

Synthesis and Properties of Novel Dicyanate with Low Dielectric and Water Absorption Performance

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ABSTRACT: The 1,4-bis (3,5-dimethyl-4-cyanatobenzyl) benzene (BBZCy) was synthesized successfully by the reaction of 1,4-bis (3,5-dimethyl-4-hydroxybenzyl)benzene (BBZ) with cyanogen chloride in the presence of triethylamine at $-5-0^{\circ}\text{C}$. Its structure was confirmed by means of FTIR, elemental analysis, MS, and ^1H NMR spectra. The monomer of BBZCy was cured by itself or cured with catalysts to form sym-triazine structure. Thermal properties of cured BBZCy were studied using DSC, DMA, TMA, and TGA. Compared

with the commercial bisphenol A dicyanate resin (BADCy), the cured BBZCy resin exhibited a lower dielectric constant (2.66 at 1 GHz), a lower dissipation factor (0.0054 at 1 GHz), lower water absorption (0.8% at 100 h), less thermal stability, and lower glass transition temperature. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3716–3723, 2011

Key words: low-dielectric polymer; *ortho*-methylation; water absorption; cyanate ester

INTRODUCTION

Cyanate ester resins (CE) have received considerable attentions in the past few years because of their importance as thermosetting resins for use in the electronics, aerospace, and adhesive industries.¹ Cyanate ester resins have many excellent properties, such as good thermal stability, high glass transition temperatures, low dielectric constants over a wide range of frequencies and temperatures, and outstanding adhesion to conducting metals.^{2,3} These properties make them the resin of choice for high performance applications where such properties are required, such as, high speed, high density, multilayer circuit boards.⁴

In designing thermoset polymers for use as printed circuit boards (PCBs) substrates, several critical performance parameters including the processibility, thermal stability, glass-transition temperature (T_g), moisture resistance, and electrical insulation properties must be considered.^{5,6} Conventional PCBs are made from glass-fiber-reinforced bisphenol A epoxy resins. However, they often fall short of the thermal and electrical performance demands of many modern high-speed devices.^{7–9} Nowadays, the trend of the rapid evolution for faster signal speed, shorter propagation delays, more powerful, and faster multilayer units paces increased demands on dielectric materials

for lower dielectric constant and dissipation properties to accomplish these goals.^{10–13} Moreover, a continuing goal in cyanate ester research is also further to depress the dielectric constant and water absorption while maintaining the attractive thermal (high T_g and thermal stability) and mechanical properties.¹⁴

The properties of cyanate ester resins are governed by both the cyanurate linkage and the connecting structure of the monomer. The monomer connecting structure, which usually consists of one, two, or three phenylene moieties, regulates the crosslinking density and results in the resin's desirable glass transition temperature. Generally, increasing the bulkiness of the hydrocarbon bridging units (e.g., methyleneisopropylidene<dicyclopentadiene<*meta*-diisopropenylbenzene (RTX-366)) progressively lowers dielectric constant by diluting dipole concentrations and decreasing electronegativity of the substituted benzene ring.¹⁵ The replacement of the connecting structure of the bisphenol backbone by cycloaliphatic or dicyclopentadiene has produced a family of cyanate functional resins with low dielectric properties.¹⁶ A chemical modification, *ortho*-methylation, also significantly lowers dielectric constant by shielding and weakening the C–O, C–N, and C=N dipoles. At the same time, bulky hydrophobic groups such as *p*-xylene moiety in the backbone and *ortho*-methylation are good for moisture resistance. Based on these, new dicyanate with *p*-xylene moiety in the backbone and *ortho*-methylation (see Fig. 1) was proposed, expected to be low dielectric constant and low moisture uptake. This study is emphasized on the synthesis of new

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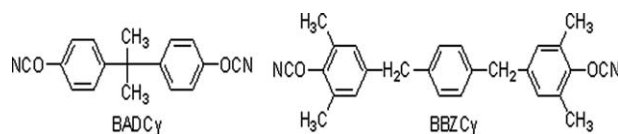


Figure 1 Chemical structures of BBZCy and BADCy dicyanates.

dicyanate with *p*-xylene moiety, its structural characterization and corresponding properties.

EXPERIMENTAL

Materials

Cyanogen chloride, triethylamine and BADCy were supplied by Shanghai HUIFENG Technical and Business. *p*-toluenesulfonic acid (PTS) was purchased from Shanghai LINGFENG Chemical Reagent. The other reagents and solvents were reagent-grade, purchased commercially and used without further purification unless otherwise specified.

General procedure for the synthesis of BBZ

A four-necked, round-bottom flask equipped with addition funnel was charged with melted 2,6-dimethylphenol (244 g, 2 mol) and PTS (5.5 g) and stirred. After the solution was heated to 130°C, 1, 4-bis(methoxymethyl) benzene (33.2 g, 0.2 mol) was added in drops to the solution over 1 h. The methanol was formed and generated out. The reaction mixture was maintained at 130°C for 4 h. After completion of the reaction, the mixture obtained was neutralized by 0.03 mol 20% potassium hydroxide solution and excess 2,6-dimethylphenol was distilled under reduced-pressure. The crude product was dissolved in toluene and extracted with water several times. The organic phase was precipitated by slowly cooling to 0°C, then filtrate the precipitation to obtain solid. The solid was recrystallized from toluene, filtered and dried under vacuum to give BBZ (40.14 g, 58%) as a yellowish white solid; m.p. = 172°C.

FTIR (KBr; cm^{-1}): 3410 (ν_{OH}), 3010, 2914, 2851, 1486, 1202, 1145, 1020, 877, 752. ^1H NMR (CDCl_3 ; δ , ppm): 7.1 (s, 4H, C_6H_2), 6.8 (s, 4H, C_6H_4), 4.5 (s, 2H, OH), 3.8 (s, 4H, CH_2), 2.2 (s, 12H, CH_3). ELEM. ANAL. Calcd for $\text{C}_{24}\text{H}_{26}\text{O}_2$: C, 83.24%; H, 7.51%; O, 9.25%; Found: C, 83.46%; H, 7.30%; O, 9.24%. MS (EI, m/z , % relative intensity): 346(M^+ , 100), 331 (M-25, 26), 211(M-125, 56).

General procedure for the synthesis of BBZCy

Cyanogen chloride (78.2 g, 1.272 mol) and dichloromethane (800 g, 9.4 mol) were added to the three-necked flask fitted with a thermometer. The reaction temperature was cooled to -5°C . A mixture contain-

ing BBZ (200 g, 0.578 mol), triethylamine (127.7 g, 1.265 mol), and butanone (400 g) was added gradually for 1 h under nitrogen and maintained at -5 to 0°C for another 2 h. After the reaction was completed, the solution was filtered, 10% sulfuric acid was added to the filtrate, and then the filtrate was washed with water several times. The organic phase was dried with anhydrous Na_2SO_4 and distilled under vacuum to remove the solvent to obtain the corresponding dicyanate (213 g, 90%) as a beige solid; m.p. = 137°C .

FTIR (KBr; cm^{-1}): 3020, 2923, 2270 (ν_{OCN}), 1478, 1178, 1139, 1026, 815, 764. ^1H NMR (CDCl_3 ; δ , ppm): 7.1 (s, 4H, C_6H_2), 6.8 (s, 4H, C_6H_4), 3.8 (s, 4H, CH_2), 2.2 (s, 12H, CH_3). ELEM. ANAL. Calcd for $\text{C}_{26}\text{H}_{24}\text{O}_2\text{N}_2$: C, 78.79%; H, 6.06%; O, 8.08%; N, 7.07%; Found: C, 78.95%; H, 6.14%; O, 7.96%; N, 6.95%. MS (EI, m/z , % relative intensity): 396 (M^+ , 35), 381 (M-15, 11), 354 (M-42, 27), 236 (M-160, 26).

Preparation of cured cyanate resins

The $\text{Co}(\text{AcAc})_2$ catalyst (at the concentration of $4.62 \text{ mmol mol}^{-1}$ ($\text{Co}(\text{AcAc})_2/\text{dicyanates}$) was pre-dissolved in nonylphenol (nonylphenol at the concentration of 3% of the total resin weight), then added to the melted BBZCy monomer or BADCy prepolymer with continuously stirring, to obtain homogeneous mixture. The mixture was then poured directly into the preheated molds (100°C) and degassed the entrapped air or any volatiles. The CEs were trimerized by thermal curing in an air convection oven according to the cure schedule: 180°C for 4 h, 200°C for 1 h, and finally 230°C for 3 h. The cured resins were ejected from the molds then cut and polished according the dimension requirements for the property measurements.

MEASUREMENTS

Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet 5700 in the form of pellet with KBr. Mass spectra were recorded using Micromass GCT (Micromass) mass spectrometer. ^1H NMR spectra were carried out on the DRX500 spectrometer (Bruker). The spectra were determined in chloroform- d_1 with tetra-methylsilane as an internal standard. Elemental analysis was determined with an Elementar Vario EL III elemental analyzer. Differential scanning calorimetric (DSC) analysis was performed on a TA Instruments modulated DSC 2910 thermal analyzer at a heating rate of $10^\circ\text{C min}^{-1}$ under flowing nitrogen ($50 \text{ cm}^3 \text{ min}^{-1}$). Glass transition temperature (T_g) was measured by a TA DMA 2980 Dynamic Mechanical Analyzer at a frequency of 1 Hz and a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere. The coefficient of thermal expansion was obtained from samples with the length of 10–20 mm at a heating rate

of $5^{\circ}\text{C min}^{-1}$ by TMA mode of NETZSCH DIL 402PC. TGA was performed on a NETZSCH STA 409 thermal analyzer at a heating rate of $10^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere from 25 to 800°C .

Dielectric measurements were performed with an Agilent 4991B measurement at room temperature by the two-parallel-plate mode. The applied voltage was 200 mV.

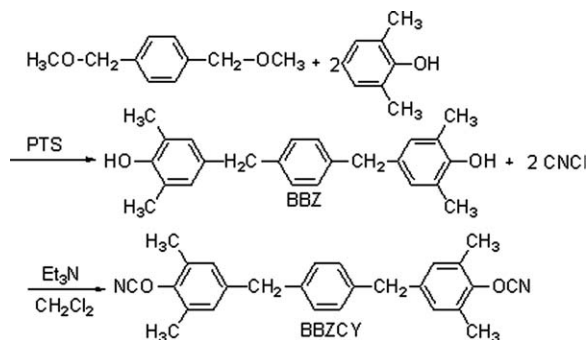
The instrument was calibrated with polytetrafluoroethylene (PTFE) sample provided by the manufacturer. Before being tested the samples ($2 \times 2 \text{ cm}^2$ and 0.2 cm thickness) were dried under vacuum at 100°C for 8 h.

Long-term water absorption was performed as follows: the samples were dried *in vacuo* at 120°C until constant weight. Then the dried samples were immersed in the boiling distilled water for the duration of the study. For weighting, Samples were taken out of the bath and surface moisture removed with a dry cloth. The water absorption was calculated as follows: $\text{weight gain} = (W/W_0 - 1) \times 100\%$, where W is the weight of a sample after it was placed in the boiling water for some time and W_0 was the weight of a sample before it was placed in the boiling water.

RESULTS AND DISCUSSION

Characterization of BBZ

BBZ, the intermediate (phenolic precursor) of cyanate ester, is prepared via the reaction between excess 2,6-dimethylphenol and 1,4-bis(methoxymethyl)benzene in the presence of toluene-4-sulfonic acid (see Scheme 1). The pure BBZ is obtained by precipitation and the supposed structure is confirmed by spectroscopy methods. In the IR spectrum of BBZ (see Fig. 2), the OH characteristic absorption peak at 3410 cm^{-1} can be observed. $^1\text{H NMR}$ spectrum of BBZ is shown in Figure 3. Protons of methyl group are at 2.19 ppm. The signal of 3.8 ppm is from the methylene protons. The aromatic protons on phenylene ring and phenoxy ring can be observed at 7.1 and 6.8 ppm, respectively. The hydroxyl protons are detected at 4.5 ppm. Its elemental



Scheme 1 Synthesis of BBZ and BBZCY.

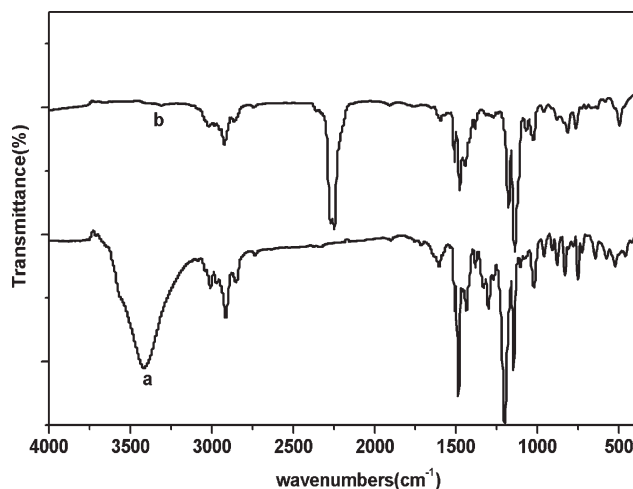


Figure 2 IR spectrum of (a) BBZ and (b) BBZCY.

analysis is in good agreement with the calculated values. Figure 4 is the mass spectrum of BBZ. The characteristic peaks of $\text{C}_{24}\text{H}_{26}\text{O}_2$ at 346, $(\text{M}-\text{CH}_3)^+$ at 331 and $(\text{M}-195)^+$ at 211 are observed. These results are consistent with the proposed structure of BBZ.

Characterization of BBZCY

The reaction mechanism of BBZCY may be a two-step process. In the first step, the bisphenol precursor BBZ was synthesized according to Scheme 1. In the second step, BBZ reacted with CNCN in the presence of triethylamine (an acid acceptor) and dichloromethane (solvent) (see Scheme 1), to convert into the resulting dicyanate. This reaction was carried out by prereacting BBZ with the triethylamine before the cyanogen chloride was added at -5 – 0°C . This modified synthetic routine reduces the formation of the diethylcyanamide byproduct.¹⁷ Triethylamine has been reported as a trimerization catalyst and another possible impurity that could contribute to the cure catalysis.¹⁸ In the synthesis of BBZCY, the resulting mixture was washed with the sulfuric acid solution which could reduce the triethylamine content.¹⁹

The IR spectrum of BBZCY exhibits several distinctive absorptions, as shown in Figure 2. The absorption peaks at 2273 and 2240 cm^{-1} are designated to $-\text{O}-\text{C}\equiv\text{N}$ stretching vibration. Compared with the IR spectrum of BBZ, the OH absorption peak at 3410 cm^{-1} is absent, which implies that phenolic OH has completely transformed into $-\text{O}-\text{C}\equiv\text{N}$. The $^1\text{H NMR}$ spectrum of BBZCY is shown in Figure 5. The same signal pattern as in BBZ is observed except for the disappearance of the signal corresponding to the hydroxyl protons. Assignments of Chemical shifts are as follow: 2.19 ppm (methyl protons), 3.82 ppm (methylene protons), 6.8 ppm (phenyl protons on the phenol ring),

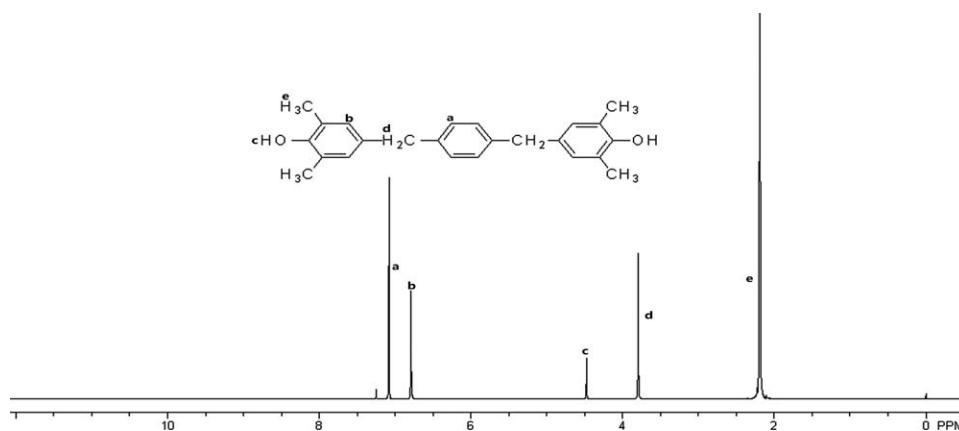


Figure 3 ^1H NMR spectrum of BBZ.

and 7.1 ppm (phenyl protons on the benzene ring). The elemental analysis is in good agreement with the calculated values. Figure 6 shows the mass spectrum of BBZCy with The peak of $\text{C}_{26}\text{H}_{24}\text{O}_2\text{N}_2$ at 396, $(\text{M}-\text{OCN})^+$ at 354 and $(\text{M}-160)^+$ at 236. The structure of BBZCy is confirmed by the spectral analyses and elemental analysis.

DSC analysis

The cure behavior of dicyanate ester is characterized by DSC. Figure 7 represents the DSC scans of dicyanate esters and the data are presented in Table I, including T_i (the cure onset temperature), T_{max} (the maximum cure temperature), and T_f (the cure end temperature). We observe an endothermic transition at $\sim 137^\circ\text{C}$ (the melting point), an exothermic transition onsetting at around 244°C and peaking at 312°C for neat BBZCy resin. Neat BADCy resin, being a prepolymer, exhibits only an exothermic transition for the neat-curing process beginning at $\sim 230^\circ\text{C}$ and peaking at about 275°C . When the catalyst is added, BBZCy resin shows the melting point (134°C), an exothermic transition starting at 194°C and a broad exothermic peaking at 273°C , whereas BADCy prepolymer exhibits an exothermic peak

beginning at around 157°C and peaking at 217°C . These thermograms indicate that the addition of the cobalt catalyst and the nonyl phenol cocatalyst lowers the initial curing temperature by about 50 and 43°C , respectively. In the presence of metal ion, the cyanate groups are believed to be coordinated easily through the metal ion to allow ring closure through a step growth or ionic path. The nonyl phenol cocatalyst is to be active hydrogen donor.²⁰

DMA

Dynamic mechanical analysis is a powerful technique measuring the glass transition temperature (T_g), particularly for polymers with rigid backbones. The peak temperature of $\tan \delta$ is assumed to be T_g because a large decrease in the storage modulus (E') occurred at the point. Figure 8 shows the dynamic analyses of cured BBZCy and cured BADCy at a heating rate of 10 K min^{-1} . These two CE resins show slightly different dynamic behaviors [storage modulus (E') and $\tan \delta$, loss tangent] by DMA. Because of the introduction of bulkier *p*-xylene moiety in the backbone and the *ortho*-methyl group, judging from the functionalities of CE resins, the

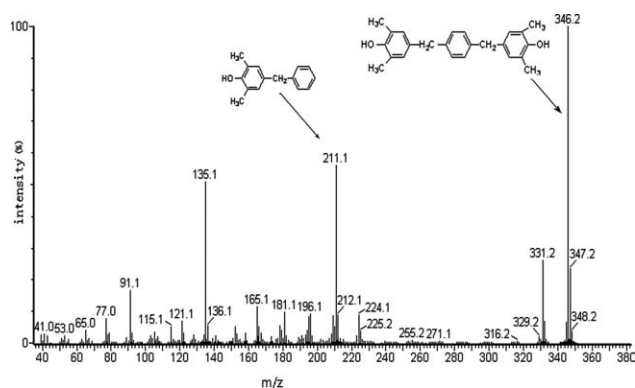


Figure 4 Mass spectrum of BBZ.

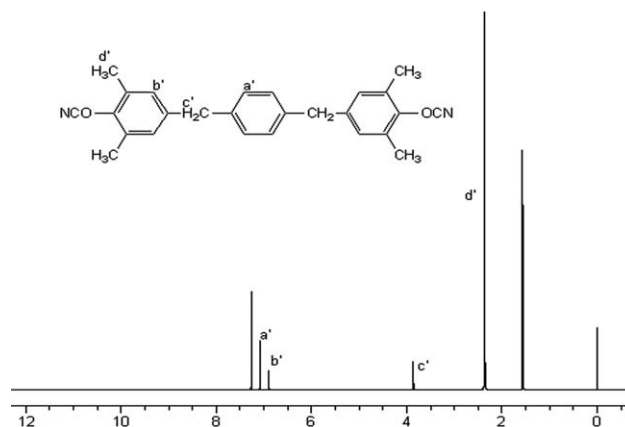


Figure 5 ^1H NMR spectrum of BBZCy.

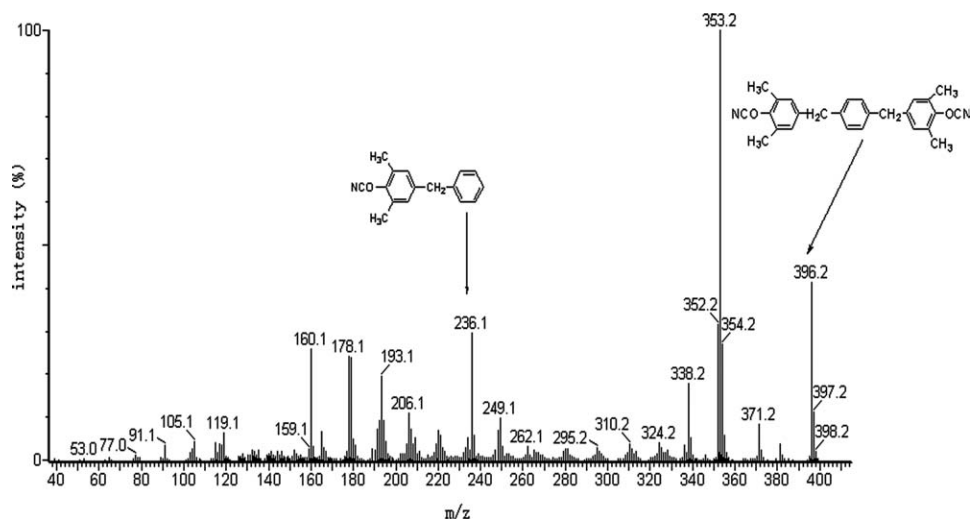


Figure 6 Mass spectrum of BBZCy.

crosslinking density of cured BBZCy is lower than that of cured BADCy. Therefore, the cured BADCy retained higher E' at both low and high temperature than that of cured BBZCy. The T_g value of cured BADCy resin is also higher than that of cured BBZCy resin. The $\tan \delta$ means that the ability of losing energy for the deformation for sample while heating. It is observed that as temperature increases, the loss tangent goes through a maximum in transition region and then decreases in the rubbery region. In the transition region, the loss tangent is high due to the initiation of the micro-Brown motion of the molecular chain segments and their stress relaxation. The position and height of $\tan \delta$ are indicative of the structure and properties of the material.²¹ The incorporation of stiffer *p*-xylene moiety in the backbone made BBZCy resin deform more difficultly than

BADCy resin, so the peak $\tan \delta$ of BBZCy resin is lower than that of BADCy resin.

TGA

TGA is the most favored technique for rapid evaluation in tracing and ranking the thermal stability and thermal degradation behavior of various polymers. The TGA thermograms of cured BBZCy and cured BADCy in nitrogen atmosphere are shown in Figure 9. $T_{5\%}$ is defined as the temperature at which the weight loss is 5% and is considered as the onset temperature for cured cyanate ester resins for comparative purposes. The relative thermal stability of the cured resins are compared by the temperature of 5% weight loss ($T_{5\%}$), and as listed in Table II, the temperatures of maximum weight loss rate and percentage char yields at 800°C are also presented in the same table. As expected, the cured cyanate ester resins showed good thermal stability, due to the triazine rings formed during curing. Cured BBZCy and cured BADCy exhibit a 5% weight loss temperature ($T_{5\%}$) at 420 and 427°C, respectively, (Fig. 9). Commonly in other published work, BADCy resin showed two stages of weight loss, which was

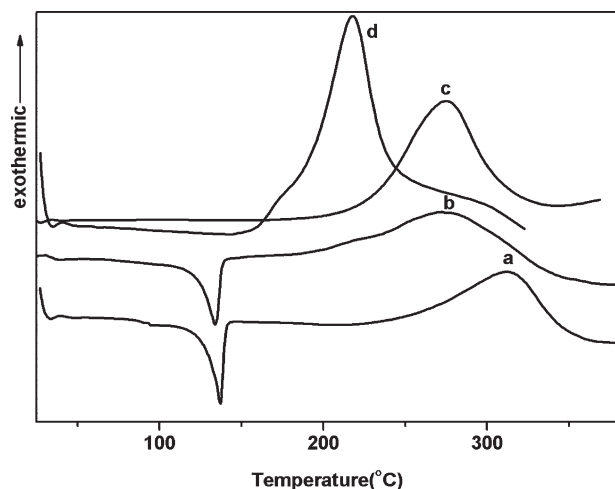


Figure 7 DSC thermograms of (a) neat BBZCy; (b) catalyzed BBZCy; (c) neat BADCy prepolymer; (d) catalyzed BADCy prepolymer.

TABLE I
DSC Analyses for Various Dicyanate Monomers

Sample	T_m (°C)	T_i (°C) ^a	T_{max} (°C) ^b	T_f (°C) ^c	ΔH (J g ⁻¹)
Neat BBZCy	137	244	312	362	-335
Catalyzed BBZCy	134	194	273	345	-383
Neat BADCy	-	230	275	332	-360
Catalyzed BADCy	-	157	218	320	-416

^a Onset temperature for curing reaction.

^b Maximum temperature of polymerization exotherm.

^c Temperature corresponding to the end of curing reaction.

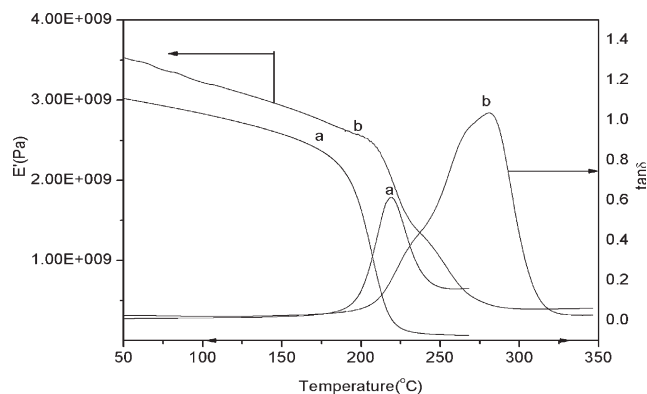


Figure 8 DMA scans of (a) cured BBZCy and (b) cured BADCy.

reflected by the two peak temperatures in the first derivative weight loss curve (DTG) (Fig. 10) and the degradation peak temperature at 452°C. BBZCy resin had one stage of weight loss and the degradation peak temperature was 449°C. It is generally accepted that the degradation mechanism of cyanate ester resins proceeds in several stages including the random scission and crosslinking between 400 and 450°C, decyclization of the triazine ring between 450 and 500°C, and decomposition of the primary residue between 500 and 750°C.^{22,23} The degradation process for BBZCy resin may be different from BADCy resin and further research is necessary to do.

Thermomechanical analysis (TMA)

Internal stress is one of the major reason for the failure of electronic encapsulation. To increase the reliability of encapsulation, internal stress must be reduced which results from the difference in the coefficient of thermal expansion (CTE) between the silicon and encapsulation material. Thermally induced dimension changes of cured resins were

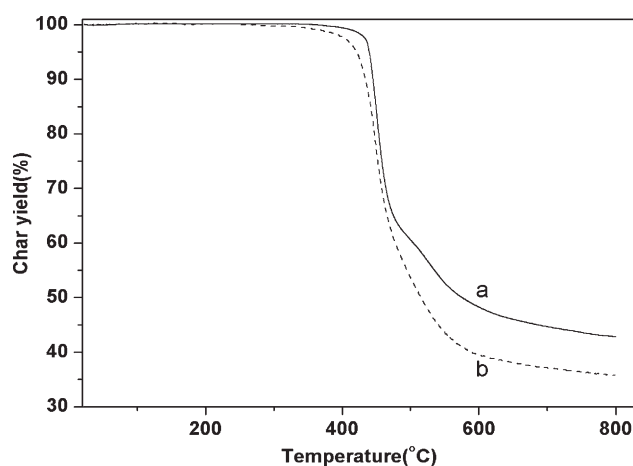


Figure 9 TGA thermograms of (a) cured BADCy and (b) cured BBZCy.

TABLE II
Thermal Degradation Results of Different Dicyanate Ester Resins

Resins	$T_{5\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	Char yield(%) at 800°C
Cured BBZCy	420	449	–	35.7
Cured BADCy	434	452	524	39.8

investigated by thermomechanical analyzer. The results of thermomechanical analyses (TMAs) are listed in Table III. The coefficients of thermal expansion (CTE) (before T_g) of the BBZCy resin and BADCy resin are $5.45 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ and $6.24 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$, respectively. Because of *p*-xylene moiety and *ortho*-methylation, BBZCY has lower crosslink density and larger free volume of resins than BADCy, increasing the coefficients of thermal expansion. However, the conjugated structure in BBZCy led by the introduction of *p*-xylene moiety makes the chain motion very difficult. The effect from conjugated structure compensates for the effect of the free volume. Therefore the coefficient of thermal expansion of BBZCy is lower than that of BADCy.

Moisture absorption

Absorbed moisture has an effect on dielectric, thermal, and mechanical properties of resins. Because of the water's contribution to polarization and energy dissipation, the dielectric constant of laminate board materials will be increased. Moisture absorption will also reduce T_g of a laminate material. In addition, moisture absorption is a serious problem both in printed circuit board fabrication and during population and soldering, causing delamination in all operations above 100°C.²⁴ The maximum moisture absorption for PCB laminates (laminare thickness

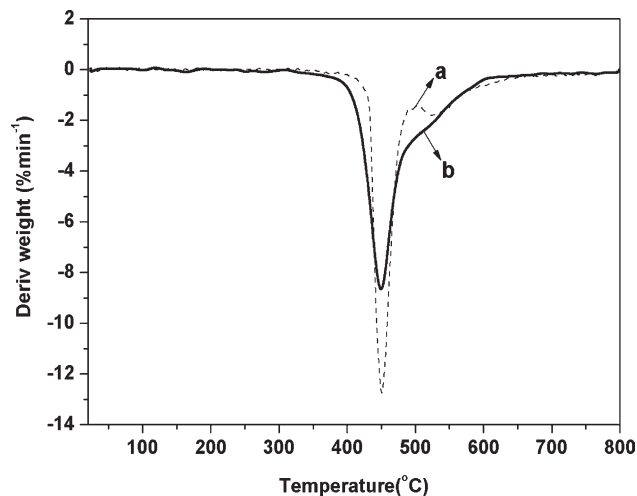


Figure 10 DTG thermograms of (a) cured BADCy and (b) cured BBZCy.

TABLE III
DMA and TMA of Cured BBZCy and BADCy

Sample	T_g ($^{\circ}\text{C}$) ^a	CTE ($10^{-5}/^{\circ}\text{C}$, $T < T_g$) ^b	Tan δ ^c
BBZCy	219	5.45	0.61
BADCy	280	6.24	1.03

^a From DMA.

^b Determined by TMA at a heating rate of $5^{\circ}\text{C min}^{-1}$.

^c Tan δ value at T_g .

< 0.5 mm) is lower than 0.8%.²⁵ The resin matrix has an influence on the moisture absorption of PCB laminates. Therefore, the low moisture absorption of CE resins is necessary for PCB laminate materials. CE resins, with weak dipoles and the absence of hydrogen bonding, are characteristic of low moisture absorption properties. Figure 11 shows the water absorption plot versus time. Compared with BADCy resin, water absorption of BBZCy resins appears to level off after about 10 h immersed in boiling water. The moisture absorption of CE resins is a function of inherent polarity of CE resins and crosslinking density. Although the introduction of *p*-xylene moiety and four methyl groups lowers the crosslinking density, the hydrophobic effect of *p*-xylene and four methyl groups will lower the water absorption effectively.²⁶ Therefore, the water absorption of cured BBZCy is much lower than that of cured BADCy.

Dielectric constant and dielectric dissipation

Table IV shows dielectric constants (D_k) and dissipation factors (D_f) of cured CE resins. The dielectric constants of cured BBZCy and BADCy at 1 GHz are 2.66 and 2.98, respectively. The dissipation factors of cured BBZCy and BADCy is 0.0054 and 0.0083, respectively. In BBZCy, the introduction of low polar

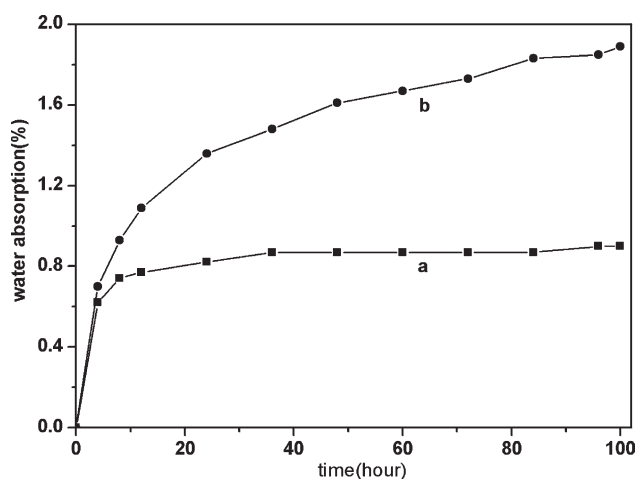


Figure 11 Plots of the weight of water absorbed over timer for (a) cured BBZCy and cured BADCy immersed at 100°C .

TABLE IV
Dielectric Properties and Moisture Absorption of Cured BBZCy and BADCy

Sample	D_k (1 GHz)	Tan δ (1 GHz)	Moisture absorption (%)
BBZCy	2.66	0.0054	0.8
BADCy	2.98	0.0083	1.89

p-xylene moiety linkage increasingly lowered D_k by diluting dipole concentrations and decreasing electronegativity of the substituted benzene ring. Moreover, four bulky *ortho*-methyl groups of BBZCy also significantly lowered D_k by shielding and weakening the C–O, C–N, and C=N dipoles. Therefore, BBZCy resin has lower D_k and D_f than BADCy.

CONCLUSIONS

A novel, *ortho*-methylated dicyanate containing *p*-xylene moiety was successfully synthesized by the reaction of cyanogen chloride with BBZ. The cured BBZCy resin has lower T_g than the BADCy system. The thermal stability of cured BBZCy resin is slightly less stable than that of the BADCy system. At the same time, BBZCy resin has lower CTE, lower dielectric constant (2.66 at 1 GHz), and dissipation factor (0.0054 at 1 GHz) than that of BADCy resin. The water absorption of cured BBZCy resin (0.8%) is lower than that of cured BADCy resin (1.8%). The combination of low CTE, low dielectric constant, low dissipation factor, and outstanding water resistance makes BBZCy a promising candidate for printed circuit board and electronic encapsulation applications.

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