	moderate	420° C.
NEPMI	50° C./min	135.7	244	high	410° C.
NEPMI	100° C./min	135.2	248	high	412° C.
BMI	10° C./min	151.7	246	very low	420° C.
BMI	50° C./min	154.7	246	very low	410° C.
Thermid 600®	10° C./min	Not observed	250	low	508° C.
Thermid 600®	50° C./min	Not	297	moderate	503° C.

TABLE 1-continued

Sample	Heating Rate	Pure Reactants			Temp. 5% Wt. loss in air
		Melt Onset (°C.)	Exotherm Temp. (°C.)	Exotherm Intensity	
600 ®		observed			

EXAMPLE 2

NEPMI was blended in various ratios with the maleimide of methylene dianiline (BMI) and thermally polymerized as described in Example 1. BMI has the following structural formula:

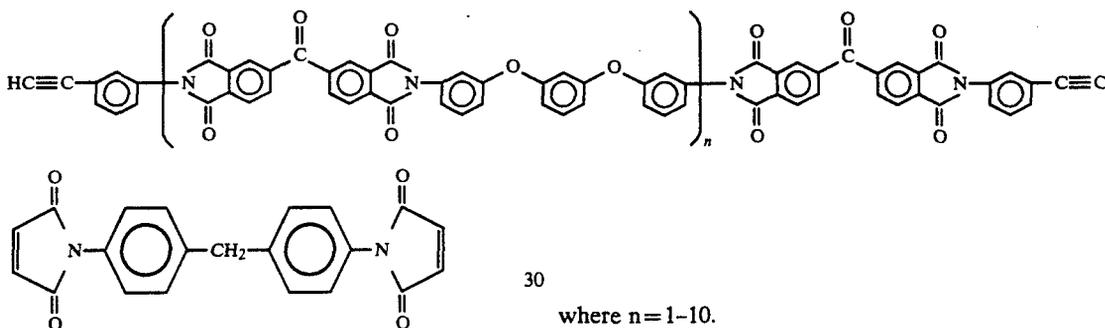
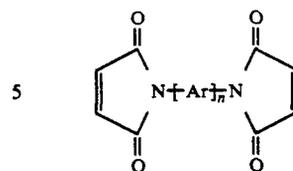


Table 2 shows the heating rate, melt temperature, exotherm temperature, temperature of 5% weight loss in air, and glass transition temperature (T_g) for the resulting polymer blends and is compared to BMI and Thermid 600 ® control polymers. It is evident from the data that the presence of NEPMI offers a significant improvement in the T_g of these polymers.

TABLE 2

Polymers from NEPMI-BMI Blends						
Ratio of NEPMI/BMI	Heating Rate	Melt Temp. (°C.)	Exotherm Temp. (°C.)	Temp. 5% wt. loss (°C.)	T _g (°C.)	
90/10	10° C./min	122.8	210	418	> 500	
90/10	50° C./min	131.3	240	432	> 500	
80/20	10° C./min	107.9	208	415	> 500	
		120				
80/20	50° C./min	110	250	410	> 500	
		135				
70/30	10° C./min	109.4	214	430	> 500	
		120				
70/30	50° C./min	111.9	250	420	> 500	
		133				
60/40	10° C./min	109.4	211	410	> 500	
		126				
60/40	50° C./min	113	251	420	> 500	
50/50	10° C./min	109.9	212	442	> 500	
50/50	50° C./min	113	248	418	> 500	
80/20	10° C./min	110	224	428	> 500	
		129				
80/20	50° C./min	113	252	418	> 500	
		137				
BMI	10° C./min	151.7	246	420	290	
Thermid 600 ®	10° C./min	None	250	508	305	

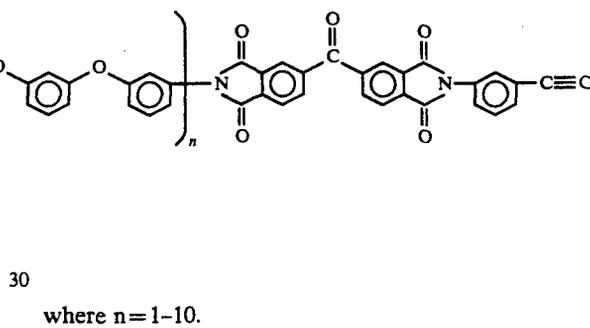
Although BMI was used in this example, other bis-maleimides can also be used which have the following structure:



10 where Ar is any aromatic moiety and n=1-50.

EXAMPLE 3

NEPMI was also blended in various ratios with the ethynyl-containing oligomeric compound Thermid 600 ® and thermally polymerized as described in Example 1. Thermid 600 ® has the following structural formula:



30 where n=1-10.

Table 3 contains data on the resulting NEPMI-Thermid 600 ® blends as compared to BMI and Thermid 600 ® control polymers.

TABLE 3

Polymers from NEPMI-Thermid 600 ®						
Ratio of NEPMI/Thermid 600 ®	Heating Rate	Melt Temp. (°C.)	Exotherm Temp. (°C.)	Temp. of 5% wt. loss (°C.)	T _g (°C.)	
90/10	10° C./min	127.6	210	415	> 500	
90/10	50° C./min	131.7	246	438	> 500	
80/20	10° C./min	127.1	218	432	> 500	
80/20	50° C./min	133.1	254	396	> 500	
70/30	10° C./min	128	-218	435	> 500	
70/30	50° C./min	132	252	440	> 500	
60/40	10° C./min	127	228	378	> 500	
60/40	50° C./min	129	276	432	> 500	
50/50	10° C./min	128	230	410	> 500	
50/50	50° C./min	130	278	462	> 500	
20/80	10° C./min	128	246	455	> 500	
20/80	50° C./min	130	288	500	> 500	
BMI	10° C./min	151.7	246	420	290	
Thermid 600 ®	10° C./min	Not Observed	250	508	305	

55 Although Thermid 600 ® was used in this example, other bisethynyl terminated oligomers known to those skilled in the art may also be employed. These compounds have the following general structure:



60 where Ar is any aromatic moiety and n=1-50.

EXAMPLE 4

65 Polymers were made by heating blends of NEPMI, Thermid 600 ®, and BMI in various ratios. The data is presented in Table 4 and compared to BMI and Thermid 600 ® control polymers.

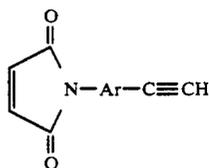
TABLE 4

Ratio of NEPMI/ BMI/ Thermid 600 ®		Heating Rate	Melt Temp. (°C.)	Exotherm Temp. (°C.)	Temp. of 5% weight loss (°C.)	T _g (°C.)
1/1/1	10° C./min	105	230	468	>500	
1/1/1	50° C./min	114	260	458	>500	
1/0.5/3	10° C./min	111	247	450	>500	
1/0.5/3	50° C./min	125	290	482	>500	
1/3/2	10° C./min	107	236	462	>500	
1/3/2	50° C./min	116	256	450	>500	
BMI	10° C./min	151.7	246	420	290	
Thermid 600 ®	10° C./min	None	250	508	305	

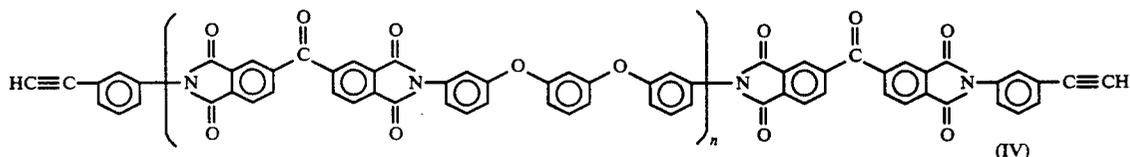
The utility of these polymers is dependent on their ability to be formed from monomers and oligomers which melt and polymerize without the evolution of volatiles. The presence of NEPMI in the polymer results in an increase in crosslink density, and thus, they do not exhibit a glass transition (T_g) below 500° C. These polymers are useful as high temperature composite matrix resins for supersonic aircraft structures and mainframe and engine applications where high T_g is a requirement.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A thermally stable, glassy, crosslinked polymer prepared from a monomer composition consisting essentially of at least one ethynyl imide (I) having the following general structural formula:

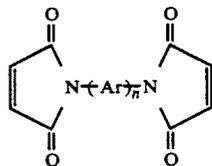


(I)

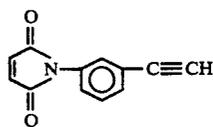


(IV)

where Ar is any aromatic moiety; and a member selected from the group consisting of:



(II)



(NEPMI),

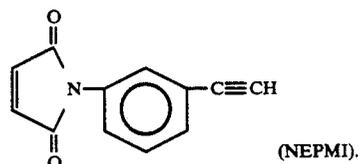
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and



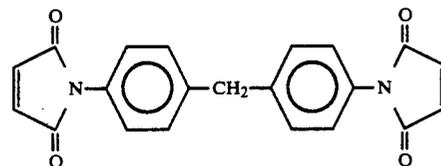
where Ar is any aromatic moiety and $n=1-50$; and said polymer has a glass transition temperature of at least 500° C.

10 2. A thermally stable, glassy, crosslinked polymer according to claim 1, wherein (I) has the following structural formula:



(NEPMI).

3. A thermally stable, glassy, crosslinked according to claim 1, wherein (II) has the following structural formula:



(BMI).

35 4. A thermally stable, glassy, crosslinked polymer according to claim 3, wherein the ratio of NEPMI to BMI is between about 90:10 and 20:80.

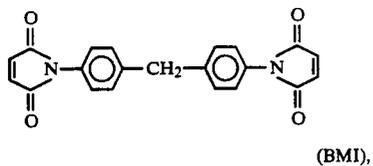
5. A thermally stable, glassy, crosslinked polymer according to claim 1, wherein (III) has the following structural formula:

where $n=1-10$.

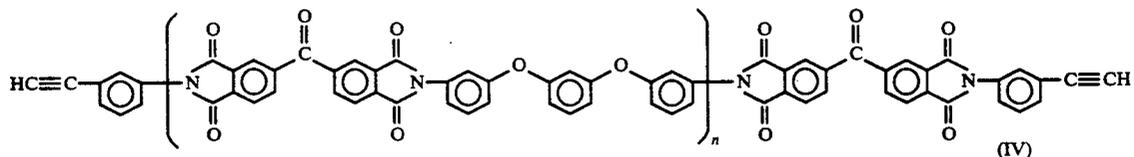
6. A thermally stable, glassy, crosslinked polymer according to claim 5, wherein the ratio of NEPMI to (IV) is between about 90:10 and 20:80.

55 7. A thermally stable, glassy, crosslinked polymer according to claim 1, wherein (I), (II), and (III) have the following structural formulas, respectively:

-continued



and



where n=1-10.

8. A thermally stable, glassy, crosslinked polymer according to claim 7, wherein the ratio of NEPMI to BMI to (IV) is 1:1:1.

9. A thermally stable, glassy, crosslinked polymer

according to claim 7, wherein the ratio of NEPMI to BMI to (IV) is 1:0.5:3.

10. A thermally stable, glassy, crosslinked polymer according to claim 7, wherein the ratio of NEPMI to BMI to (IV) is 1:3:2.

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