

# Dielectric and Thermal Properties of Polymer Network Based on Bismaleimide Resin and Cyanate Ester Containing Dicyclopentadiene or Dipentene. III

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**ABSTRACT:** A series of bismaleimide-triazine (BT) resins were prepared from commercial bismaleimide (DDMBMI) and 2,6-dimethylphenol-dicyclopentadiene dicyanate ester (DCPDCY) or 2,6-dimethylphenol-dipentene dicyanate ester (DPCY). The thermal properties of cured BT resins containing DCPD or DP were studied using a dielectric analyzer (DEA), dynamic mechanical analyzer (DMA), and thermal gravimetric analyzer (TGA). These data were compared with that of DDMBMI cured with bisphenol A dicyanate ester

(BADCY). The cured DDMBMI/DCPDCY or DDMBMI/DPCY exhibits a lower dielectric constant, dissipation factor, and moisture absorption than those of DDMBMI/BADCY. The effects of blend composition on the glass transition temperatures and thermal stability are discussed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1942–1951, 2007

**Key words:** thermosets; curing of polymers; crosslinking; dielectric properties; thermal properties; performance polymers

## INTRODUCTION

Conventional electronic circuit boards are made from glass-fiber reinforced epoxy resins. However, they often fall short of the thermal and electrical performance demands of many modern high-speed devices. With current trends toward increased circuit densities, shorter propagation delays, elevated operating temperatures, and higher reliability, advanced materials such as bismaleimide (BMI),<sup>1,2</sup> cyanate ester (CE),<sup>3–5</sup> and bismaleimide-triazine (BT) resins<sup>6–10</sup> are required to satisfy these demands. Among these materials, bismaleimide-triazine is considered to be the most promising system.

Skylex BT resins are marketed by Mitsubishi Gas and Chemical (Tokyo, Japan), which comprise blends of 4,4-bismaleimidodiphenylmethane (DDMBMI) and the dicyanate of bisphenol A (2,2-bis(4-cyanatophenyl)isopropylidene) in the form of BT resins.<sup>11,12</sup> These resins have substantially better resistance to catastrophic loss of insulation resistance than the current epoxy or bismaleimide systems. With superior properties, such as reduction in moisture absorption, excel-

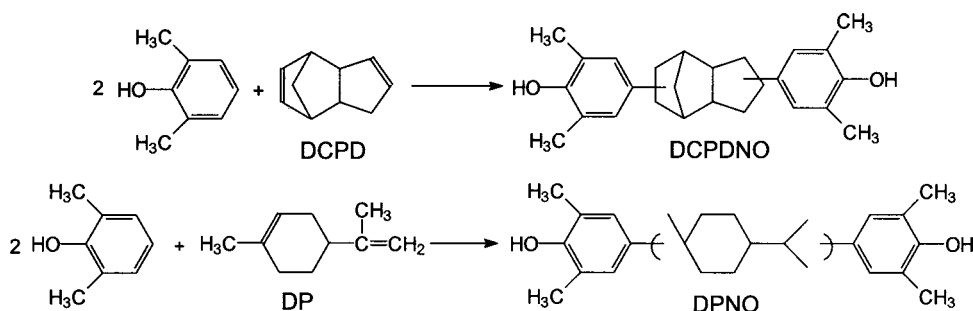
lent chemical resistance, good dimensional stability, low dielectric constant, and low dielectric loss, BT resins are attractive as substrate for circuit boards and semiconductor encapsulants applications for which high reliability is critical.

Dicyclopentadiene (DCPD) is a byproduct of C<sub>5</sub> streams in oil refineries, and is a raw material for low dielectric polymers due to their low polarity, low moisture absorption, and relatively low cost. Dipentene (DP), similar to DCPD, a cheap byproduct from naphtha cracking, is inexpensive and has a functional group (C=C) similar to DCPD. Nelson et al.,<sup>13</sup> Hiroaki et al.,<sup>14</sup> and Wang et al.<sup>15,16</sup> synthesized low dielectric DCPD containing epoxy resins derived from the novolac of phenol and dicyclopentadiene in the presence of a Lewis acid and then converted the resulting novolacs to epoxy resins. A large cycloaliphatic moiety [dipentene (DP)] has been incorporated into a polymer backbone.<sup>17</sup> In our previous studies,<sup>18,19</sup> 2,6-dimethyl phenol-dicyclopentadiene novolac and 2,6-dimethyl phenol-dipentene novolac were synthesized from dicyclopentadiene, dipentene, and 2,6-dimethyl phenol, and then converted to the corresponding epoxy resin by reaction with epichlorohydrin. The experimental results show that DCPD-containing and DP-containing epoxies exhibit a low dielectric constant and low moisture absorption. The results led us to do more research on DCPD and DP.

Although many studies have been devoted to BT resins, few concern BT resins containing a DCPD or DP structure. The object of this research was to investigate

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**Scheme 1** The synthetic equation of DCPDNO and DPNO.

the curing characteristics of a series of novel BT resins that were prepared from the commercial 4,4-bismaleimidophenyl methane (DDMBMI) and DCPD-containing or DP-containing dicyanate esters. The resulting BT resins were expected to have a lower dielectric constant and moisture absorption than commercial BT resins based on DDMBMI/bisphenol A dicyanate ester because of the DCPD and DP unit in the backbone structure, and to also retain the attractive thermal and mechanical properties. The dielectric properties, thermal properties, dynamic mechanical analysis, and moisture resistance of the cured BT resins were also investigated to understand the structure-properties relationship.

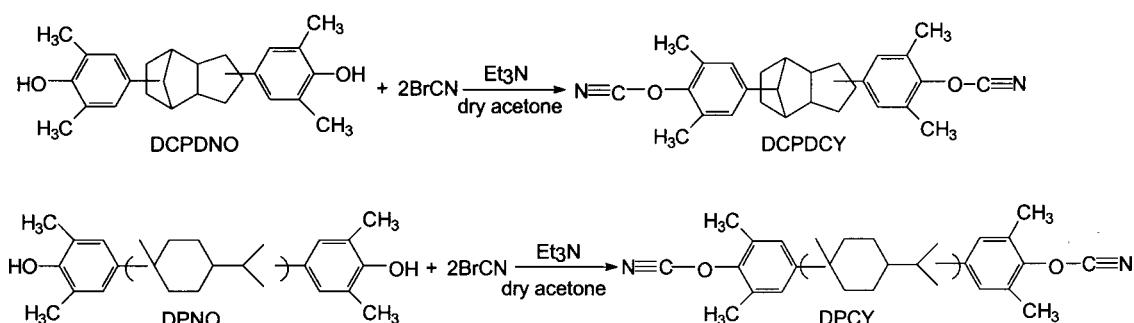
## EXPERIMENTAL

### Materials

2,6-Dimethylphenol, dicyclopentadiene (DCPD), dipentene (DP), anhydrous aluminum chloride, and molecular sieve were purchased from Acros (Somerville, NJ). Cyanogen bromide (Br-CN) was purchased from Showa Chemical (Tokyo, Japan). 4,4-Bismaleimidodiphenylmethane (DDMBMI) was purchased from TCI (Portland, OR). BADCY (B-10) was kindly supplied by Rhone-Poulenc (Santa Clara, CA). Triethylamine was purchased from Ferak (Berlin, Germany). Acetone was purchased from TEDIA (Fairfield, OH) and stored in a 4 Å molecular sieve. The other solvents used were commercial products (LC grade) and used without further purification.

### Measurements

Differential scanning calorimetry (DSC) scans were obtained from samples of about 5–10 mg in a nitrogen atmosphere ( $20 \text{ cm}^3 \text{ min}^{-1}$ ) at a heating rate of  $10^\circ\text{C}/\text{min}$  using a Perkin-Elmer (Norwalk, CT) DSC 7. TGA was performed with a Perkin-Elmer TGA 7 at a heating rate of  $20^\circ\text{C}/\text{min}$  under nitrogen ( $20 \text{ cm}^3 \text{ min}^{-1}$ ) from  $30^\circ\text{C}$  to  $800^\circ\text{C}$ . DMA was carried out with a Perkin-Elmer DMA 7e. The storage modulus  $E'$  and  $\tan \delta$  were determined as the sample was subjected to temperature scan mode at a programmed heating rate of  $10^\circ\text{C}/\text{min}$  from ambient to  $350^\circ\text{C}$  at a frequency of 1 Hz and an amplitude of  $6 \mu\text{m}$ . A sample 15 mm in length, 10 mm in width, and  $\sim 1.5$  mm in thickness was used. The test method was performed by three-point bending mode with a tension ratio at 110%. Dielectric measurements were performed with an Agilent (Palo Alto, CA) 4291B measurement system at a temperature of  $30^\circ\text{C}$  by the two parallel plate mode at 1M or 1G Hz. The applied voltage was 1 volt. Before testing, samples ( $1 \times 1 \text{ cm}^2$  and 0.3 cm thickness) were dried under vacuum at  $100^\circ\text{C}$  for 8 h. Moisture absorption was tested as follows: Samples at  $1 \times 1 \text{ cm}^2$  and 0.1 cm thickness were dried under vacuum at  $120^\circ\text{C}$  until the moisture was expelled. After cooling to room temperature, the sample was weighed and then placed in  $100^\circ\text{C}$  water for 48 h and weighed. The moisture absorption was calculated as percent weight gain =  $(W/W_0 - 1) \times 100\%$ , where  $W$  = weight of sample after placing in  $100^\circ\text{C}$  water for 48 h, and  $W_0$  = weight of sample before placing in water.



**Scheme 2** The synthetic equation of DCPDCY and DPCY.

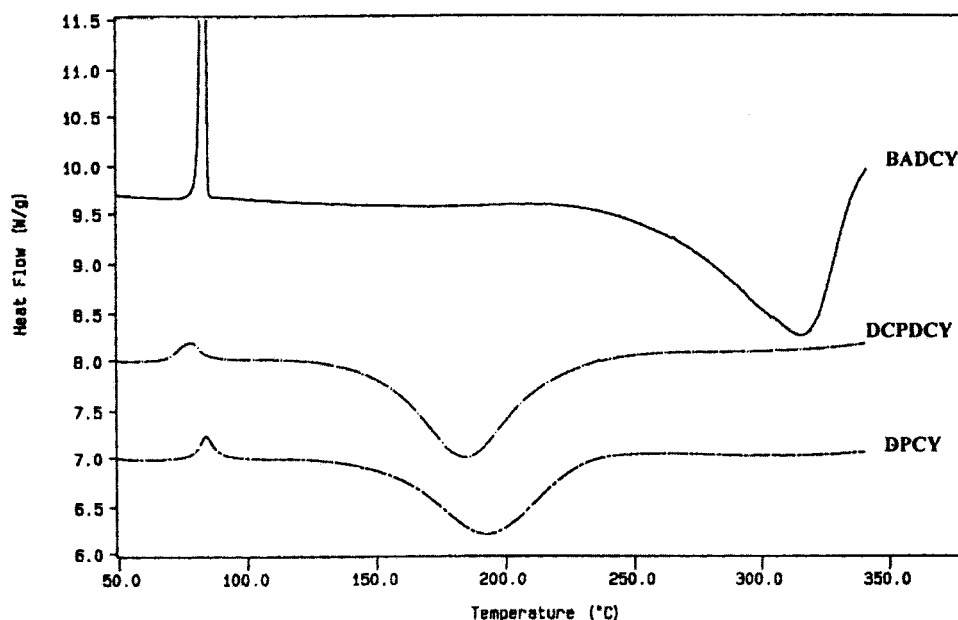


Figure 1 DSC analysis with a heating rate of 10°C/min for various cyanate esters: BADCY, DCPDCY, DPCY.

### Monomer synthesis

General procedure for the synthesis of novolac compounds

A 0.7143 mol of 2,6-dimethylphenol and 0.015 mol of  $\text{AlCl}_3$  were added to a four-necked round-bottomed flask equipped with a nitrogen inlet, heating mantle, stirrer, thermocouple, and temperature controller. The reaction mixture was gradually heated to 120°C, 0.1 mol of DCPD or 0.1 mol of DP was added gradually over a period of 2 h, and the mixture was maintained at 120°C, for another 4 h. After the reaction was completed, 0.06 mol of 5 wt %  $\text{NaOH}_{(aq)}$  was added and the mixture was stirred for 1 h. The reaction mixture was filtered and the filtrate was washed three times with water. Next, the organic phase was separated and distilled in a rotary evaporator to remove excess 2,6-dimethylphenol. The crude products were dissolved in toluene and extracted with water several times. The organic phase was distilled to remove toluene and water and a deep-brown 2,6-dimethylphenol-DCPD novolac (DCPDNO) or pale-yellow 2,6-dimethylphenol-DP novolac (DPNO) were obtained in almost quantitative yield. The reaction equation is shown in Scheme 1.

DCPDNO: Yield: 91%, IR (KBr)  $\text{cm}^{-1}$ : 3400 ~ 3230  $\text{cm}^{-1}$  (—OH), 1450 ~ 1490  $\text{cm}^{-1}$  (aromatic ring),  $^1\text{H-NMR}$   $\delta$  (ppm): 7.9(s, 2H, —OH), ~ 6.75(m, 4H, aromatic), 0.7(s, 12H, —CH<sub>3</sub>), 1.2 ~ 2.5(m, 14H, -aliphatic). Elemental analyses for  $\text{C}_{26}\text{H}_{32}\text{O}_2$ : C: 82.90%, H: 8.60%, O: 8.50% (theoretical) and C: 82.73%, H: 8.50%, O: 8.77% (experimental). FAB mass spectrometry (FABMS;  $m/z$ ): 376 (62,  $\text{M}^+$ ).

DPNO: Yield: 89%, IR (KBr)  $\text{cm}^{-1}$ : 3755 ~ 3066  $\text{cm}^{-1}$  (—OH), 1450 ~ 1490  $\text{cm}^{-1}$  (aromatic ring),  $^1\text{H-NMR}$   $\delta$  (ppm): 7.85(s, 2H, —OH), 6.60 ~ 6.87(m, 4H, aromatic), 0.4 ~ 3.2(m, 30H, -aliphatic). Elemental analyses for  $\text{C}_{26}\text{H}_{36}\text{O}_2$ : C: 82.10%, H: 9.50%, O: 8.40% (theoretical) and C: 81.89%, H: 9.59%, O: 8.52% (experimental). FAB mass spectrometry (FABMS;  $m/z$ ): 380 (30,  $\text{M}^+$ ).

General procedure for the synthesis of cyanate ester compounds

The dicyanate monomer was synthesized using a modified procedure reported by Hwang and Wang<sup>7</sup> (Scheme 2). To a 250-mL four-necked flask was charged 75 mL of acetone and cooled to -25°C. Then 25 g of cyanogen bromide ( $\text{BrCN}$ , 0.236 mole) was dissolved in acetone and maintained at -25°C with stirring. Under nitrogen atmosphere, 0.104 mole of novolac and 0.21 mole of triethylamine in 25 mL anhydrous acetone was added dropwise into the flask and maintained at -15°C. After the addition was completed, the temperature was allowed to equilibrate to -5°C. The solution was filtered and washed with anhydrous acetone. To the filtrate was added 100 mL of  $\text{CH}_2\text{Cl}_2$  and washed with 10% of  $\text{NaCl}_{(aq)}$  and water. The organic

TABLE I  
DSC Analysis with a Heating Rate of 10°C/min  
for Various Cyanate Esters

Cyanate esters	$T_m$ (°C)	$T_i$ (°C)	$T_{exo}$ (°C)
BADCY	83	257	316
DCPDCY	78	161	188
DPCY	84	155	192

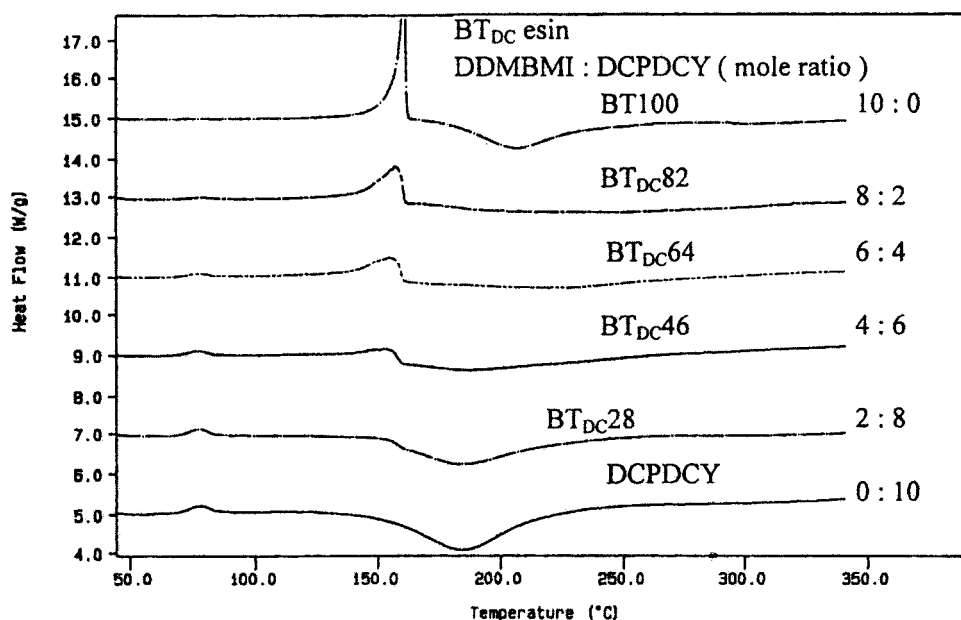


Figure 2 DSC analysis for various mole ratios of DDMBMI/DCPDCY ( $BT_{DC}$ ) resins.

layer was dried with anhydrous sodium carbonate and then evaporated in a rotary evaporator. The dicyanate monomer was obtained.

DCPDCY: Yield: 87%, IR(KBr)  $cm^{-1}$ : 1200 ~ 1220  $cm^{-1}$  (C-O-C), 1450 ~ 1490  $cm^{-1}$  (aromatic ring), 2235 ~ 2270  $cm^{-1}$  (—OCN), 2950 ~ 2975  $cm^{-1}$  (—CH<sub>3</sub>), <sup>1</sup>H-NMR  $\delta$  (ppm): 7.0 ~ 7.3(m, 4H, aromatic), 2.3(s, 12H, —CH<sub>3</sub>), 1.04 ~ 2.7(m, 14H, -aliphatic). Elemental analyses for C<sub>28</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>: C: 78.87%, H: 7.04%, N: 6.57%, O: 7.52% (theoretical) and C: 78.62%, H: 7.09%, N: 6.66%, O: 7.63% (experimental). FAB mass spectrum of DPCY with the peaks of C<sub>28</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub> at 426(23, M<sup>+</sup>), 279(16, M-147).

DPCY: Yield: 85%, IR(KBr)  $cm^{-1}$ : 1200 ~ 1220  $cm^{-1}$  (C-O-C), 1450 ~ 1490  $cm^{-1}$  (aromatic ring), 2235 ~ 2270  $cm^{-1}$  (—OCN), 2950 ~ 2975  $cm^{-1}$  (—CH<sub>3</sub>), <sup>1</sup>H-NMR  $\delta$  (ppm): 7.0 ~ 7.3(m, 4H, aromatic), 2.3(s, 12H, —CH<sub>3</sub>), 0.4 ~ 2.5(m, 18H, -aliphatic). Elemental analyses for C<sub>28</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub>: C: 78.10%, H: 8.00%, N: 6.50%, O: 7.40% (theoretical) and C: 77.86%, H: 8.01%, N: 6.53%, O: 7.60% (experimental). FAB mass spectrum of DPCY with the peaks of C<sub>28</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub> at 430(32, M<sup>+</sup>), (M-CN+1)<sup>+</sup> at 405.

#### DSC scans of uncured resins and their curing procedure

The DSC curves of BADCY, DCPDCY, and DPCY are shown in Figure 1 and curing characteristics are given in Table I. The melting temperature ( $T_m$ ), onset of exotherm ( $T_i$ ), and peaks of exotherm ( $T_{exo}$ ) were 83, 257, and 316°C for BADCY, 78, 161, and 188°C for DCPDCY, and 84, 155, and 192°C for DPCY, respectively. The lower exothermic temperature of DCPDCY and DPCY imply higher reactivity of DCPDCY and DPCY than that of BADCY.

Figure 2 shows the DSC scans for various mole ratios of DDMBMI/DCPDCY ( $BT_{DC}$ ) resins. Based on the DSC analyses, DDMBMI/dicyanate ester with mole ratios of 10/0, 8/2, 6/4, 4/6, 2/8, and 0/10 were mixed and then heated on a hotplate at about 150°C with continuous stirring until homogeneous solutions were obtained. The homogeneous mixture was cured in oven at 180°C for 2 h, 200°C for 8 h, and 220°C for another 5 h under dry nitrogen.

#### RESULTS AND DISCUSSION

The desired dicyanate ester monomers were synthesized in a previous study.<sup>5,20</sup> The first step is DCPD

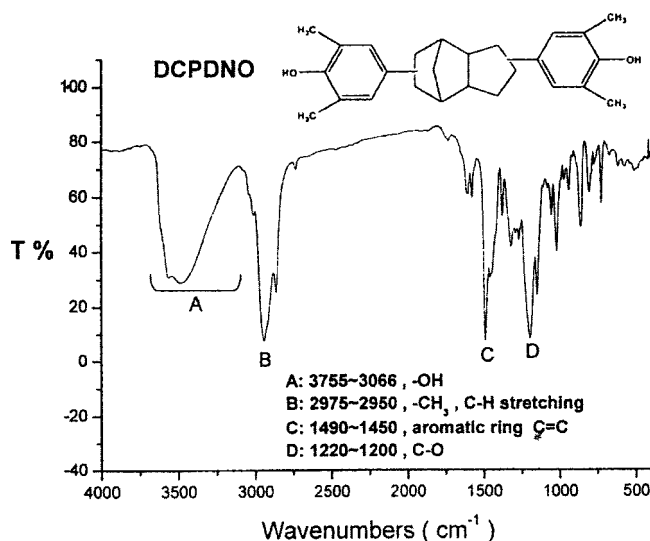


Figure 3 FT-IR spectrum of DCPDNO.

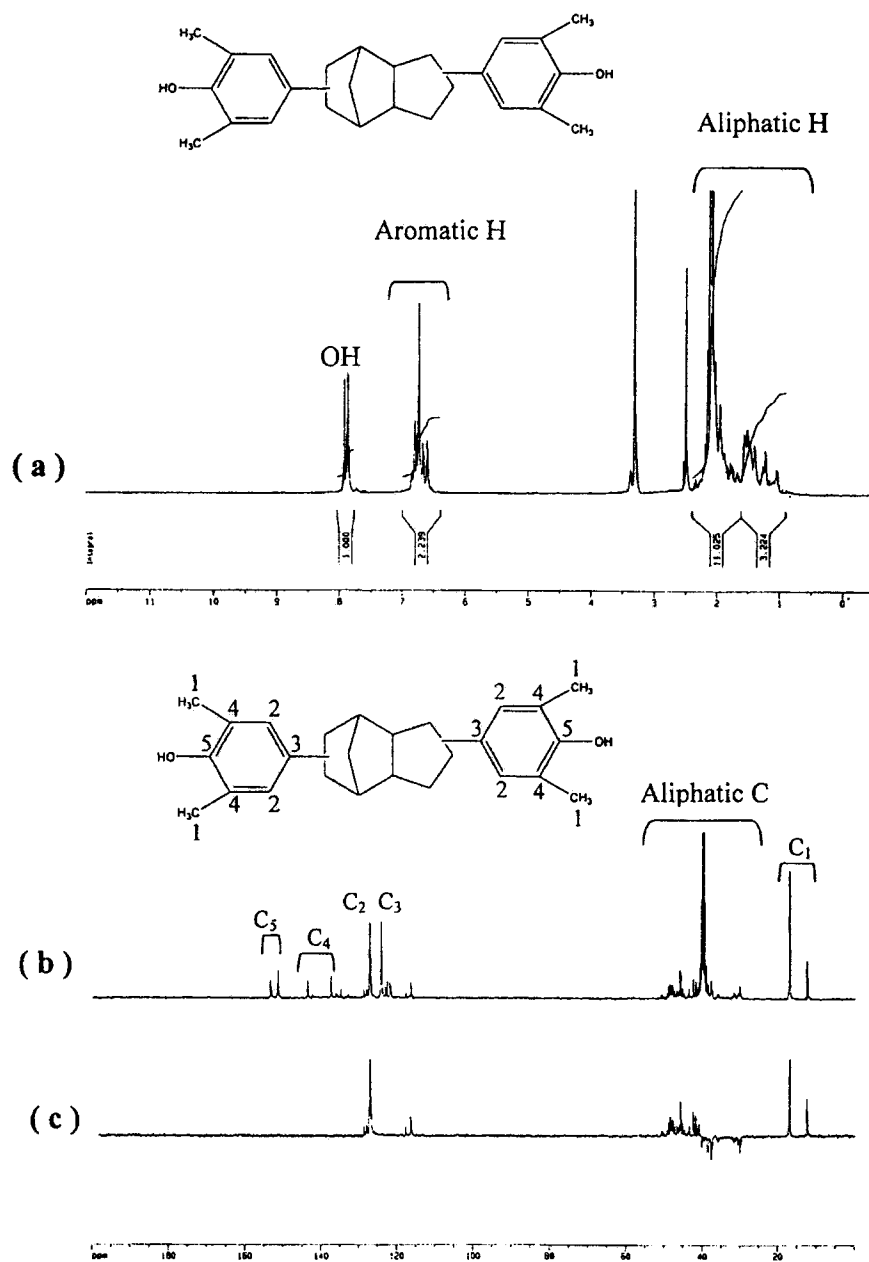


Figure 4  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and DEPT 135 spectra of DCPDNO.

or DP reacting with  $\text{AlCl}_3$  to form several different types of carbocations. The carbocations may react with the excess amount of 2,6-dimethylphenol to form DCPDNO or DPNO. The disappearance of a characteristic absorption peak of  $-\text{CH}=\text{CH}-$  at  $770\text{--}690\text{ cm}^{-1}$  and  $3040\text{--}3010\text{ cm}^{-1}$  on the IR spectra were used as criteria for the completion of reaction of DCPD or DP compounds. The typical IR spectra of 2,6-dimethylphenol DCPD novolac (DCPDNO) are shown in Figure 3. The characteristic absorption peaks of the aromatic ring at  $1490\text{--}1450\text{ cm}^{-1}$ , and OH absorption peaks around  $3755\text{--}3066\text{ cm}^{-1}$ , were observed. The structures of the intermediate novolacs were confirmed by IR,  $^1\text{H-NMR}$ , mass spectra, and elemental

analyses. The typical NMR spectra of 2,6-dimethylphenol-DCPD novolac (DCPDNO) are shown in Figure 4. The  $^1\text{H-NMR}$  signal at 5.4 and 5.9 ppm disappears due to the olefinic protons of the  $-\text{CH}=\text{CH}-$  functional groups reacting with 2,6-dimethylphenol. The characteristic peaks of saturated hydrogens at  $0.7 \sim 2.35\text{ ppm}$  and aromatic rings around  $6.65 \sim 7.83\text{ ppm}$  and the OH absorption peaks at 7.9 ppm were all observed. The  $^{13}\text{C-NMR}$  and DEPT135 spectra of DCPDNO are also shown in Figure 4. The  $4^\circ$  carbons  $\text{C}_3$ ,  $\text{C}_4$ ,  $\text{C}_5$  have disappeared in the DEPT135 spectrum.

The cyanate ester monomer formation is described in Scheme 2. The cyanate ester compounds were syn-

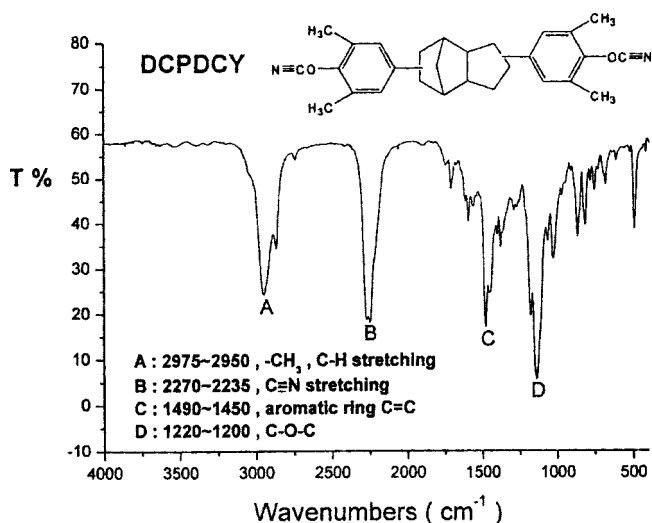
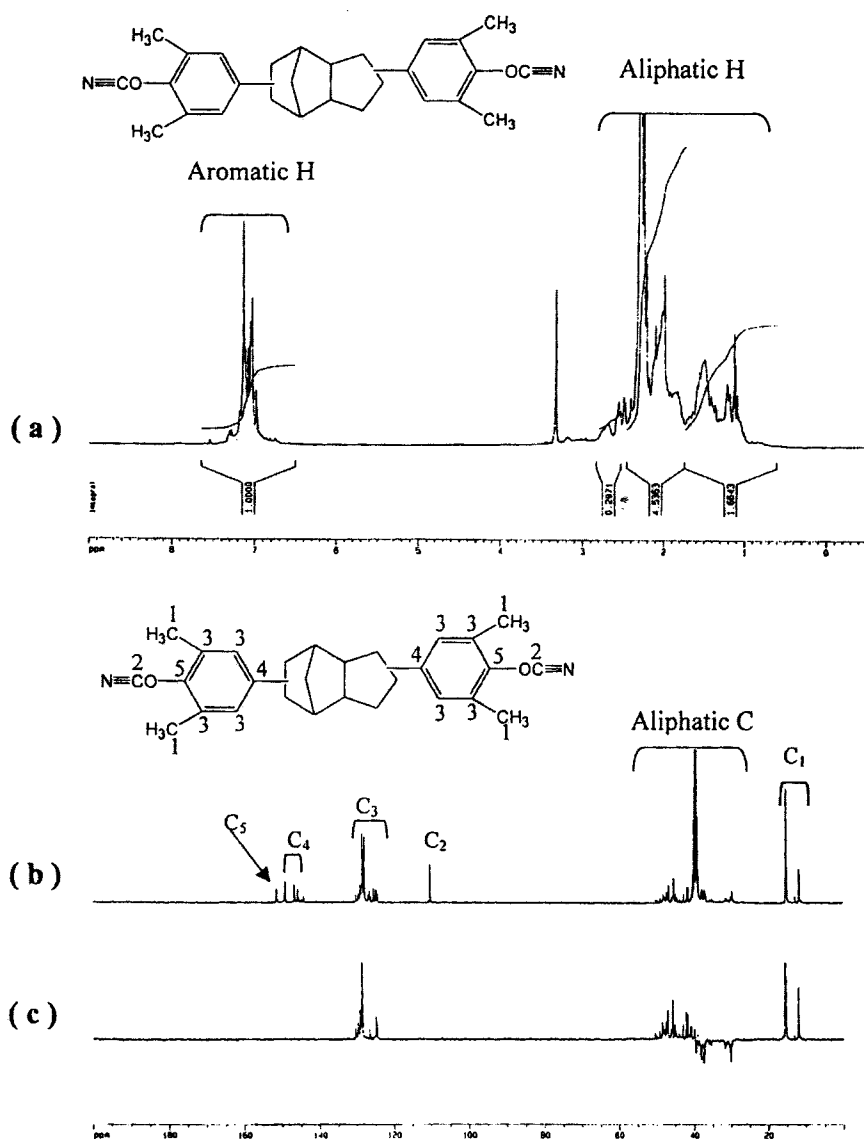


Figure 5 FTIR spectrum of DCPDCY.

thesized from novolac (DCPDNO or DPNO) and cyanogen bromide in the presence of triethylamine as an acid acceptor with acetone as a solvent. The reaction was exothermic and novolac was added slowly to keep the reaction at the desired rate. A high reaction temperature would lead to unwanted formation of diethyl cyanamide.<sup>21</sup> The typical infrared spectrum of the dicyanate ester (DCPDCY) exhibited several distinctive absorptions, as shown in Figure 5. The dicyanate showed strong absorptions at 2270 and 2235  $\text{cm}^{-1}$ , assigned to cyanate  $\text{C}\equiv\text{N}$  stretching vibration, and lacked the absorption at 3755–3066  $\text{cm}^{-1}$  associated with the phenolic OH stretching vibration. Consequently, the reaction could be monitored by means of these absorptions. The conversion of the DCPDNO monomer to dicyanate ester is shown in Figure 6 and confirmed by the disappearance of the phenolic proton in  $^1\text{H-NMR}$ . The  $^{13}\text{C-NMR}$  and DEPT135 spectra

Figure 6  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and DEPT 135 spectra of DCPDCY.

**TABLE II**  
Dielectric Constant( $D_r$ , U) at Room Temperature for Various Mole Ratio BT Resins

Bismaleimide/dicyanate ester (mole ratio)	DDMBMI/BADCY (BT)		DDMBMI/DCPDCY (BT <sub>DC</sub> )		DDMBMI/DPCY (BT <sub>DP</sub> )	
	1 MHz	1 GHz	1 MHz	1 GHz	1 MHz	1 GHz
10/0	4.03	3.89	4.03	3.89	4.03	3.89
8/2	3.94	3.62	3.69	3.56	3.69	3.58
6/4	3.52	3.30	3.38	3.29	3.50	3.29
4/6	3.27	3.05	3.10	3.01	3.13	3.06
2/8	3.22	3.01	2.83	2.76	2.84	2.79
0/10	2.95	2.92	2.58	2.53	2.61	2.56

of DCPDCY with the characteristic peak of the CN triple bond at  $\sim 110$  ppm, whereas the  $4^\circ$  carbons  $C_2$  (OCN) has disappeared in the DEPT135 spectrum. Because there are constitutional isomers for the 2,6-dimethylphenol adduct, the peaks are somewhat complex, especially for aliphatic carbons. However, they agree with the structure of the novolacs and cyanate esters.

#### Dielectric constant and dissipation factor

Tables II and III show the dielectric constants and dissipation factors of cured BT resins. The dielectric constants of cured BADCY, DCPDCY, and DPCY at 1 GHz are 2.92, 2.53, 2.56, respectively. The dissipation factors (mU) of cured BADCY, DCPDCY, and DPCY at 1 GHz are 24.33, 3.61, 5.95, respectively. No matter how much mole ratio of bismaleimide/dicyanate ester were used, the dielectric constants and dissipation factors of the BT<sub>DC</sub> and BT<sub>DP</sub> systems were lower than those of the bisphenol A system (BT system). The dielectric constant and dissipation factor decreased in the following order: BT > BT<sub>DP</sub> > BT<sub>DC</sub>. The dielectric constant could be reduced by increasing the free volume of the molecule or by a decrease in the polarization.<sup>19,22,23</sup> BT<sub>DC</sub> and BT<sub>DP</sub> systems with low polar aliphatic DCPD or DP linkages and four bulky *ortho*-methyl groups led to more spacing between the polymer molecules, and this resulted in less efficient chain packaging and an increase in the free volume of the polymer,<sup>24</sup> which reduced the

dielectric constant and dissipation factor of the BT<sub>DC</sub> and BT<sub>DP</sub> systems. Furthermore, the presence of low polar aliphatic DCPD or DP linkages may reduce interchain electronic interaction and increase hydrophobicity, thus decreasing the dielectric constant and dissipation factor. From Tables II and III, the higher the dicyanate ester content in the formulation, the lower the dielectric constant and dissipation factor of the cured BT resins; this could also be attributed to the high degree of the polar symmetry structure of triazine, which tends to balance the pull of electrons and results in low dipole moments and low energy storage in an electromagnetic field. The introduction of dicyanate ester into BT resin systems reduces the amount of DDMBMI, and thus the concentration of dipoles in the structure of the cured resins. Spacing with low polar aliphatic DCPD or DP linkages may act as dielectric diluents of the cyanate linkage structures, which further improves the dielectric properties.

The dielectric constant of cured resin systems show a slight decrease in value at higher frequencies. Similar observations were found on the dielectric constant of dicyclopentadiene-modified polycyanate resin over the frequency range from 1 KHz to 1 GHz.<sup>25</sup> The lower dissipation factors proportionally reduce power loss and heat production in multi-chip modules (MCMs) which, in turn, means that operating speeds are increased, crosstalk (the interaction between electric fields of adjacent electrical conductors) is reduced, and dimensional stability is maintained.<sup>26</sup>

**TABLE III**  
Dissipation Factor( $D_f$ , mU) at Room Temperature for Various Mole Ratio BT Resins

Bismaleimide /dicyanate ester (mole ratio)	DDMBMI/BADCY (BT)		DDMBMI/DCPDCY (BT <sub>DC</sub> )		DDMBMI/DPCY (BT <sub>DP</sub> )	
	1 MHz	1 GHz	1 MHz	1 GHz	1 MHz	1 GHz
10/0	163.88	43.32	163.88	43.32	163.88	43.32
8/2	150.58	39.95	103.97	37.08	121.18	38.33
6/4	125.32	39.33	76.84	36.17	87.60	37.68
4/6	109.85	37.75	72.74	30.63	70.49	29.52
2/8	98.13	33.41	64.49	19.42	66.74	25.33
0/10	64.39	24.33	20.21	3.61	29.33	5.95

**TABLE IV**  
Moisture Absorption of Various Mole Ratio BT Resins

Sample ID	Mole ratio	Moisture absorption (%)			
		12 h	24 h	36 h	48 h
DDMBMI/BADCY (BT100)	10/0	4.23	5.23	5.34	5.46
BT82	8/2	3.44	4.42	4.54	4.63
BT64	6/4	3.01	4.08	4.14	4.19
BT46	4/6	2.5	2.91	3.04	3.07
BT28	2/8	1.77	2.88	2.96	2.98
BT010	0/10	1.49	1.73	1.75	1.77
DDMBMI/DCPDCY (BT <sub>DC</sub> 100)	10/0	4.23	5.23	5.34	5.46
BT <sub>DC</sub> 82	8/2	3.33	4.21	4.31	4.50
BT <sub>DC</sub> 64	6/4	2.73	3.43	4.01	4.09
BT <sub>DC</sub> 46	4/6	1.94	2.51	2.98	3.04
BT <sub>DC</sub> 28	2/8	1.34	1.75	1.81	1.84
BT <sub>DC</sub> 010	0/10	0.80	0.87	0.88	0.88
DDMBMI/DPCY (BT <sub>DP</sub> 100)	10/0	4.23	5.23	5.34	5.46
BT <sub>DP</sub> 82	8/2	3.40	4.30	4.44	4.51
BT <sub>DP</sub> 64	6/4	2.90	3.80	4.10	4.11
BT <sub>DP</sub> 46	4/6	2.29	2.74	3.27	3.34
BT <sub>DP</sub> 28	2/8	1.53	1.78	1.82	1.87
BT <sub>DP</sub> 010	0/10	0.91	0.95	0.95	0.95

### Moisture resistance

The absorbed moisture acts as plasticizer, which reduces the mechanical and thermal properties of cured resins and also has a detrimental effect on dielectric properties. Moisture absorption will reduce  $T_g$  of a laminate material and may cause a "popcorn phenomenon" when in contact with solder at a high temperature. Moisture absorption will also ionize the ionic impurities (e.g.,  $Cl^-$ ) and, therefore, corrode the integrated circuits. Furthermore, moisture absorption will increase the dielectric constant of laminate board

materials. Therefore, lower moisture absorption is necessary for laminate materials.<sup>24,27</sup> As seen in Table IV, All cured DDMBMI/DCPDCY or DDMBMI/DPCY resins showed lower moisture absorption than the control bisphenol A dicyanate ester system. The higher the dicyanate ester content in the formulation, the lower moisture absorption of the cured BT resins, which further proves the low moisture absorption of dicyclopentadiene or dipentene linkage. The lower moisture absorption may be attributed to the hydrophobic nature of aliphatic DCPD or DP structure and the *ortho*-methyl groups in DCPDCY and DPCY.

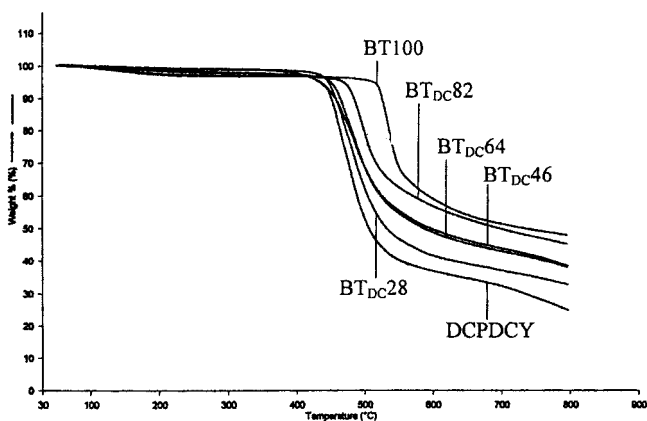
### Thermal stability of polymers

The relative thermal stability of cured resins were compared at the temperature of 5%, 10% weight loss ( $T_{5\%}$ ,  $T_{10\%}$ ) and percent char yield at 700°C ( $Y_c$ ). The TGA data for cured resins at various molar ratio of DDMBMI/dicyanate esters containing dicyclopentadiene and dipentene are listed in Table V. TGA thermograms for various mole ratio of BT<sub>DC</sub> resins are shown in Figure 7. The cured resins of DDMBMI/DCPDCY and DDMBMI/DPCY in various mole ratio exhibited 5% weight loss decomposition temperature ( $T_{5\%}$ ) ranging between 429 and 509°C in nitrogen and the anaerobic char yields at 600°C ranged between 23 and 58%. As would be expected, DDMBMI/DCPDCY and DDMBMI/DPCY resin systems show very good thermal stability. The thermal stability of cured resins slightly decreased with the increase in the cyanate ester molar ratio, which may be due to the lower crosslink density of dicyanate ester system. The same trends were observed in the char yields shown in Table IV. The 5% degradation temperature of neat DCPDCY and DPCY are 430°C and 429°C, respectively,

**TABLE V**  
TGA Analysis for Various Mole Ratio BT Resins

Sample	Mole ratio	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield at 600°C (%)	Char yield at 700°C (%)
DDMBMI/BADCY (BT100)	10/0	509	523	58.81	51.25
BT82	8/2	453	470	59.20	52.83
BT64	6/4	396	442	57.24	51.27
BT46	4/6	398	423	53.37	47.98
BT28	2/8	395	428	51.05	46.04
BT010	0/10	441	457	45.4	40.86
DDMBMI/DCPDCY (BT <sub>DC</sub> 100)	10/0	509	523	58.81	51.25
BT <sub>DC</sub> 82	8/2	466	482	56.58	49.67
BT <sub>DC</sub> 64	6/4	448	462	48.54	42.74
BT <sub>DC</sub> 46	4/6	432	454	49.47	43.63
BT <sub>DC</sub> 28	2/8	444	455	41.35	36.78
BT <sub>DC</sub> 010	0/10	430	449	36.64	32.05
DDMBMI/DPCY (BT <sub>DP</sub> 100)	10/0	509	523	58.81	51.25
BT <sub>DP</sub> 82	8/2	464	482	52.39	45.49
BT <sub>DP</sub> 64	6/4	446	463	43.69	38.11
BT <sub>DP</sub> 46	4/6	443	461	42.10	36.47
BT <sub>DP</sub> 28	2/8	445	456	30.60	22.17
BT <sub>DP</sub> 010	0/10	429	448	23.61	17.64



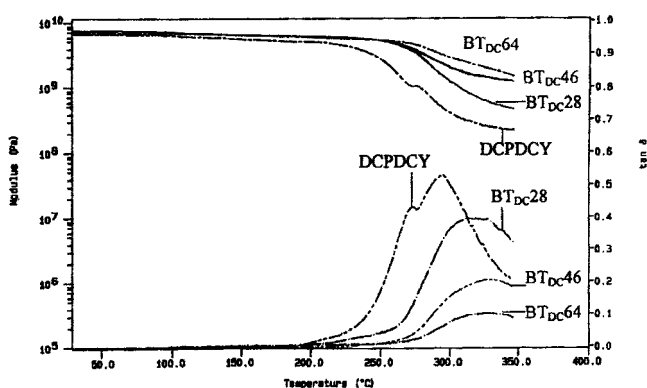


**Figure 7** TGA thermograms for various mole ratios of  $BT_{DC}$  resins.

which is lower than the  $441^{\circ}C$  for that of neat BADCY. The char yield at  $700^{\circ}C$  for DCPDCY and DPCY are 32.05% and 17.64%, respectively, which is much lower than the 40.9% for that of neat BADCY. These differences may be attributed to the aliphatic structure of dicyclopentadiene, dipentene, and the methyl group, which reduce the flame retardancy.

#### Dynamic mechanical properties of polymers

The glass transition temperature ( $T_g$ ) of the crosslinked resins could not be detected by DSC and this could be attributed to the fact that the resin was highly crosslinked and the change in  $C_p$  was very small. The typical DMA plots of the storage moduli as a function of temperature for DDMBMI/DCPDCY ( $BT_{DC}$ ) resins are shown in Figure 8. The peak of  $\tan \delta$  was identified as the  $T_g$  because a large decrease in  $G'$  occurred at the point. The  $T_g$  of the cured resins with various molar ratios of the DDMBMI/dicyanate ester were examined and are listed in Table VI. As would be expected, DDMBMI/DCPDCY and DDMBMI/DPCY resin systems show very good thermal stability. The higher the bismaleimide content in the formulation, the higher



**Figure 8** DMA results of DDMBMI/DCPDCY resins with various mole ratios.

**TABLE VI**  
DMA Analysis for Various Mole Ratio BT Resins

Sample	Mole ratio	$T_g$ ( $^{\circ}C$ )	Height of $\tan \delta$
DDMBMI/BADCY (BT100)	10/0	> 350	—
BT82	8/2	300	0.036
BT64	6/4	293	0.113
BT46	4/6	289	0.185
BT28	2/8	288	0.367
BT010	0/10	287	0.512
DDMBMI/DCPDCY ( $BT_{DC}100$ )	10/0	> 350	—
$BT_{DC}82$	8/2	335	0.052
$BT_{DC}64$	6/4	328	0.102
$BT_{DC}46$	4/6	317	0.194
$BT_{DC}28$	2/8	297	0.343
$BT_{DC}010$	0/10	271	0.424
DDMBMI/DPCY ( $BT_{DP}100$ )	10/0	> 350	—
$BT_{DP}82$	8/2	295	0.066
$BT_{DP}64$	6/4	292	0.146
$BT_{DP}46$	4/6	286	0.244
$BT_{DP}28$	2/8	279	0.512
$BT_{DP}010$	0/10	258	0.586

the modulus of the cured BT resins. The glass transition temperature of cured resins slightly decreased with the increase in the dicyanate ester molar ratio because of less crosslink density than neat DDMBMI.

#### CONCLUSIONS

A series of DCPD-containing or DP-containing novel bismaleimide-triazine resins were prepared from various mole ratio DCPDCY or DPCY and commercial bismaleimide (DDMBMI). Because of the hydrophobic effect of the cycloaliphatic DCPD or DP structure and the *ortho*-methyl groups, the cured DCPD-containing or DP-containing BT resins exhibited lower moisture absorption than that of DDMBMI cured with the BADCY. Because of higher free volume and low polarity of cycloaliphatic DCPD and DP linkages, cured DCPD-containing and DP-containing BT resins exhibited a low dielectric constant and dissipation factor. The glass transition temperature and thermal stability of cured resins slightly decreased with the increase in the cyanate ester molar ratio. But all dicyclopentadiene-based or dipentene-based cured BT resins still retain good heat-resistant properties. The combination of low dielectric constant, low dissipation factor, and outstanding resistance to moisture absorption make DDMBMI/DCPDCY and DDMBMI/DPCY BT resins attractive candidates in printed circuit board applications.

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