The synthesis of rod-like polyimides terminated with biethenylene and the application of them to improvement of dimensional stability of material

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Abstract:

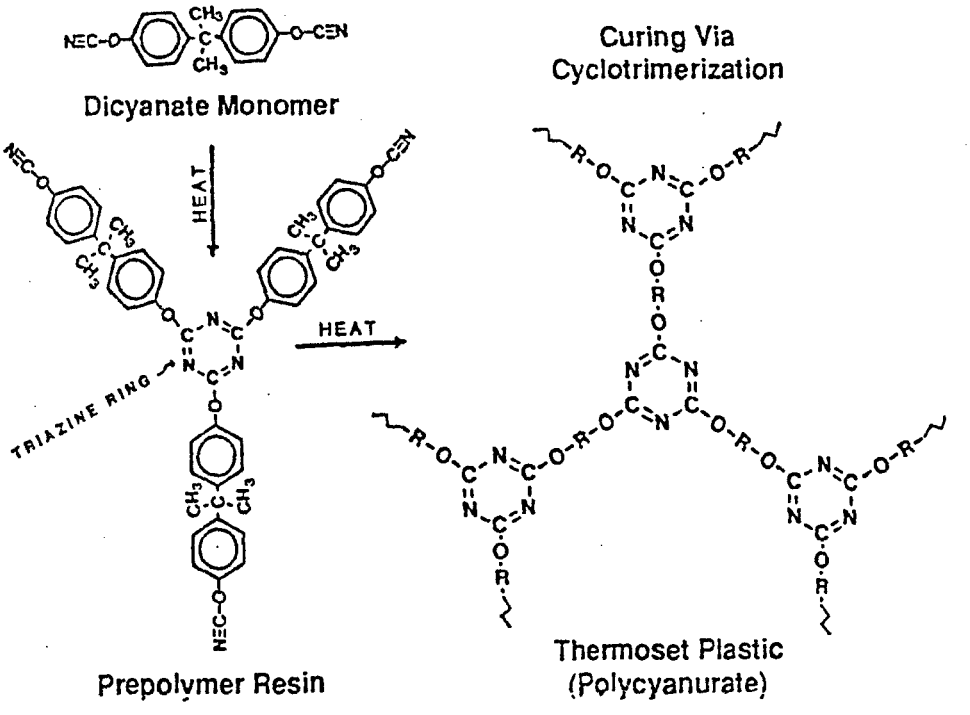
Several rod-like polyimides terminated with biethenylene were synthesized. Some of them can controlled the coefficient of thermal expansion (CTE) of BT resin and the improved BT resin did not sacrifice its excellent properties.

Key Words:

Reactive Rod-like Polyimide, BT Resin, Laminate, Coefficient of Thermal Expansion (CTE).

Arocy B-10 (2,2'-bis(cyanatophenylOpropane) functionality cyclotrimerizes upon heating-catalyzing via step-growth mechanism to form a thermoset plastic, polycyanurate [1].

Figure 1



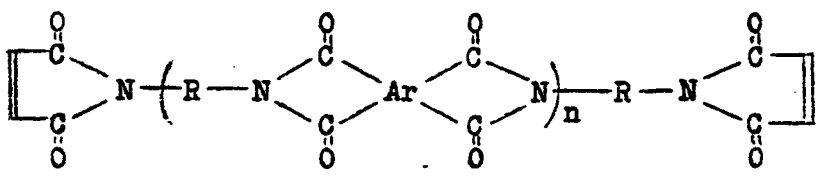
This cyclotrimerization ultimately forms a cross-linked network

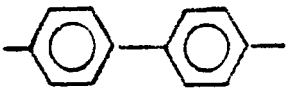
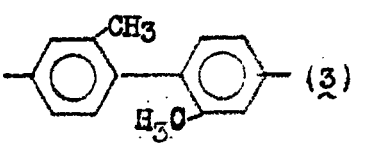
characterized as bisphenol units and triazine rings linked by oxygen atoms. The polymer obtained in this way possesses good thermostability, low dielectric constant, excellent mechanical strength, adhesion, toughness and low shrinkage characteristic. To blend the B-staged Arocy B-10, which is named T resin, with the B-staged bismaleimide, which is named B-resin give the socalled BT resin.

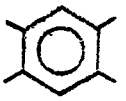
The study on BT resin[2] showed that the glass transition temperature (Tg) of BT resin after curing increased with increasing amount of the bismaleimide component. BT resin after curing has less coefficient of thermal expansion (CTE) than pure T resin has. This phenomenon is raised by the small CTE of bismaleimide. However, bismaleimide only has a little effect on the CTE of BT resin, because the difference of CTEs between B resin and T resin is small. The former is 2.14×10^{-5}, while the latter is 2.81×10^{-5}. When the mol ratio of B resin component is 60%, the CTE of BT resin after curing is 2.45×10^{-5}, about 13% less than the CTE of Arocy B-10 after curing.

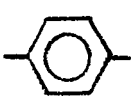
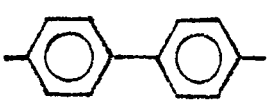
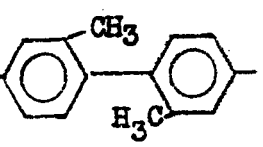
Namata et al reported [3] that some rod-like polyimides had very small CTE, because these rod-like polymer molecules were forced to restrain their thermal shake within the intermolecular spaces, just like glass fiber does in FRP. The rod-like structure comes from the linear diamine, such as p-PDA, 4,4'-BPA, some 2,2'-disubstituted-4,4'-BPA and some aromatic tetracarboxylic dianhydride, such as PMDA, BPDA etc. Their study also showed that the CTE of polyimides can be controled by copolymerization or blending of polyamic acids. The larger the weight fraction of the low thermal expansion polyimide, the lower the CTE becomes. It seemed that there is a linear relationship between the CTE and the monomer ratio. For getting the laminate of small CTE, we attempt to improve BT resin with rod-like polyimides terminated with biethenylene.

There already have been a lot of reports [4] about the synthesis of polyimides terminated with various reactive groups. However, as far as we know, there is no a special report about the synthesis of rod-like polyimides terminated with reactive group to prepare a resin with small CTE. We synthesized the following compounds from 4,4'-BPA, p-PDA, 2,2'-dimethyl-4,4'-BPA , PMDA and maleic anhydride (MA):



n = 0
R =  (1),  (2),  (3)

n = 1, Ar =  ,

R =  (4),  (5),  (6)

Imidation was achieved by heating polyamic acid in DMF. Some of properties of these polyimides are showed in Table 1.

Table 1, IR and Thermoanalytic date of the synthesized PIs

Compounds	Yield (%)	IR (cm^{-1})	DSC (C)	TGA* Weight Loss (%)	TGA* Temperature (C)
1	64.6	1410	202.0	2.0	70.7
		700		5.0	130.7
		630		14.9	171.4
				50.0	398.0
2		1406	193.5	2.0	148.2
		696		4.9	172.4
		625		15.0	231.4
				49.9	420.3
3	97.8	1390	180.5	1.2	88.9
		696		5.0	182.8
		610		15.0	364.4
				49.3	513.5
4	80.3	1390	160.5	1.9	107.5
		734		4.9	155.6
				14.9	343.1
				49.4	538.9
5	89.0	1390	135.8	2.0	87.1
		732		5.0	143.3
				14.9	330.2
				49.1	527.8
6	96.3	1386	154.7	2.0	89.1
		734		4.9	123.0
				15.0	331.2
				49.5	538.4

* in air stream.

Our primary study indicated that our idea was correct. The properties of laminates of copper foil/woven quartz dipped with resin (B/T/6 system in 40/50/10 weight ratio) are showed in Table 2. The CTEs in-plane (X.Y.) and in-aplomb (Z) of the laminate of improved resin by 10% compound 6 are only 50% and 30% of the CTEs of the laminate of unimproved BT resin respectively. The copper peel strength is 14 N/cm indicating the good toughness of the improved resin.

Table 2, Some properties of laminates of woven quartz/BT resin

		Woven quartz/ improved BT resin *	WovenQuartz/ BT resin [5]
CTE (10^{-6})	X.Y.	3.1	6 ~ 6.5
	Z	13	60
Dielectric constant (1 MHz)		3.6	3.6
Dissipation factor (1 MHz)		6.7×10^{-3}	2.7×10^{-3}
Cu peel strength (N/cm)		14	

* The component of BT resin was B/T/6 system in 40/50/10 weight ratio.

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