

Synthesis and Characterization of Novel Low-Dielectric Cyanate Esters. II

Jeng-Yueh Shieh,¹ Shih-Peng Yang,² Chun-Shan Wang²

¹Department of Industrial Safety and Hygiene, Chung Haw College of Medical Technology, Tainan, Taiwan, 717, Republic of China

²Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan, 701, Republic of China

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ABSTRACT: A novel cyanate ester, 2,6-dimethyl phenol dipentene cyanate ester (DPCY), was successfully synthesized from cyanogen bromide with 2,6-dimethyl phenol dipentene novolac, which was synthesized from dipentene and 2,6-dimethyl phenol. For the purpose of increasing the mobility of residual DPCY during the final stage of curing and achieving a complete reaction of cyanate groups, a small quantity of a monofunctional cyanate ester, 4-*tert*-butyl phenol cyanate ester, was added to DPCY to form a cyanate ester copolymer. The thermal properties of the cured cyanate ester resins were studied by dynamic mechanical anal-

ysis, dielectric analysis, and thermogravimetric analysis. These data were compared with those of the commercial bisphenol A cyanate ester system. The cured modified cyanate ester exhibited a dielectric constant of 2.59–2.50, a dissipation factor of 0.0055–0.0089, and moisture absorption of 0.91–1.17%; these values were all lower than those of the as-cured bisphenol A dicyanate system. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 369–379, 2005

Key words: dielectric properties; high performance polymers; thermal properties

INTRODUCTION

Cyanate esters, possessing excellent mechanical properties, thermal stability, and low dielectric constants over a wide range of frequencies and temperatures with good flame retardancy, are high-performance thermosetting resins used in the electronics and aerospace industries.^{1–5} They can also be mixed with many kinds of thermosetting resins to form compatible blends for aerospace and electronic applications.^{6–13} Electronic applications include printed wiring circuit boards, thin cards, multichip module laminates, chip encapsulations, and sheet molding compounds.^{14–18} Resin compositions with cyanate esters have been demonstrated to be useful as die attachment adhesives, underfillings, and encapsulants; the characteristics of the resins can be varied over a wide range through copolymerization with functionalized comonomers such as epoxies, phenols, rubbers, and thermoplastic.^{19–21}

In designing thermoset polymers for use as printed wiring board substrates, researchers must consider several critical performance parameters. These param-

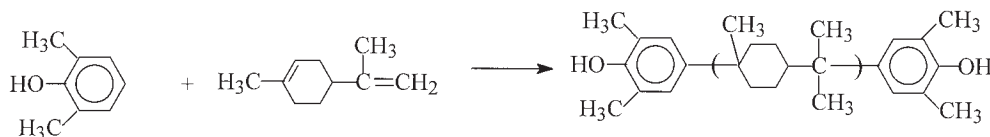
eters include the processibility, thermal stability, glass-transition temperature (T_g), moisture resistance, and electrical insulation properties. Conventional electronic circuit boards are made from glass-fiber-reinforced bisphenol A epoxy resins. However, they often fall short of the thermal and electrical performance demands of many modern high-speed devices. The demands for future printed circuit boards include multiple layers, low thermal expansion, high thermal stability, and low dielectric properties.

A large cycloaliphatic moiety [dipentene (DP)] has been incorporated into polymer backbones.^{22,23} DP is a byproduct of C₅ streams in oil refineries; it is low-cost and has high reactivity. A previous study²³ has demonstrated that this hydrophobic, nonpolar bridging group contributes to excellent moisture resistance and to a dramatic reduction in the dielectric constant without detrimentally affecting thermal performance and while maintaining epoxy-like processibility. In this study, the DP structure was incorporated into a dicyanate ester system because cyanate ester is well known for its excellent dielectric properties.²⁴ The combination of the DP structure with cyanate ester was expected to produce a synergistic effect.

The curing of cyanate ester includes the cyclotrimerization of three aryl cyanates (Ar—O—C≡N) to form a cyanurate structure. The major problem with a dicyanate ester curing system is that the high crosslink density and very high viscosity during the final stage of curing reduce the mobility of unreacted residual

Correspondence to: J.-Y. Shieh (cswang@mail.ncku.edu.tw).

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Scheme 1 Synthesis of DPNO.

cyanate groups, and a complete reaction of cyanate groups cannot be accomplished.²⁵ The remaining residual polar functional group of O—C≡N increases the moisture absorption and dielectric constant. Therefore, in this study, the synthesized novel DP dicyanate ester was combined with a small amount of a monocyanate ester compound, 4-*tert*-butyl phenol cyanate ester (4TPCY), to reduce the crosslink density for the purpose of increasing the mobility during the final stage of curing. The combined effects of 2,6-dimethyl phenol dipentene cyanate ester (DPCY) and the slight reduction in the crosslink density on the dielectric properties and physical properties were investigated, and their thermal, mechanical, and dielectric property test results were compared with those of an as-cured bisphenol A dicyanate ester.

EXPERIMENTAL

Materials

4-*tert*-Butyl phenol and cyanogen bromide (BrCN) from Acros Co (Pittsburgh, PA) were used as received. DP, 2,6-dimethyl phenol, 4-*tert*-butyl phenol, anhydrous aluminum chloride, and molecular sieves were also purchased from Acros. All the solvents were commercial products (liquid chromatography-grade) and were used without further purification. Copper acetyl acetonate was used as a catalyst. For the synthesis of the monofunctional cyanate ester, acetone was dehydrated with CaH₂ before use.

Measurements

¹H-NMR spectra were registered with a Bruker Avance 600 spectrometer (Rheinstetten, Germany) with dimethyl sulfoxide-*d*₆ as a solvent. Elemental analyses were carried out with a Heraeus CHN rapid elemental analyzer (Hanau, Germany). Fourier transform infrared spectra were recorded on a Nicolet Magna 550 spectrometer (Madison, WI) with KBr pellets or with 10–15- μ m film. Spectra in the optical range of 400–4000 cm⁻¹ were obtained through the averaging of 32 scans at a resolution of 4 cm⁻¹. Differential scanning calorimetry (DSC-7, PerkinElmer, Norton, OH) measurements were used in this work. Samples of approximately 5–10 mg were sealed in hermetic aluminum pans and scanned in the calorimeter at a heating rate of 10°C/min in the range of

50–340°C under an N₂ atmosphere, and the *T*_g values were taken as the change in the specific heat in the heat-flow curves. Thermogravimetric analyses (TGAs) were performed on a PerkinElmer TGA-7 thermal analyzer at a heating rate of 10°C/min in N₂ at a purge pressure of 25 psi within the temperature range of 100–800°C. The dielectric constant and dissipation factor were measured with an Agilent 4291B measurement system (Palo Alto, CA) at 30°C in a nitrogen atmosphere at a flow rate of 500 cm³/min in the two parallel-plate mode at 1 GHz. The applied voltage was 1 V.

Synthesis of 2,6-dimethyl phenol dipentene novolac (DPNO)

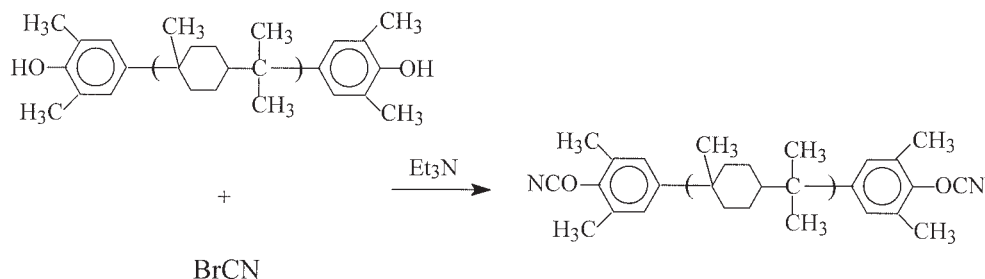
DPNO was synthesized according to a reported procedure²³ in a yield of 89%. The reaction equation is shown in Scheme 1.

ANAL. Calcd for C₂₆H₃₆O₂: C, 82.10%; H, 9.47%. Found: C, 82.01%; H, 9.51. Electron-impact mass spectrometry (EIMS; *m/z*): 380 (30 M⁺).

Synthesis of DPCY

The dicyanate monomer was synthesized with a modified procedure reported by Grigat and Putter²⁶ (Scheme 2). To a 250-mL, four-necked flask was charged 75 mL of acetone, and this was cooled to -25°C. BrCN (25 g, 0.236 mol) was dissolved in acetone and kept at -25°C with stirring. Under a nitrogen atmosphere, 0.104 mol of DPNO and 0.21 mol of triethylamine in 25 mL of anhydrous acetone were added dropwise to the flask, which was maintained under -15°C. After the addition was complete, the temperature was allowed to equilibrate to -5°C. The solution was filtered, and NaBr on the filter was washed with anhydrous acetone. To the combined filtrate was added 100 mL of CH₂Cl₂, and this was washed with 100 mL of 1% NaCl (aqueous) and water. The organic layer was dried with anhydrous sodium carbonate and then evaporated in a rotary evaporator. The dicyanate monomer was obtained (Scheme 2).

Yield: 85%. ANAL. Calcd for C₂₈H₃₄N₂O₂: C, 78.10%; H, 8.00%; N, 6.50%. Found: C, 77.87%; H, 8.04%; N, 6.53%. EIMS (*m/z*): 430 (32. M⁺).



Scheme 2 Synthesis of DPCY.

Synthesis of the monofunctional cyanate esters

To a 250-mL reaction vessel equipped with a temperature controller, a stirrer, a reflux condenser, and a feeder was added 75 mL of dehydrated acetone. The temperature of the reactor was cooled to -15°C , and 25 g (0.236 mol) of BrCN was slowly added with stirring; the temperature was further reduced to -25°C . A mixture of 31.20 g (0.208 mol) of 4-*tert*-butyl phenol, 21.21 g (0.21 mol) of triethylamine, and 25 mL of dehydrated acetone was slowly added from the feeder to the reactor while the temperature was kept under -16°C . The reaction was allowed to warm to -5°C and then was filtered for the removal of triethylammonium hydrogen bromide. To the filtrate was added 100 mL of dichloromethane, and it was then washed with 100 mL of a 1% aqueous NaCl solution followed by 100 mL of cold deionized water. The organic phase was collected and dried with dehydrated sodium carbonate. Then, the solution was filtered, and the solvent was removed *in vacuo* to produce 4TPCY as a liquid. The reaction is shown in Scheme 3.

Yield: 90%. ANAL. Calcd for $\text{C}_{11}\text{H}_{13}\text{NO}$: C, 75.43%; H, 7.43%; N, 8.00%. Found: C, 75.34%; H, 7.38%; N, 8.09%. EIMS (m/z): 175 (78. M^+).

Curing procedure

The curing procedure for DPCY with various amount of monofunctional cyanate esters was performed with the following steps. Mixtures consisting of DPCY and 4TPCY in various molar ratio (0.05, 0.10, 0.15, and 0.20) were prepared. Copper acetyl acetonate (10 ppm) was used as a curing accelerator. The mixtures were placed in molds at 80°C to produce thermosettable

cyanate ester solutions and were cured in molds at 150°C for 2 h, at 180°C for 2 h, and at 200°C for 2 h to produce cured specimens. The products were designated DPCY-A, DPCY-B, DPCY-C, DPCY-D, and DPCY-E. (Scheme 4).

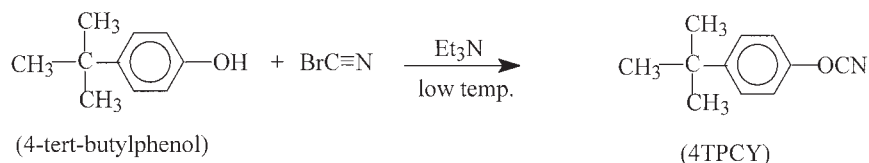
RESULTS AND DISCUSSION

Characterization of DPNO

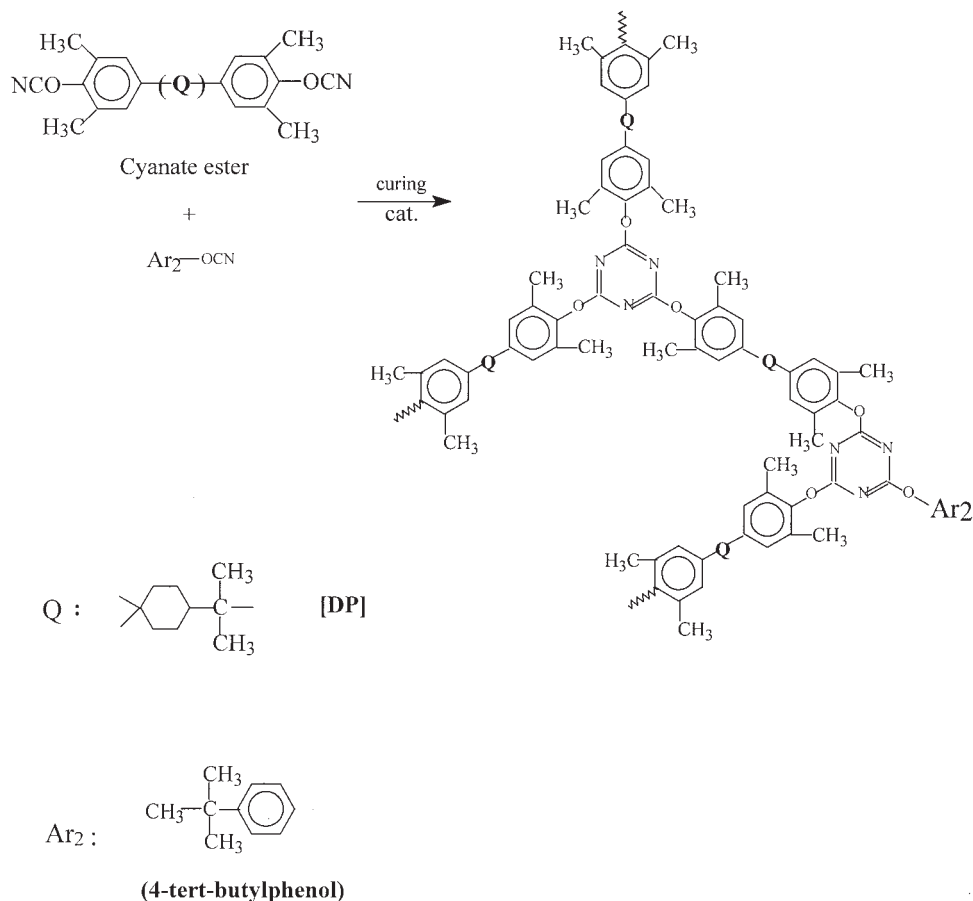
The reaction mechanism may be a two-step process, as described in our previous study.²³ In the first step, DP reacted with AlCl_3 to form carbocations with four possible structures. The four possible carbocations (I–IV; Fig. 1) then reacted with 2,6-dimethyl phenol in the second step. Which reaction occurred more easily and which product was predominant were difficult to determine and are not discussed in this article. A typical reaction is shown in Scheme 1.

The IR spectra of DP and DPNO are shown in Figure 2(a,b), respectively. The characteristic absorption peaks of $-\text{HC}=\text{CH}-$ at 1667–1640 and 3040–3010 cm^{-1} are evident in Figure 2(a). However, these characteristic absorption peaks disappear in Figure 2(b), and this implies that all the $-\text{HC}=\text{CH}-$ functional groups had reacted with 2,6-dimethyl phenol. The characteristic absorption peaks of the aromatic ring at 1490–1450 cm^{-1} and the OH absorption peaks of novolac at 3755–3066 cm^{-1} can be observed in Figure 2(b).

The $^1\text{H-NMR}$ spectra of DP and DPNO are shown in Figure 3(a,b), respectively. The signals of the aliphatic hydrogens in DP in the range of 1.52–2.13 ppm are shown in Figure 3(a). The signals at 4.78 and 5.42 ppm are from $-\text{HC}=\text{CH}-$. However, the signals at 4.78 and 5.42 ppm disappear in Figure 3(b), and this im-



Scheme 3 Synthesis of monofunctional phenol-based cyanate esters.



Scheme 4 Curing of monofunctional cyanate ester modified DPCY.

plies that all the —HC=CH— functional groups had reacted with 2,6-dimethyl phenol. The characteristic peaks of the aromatic ring at 6.60–6.87 ppm and the OH absorption peaks at 7.85 ppm can all be observed in Figure 3(b).

Characterization of DPCY

The formation of the cyanate ester monomer is described in Scheme 2. The cyanate ester compounds were synthesized from dipentene novolac and BrCN 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 have led to the unwanted formation of diethyl cyanamide.⁹ Typical IR spectra of DPCY exhibited several distinctive absorptions, as shown in Figure 2(b,c). The dicyanate showed strong absorptions at 2270 and 2235 cm^{-1} , which were assigned to cyanate $\text{C}\equiv\text{N}$ stretching vibration, and lacked the absorption at 3755–3066 cm^{-1} associated with the phenolic OH stretching vibration. Consequently, the reaction could be monitored with these absorptions. The shift and splitting pattern of the

$^1\text{H-NMR}$ spectrum showed saturated hydrogens at 0.39–2.73 ppm and aromatic rings around 6.97–7.24 ppm [Fig. 3(c)]. Figure 3 (including OH and OCN for comparison) also shows that DPCY cyanate ester was formed when the peak at $\delta = 7.85$ ppm (OH) disappeared.

Characterization of 4TPCY

The synthesis of 4TPCY was performed with 4-*tert*-butyl phenol and BrCN according to Scheme 3. The IR spectra of 4-*tert*-butyl phenol and 4TPCY are shown in Figure 4(a,b), respectively. The characteristic absorption peak of aromatic —OH at 3755–3066 cm^{-1} is evident in Figure 4(a). However, the characteristic absorption peak disappears in Figure 4(b), and this implies that all the aromatic —OH functional groups had reacted with BrCN. The characteristic absorption peak of $\text{—C}\equiv\text{N}$ at 2270–2235 cm^{-1} can be observed in Figure 4(b). The $^1\text{H-NMR}$ spectra of 4-*tert*-butyl phenol and 4TPCY are shown in Figure 5(a,b), respectively. The disappearance of Ph—OH at $\delta = 9.2$ ppm in Figure 5(b) indicates that the reaction was completed and that 4TPCY was formed.

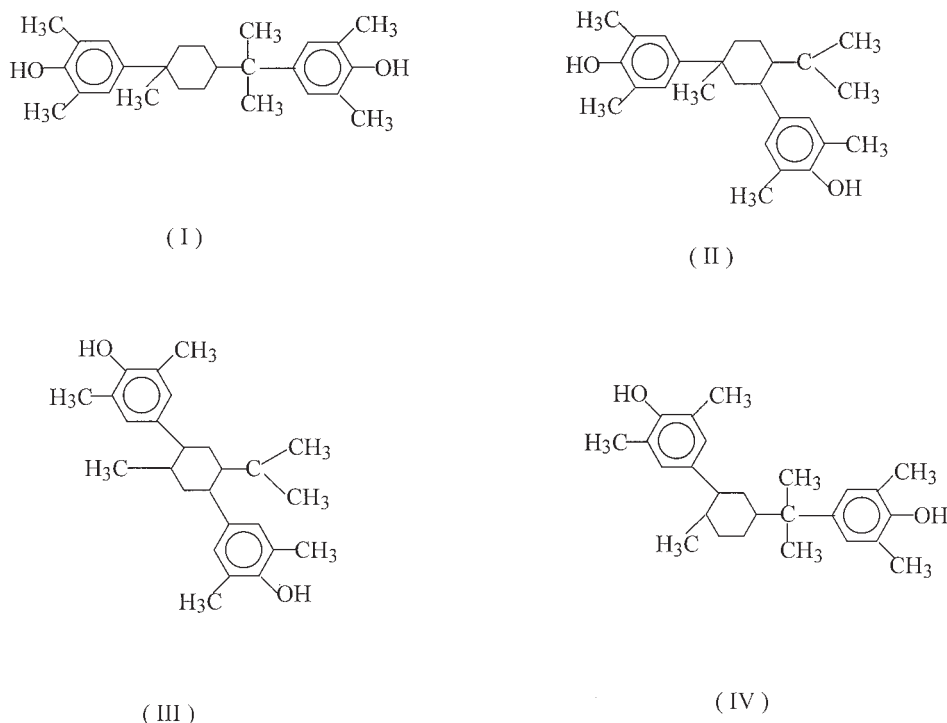


Figure 1 Four possible structures of DPNO.

Dynamic viscoelastic analyses of the cured cyanate esters

Dynamic viscoelastic analysis can provide information about the microstructure of the cured polymer. The $\tan \delta$ curve for the control network exhibits a major relaxation observed in most thermoset polymers.²⁷ The transition corresponds to the major T_g value of the cured cyanate esters, above which significant chain motion took place. Figure 6 shows the storage modulus and $\tan \delta$ values of cured bisphenol A cyanate ester (BADCY) and DPCY-A. The T_g values of all the cured cyanate ester copolymers are listed in Table I. The results indicated that the cured DPCY-A had a lower T_g (261°C) than the control BADCY (282°C). The results may be attributed to the fact that the crosslink density of the DPCY network was lower than that of BADCY because of the nonpolar DP structure, which had a higher free volume than the bisphenol A system.

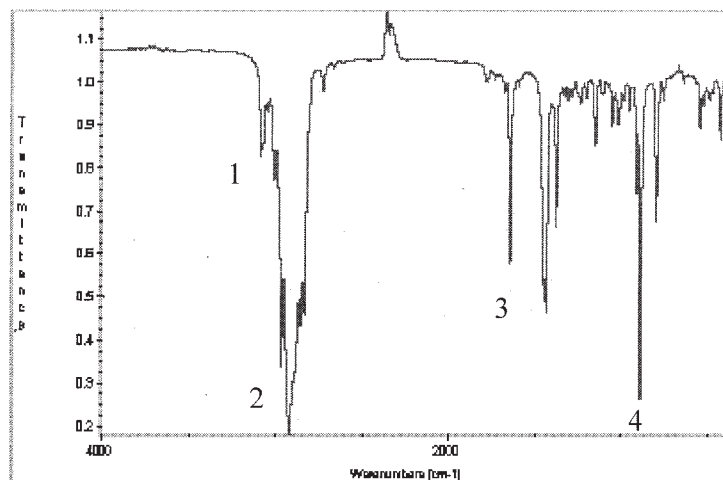
Table I indicates that the T_g 's of the cured cyanate ester copolymers slightly decreased (261–244°C) with an increase in the monofunctional cyanate ester content, and this may be attributed to the reduction in the crosslink density of the cured products. It may be that the monofunctional cyanate ester reacted with DPCY and reduced its —OCN functionality and consequently reduced its crosslink density. However, when the amount of 4TPCY was within the molar ratio range of 0.05–0.20, T_g 's of the cured cyanate esters were greater than 240°C, being much higher than

those of traditional epoxy-based laminates (~150°C) and epoxy/cyanate ester composite laminates (~180°C).²⁸

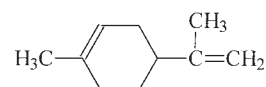
Thermal properties of the cured cyanate esters

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 results for various cured cyanate esters copolymers containing DPCY and 4TPCY under nitrogen are shown in Table I. The results indicated that most cyanate ester copolymers had a 5% decomposition temperature ($T_{d5\%}$) of more than 420°C. $T_{d5\%}$ slightly decreased with an increase in the amount of 4TPCY. The same trends can be observed for the char yields in Table I.

The thermal stability of the cured resins decreased with an increase in the monofunctional cyanate ester (4TPCY) molar ratio, and this may be due to the lower crosslink density of 4TPCY containing the dicyanate ester.²⁹ The thermal stabilities of the DPCY systems were slightly lower than those for the bisphenol A system. These differences may also be attributed to the aliphatic structure of DP and the methyl group, which reduced the thermostability. Furthermore, the lower molecular interaction, due to the higher free volume of the DP system, may also have reduced the thermostability of the DP system.



(a)



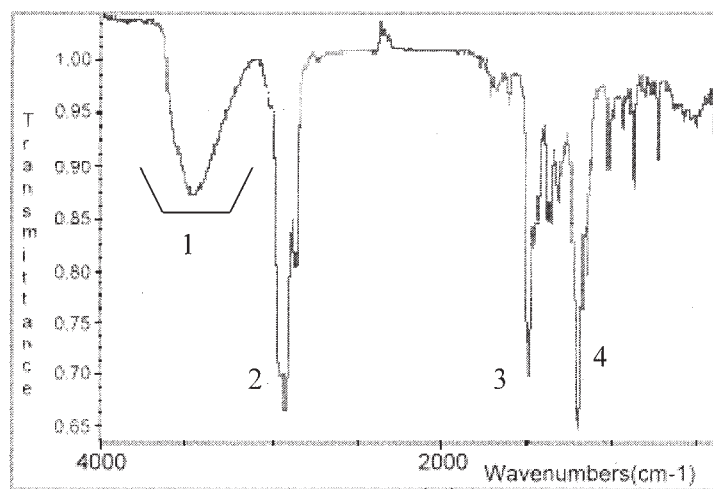
DP

1 : 3040~3010 cm^{-1} , Olefinic C-H stretching

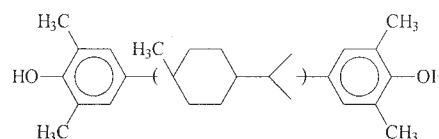
2 : 2975~2950 cm^{-1} , -CH₃, C-H stretching

3 : 1667~1640 cm^{-1} , Olefinic C=C stretching

4 : 1000~650 cm^{-1} , Olefinic C-H bending



(b)



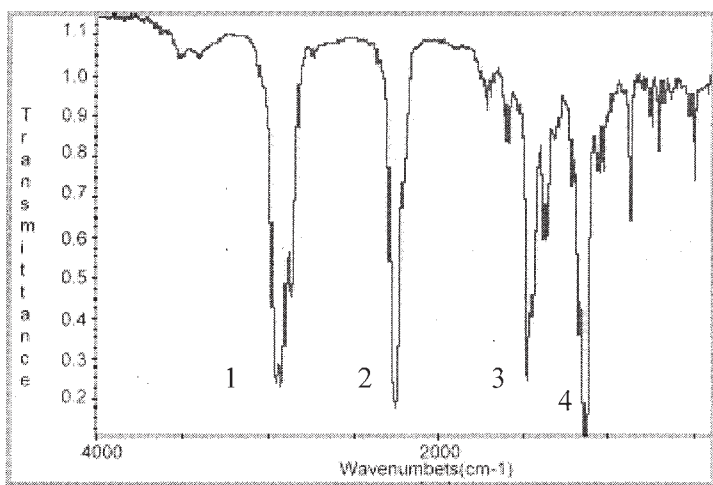
DPNO

1 : 3755~3066 cm^{-1} , -OH

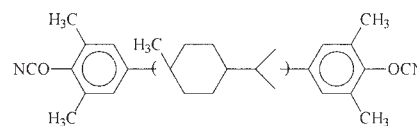
2 : 2975~2950 cm^{-1} , -CH₃, C-H stretching

3 : 1490~1450 cm^{-1} , aromatic ring C=C

4 : 1220~1200 cm^{-1} C-O



(c)



DPCY

1 : 2975~2950 cm^{-1} , -CH₃, C-H stretching

2 : 2270~2235 cm^{-1} , C≡N stretching

3 : 1490~1450 cm^{-1} , aromatic ring C=C

4 : 1220~1200 cm^{-1} , C-O-C

Figure 2 IR spectra of (a) DP, (b) DPNO, and (c) DPCY.

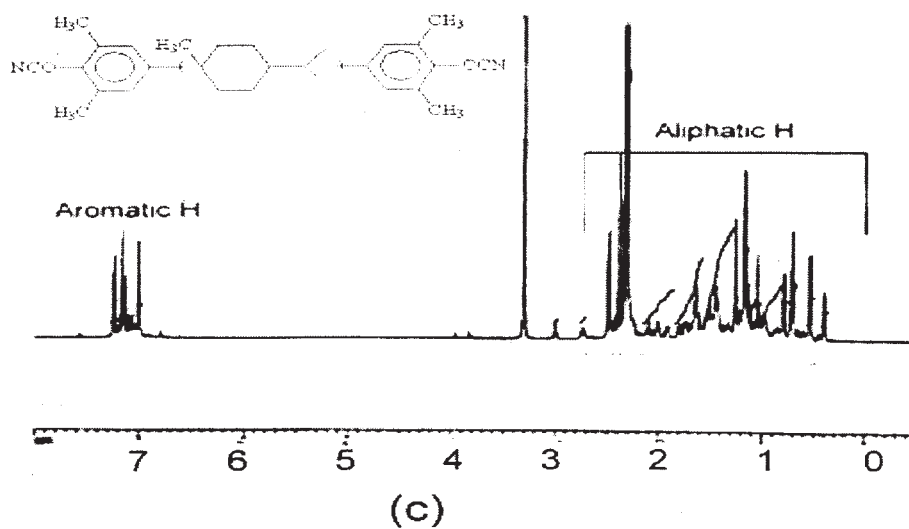
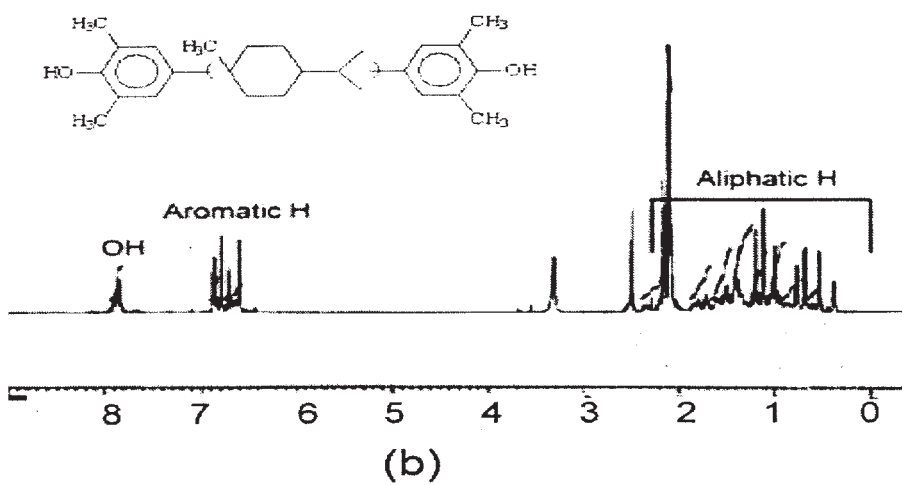
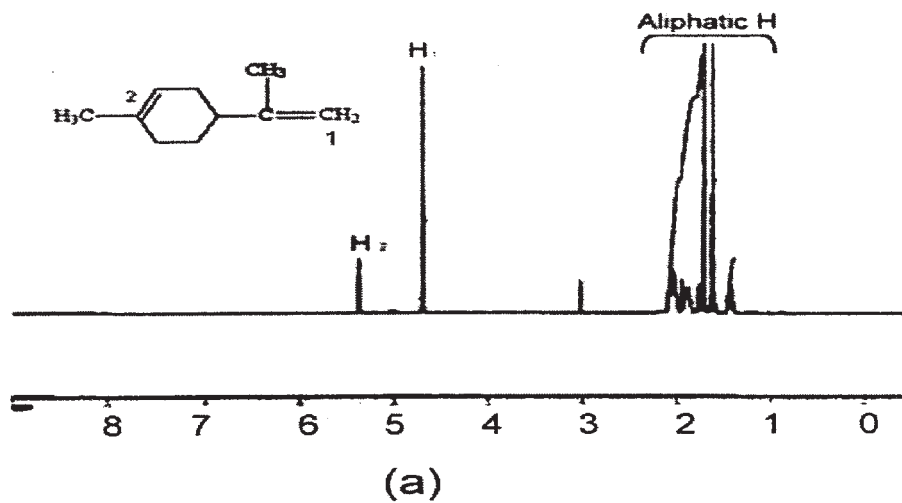
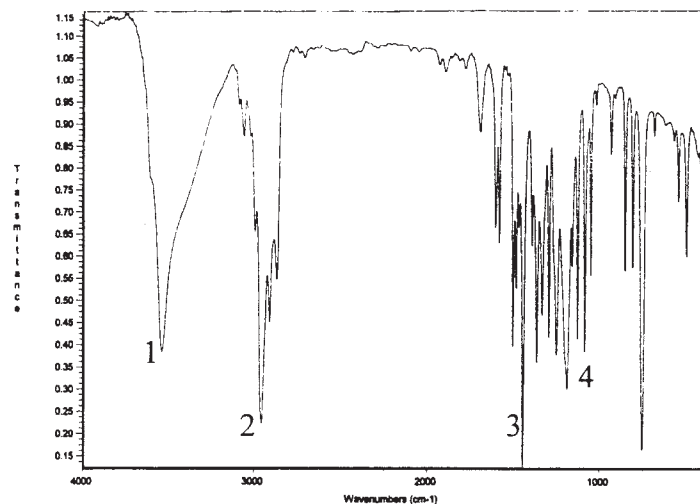
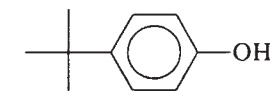
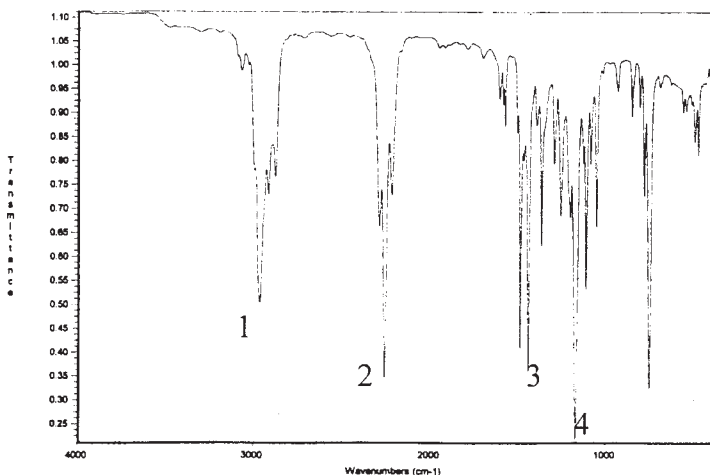


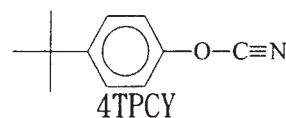
Figure 3 ¹H-NMR spectra of (a) DP, (b) DPNO, and (c) DPCY.



(a)

4-*tert*-butylphenol1 : 3755~3066cm⁻¹, OH2 : 2975~2950cm⁻¹, -CH₃, C-H stretching3 : 1490~1450cm⁻¹, aromatic ring C=C4 : 1220~1200 cm⁻¹, C-O

(b)



4TPCY

1 : 2975~2950cm⁻¹, -CH₃, C-H stretching2 : 2270~2235cm⁻¹, C≡N stretching3 : 1490~1450cm⁻¹, aromatic ring C=C4 : 1220~1200cm⁻¹, C-O-CFigure 4 IR spectra of (a) 4-*tert*-butyl phenol and (b) 4TPCY.

Moisture absorption

The absorbed moisture acted as a plasticizer, reducing the mechanical and thermal properties of the cured resins. Moisture absorption reduces T_g of a laminate material and may cause a popcorn effect when in contact with solder at a high temperature. Moisture absorption also ionizes ionic impurities (e.g., Cl^-) and, therefore, corrodes integrated circuits. Furthermore, moisture absorption increases the dielectric constant of laminate board materials. Therefore, lower moisture absorption is necessary for laminate materials.³⁰ Before the moisture absorption was tested, each sam-

ple was prepared as follows. The sample (1 cm × 1 cm × 0.1 cm) was dried *in vacuo* at 120°C until the moisture was expelled. After cooling to room temperature, the sample was weighed, placed in 100°C water for 24 h, and weighed again. The moisture absorption was calculated as the weight gain percentage $[(W/W_0 - 1) \times 100]$, where W_0 is the weight of the sample before being placed in water and W is the weight of the sample after it is immersed in 100°C water for 24 h].

Table II shows the moisture absorption of the cured cyanate ester copolymers. The moisture absorption of the cured 4TPCY/DPCY copolymers was 0.91–1.17%,

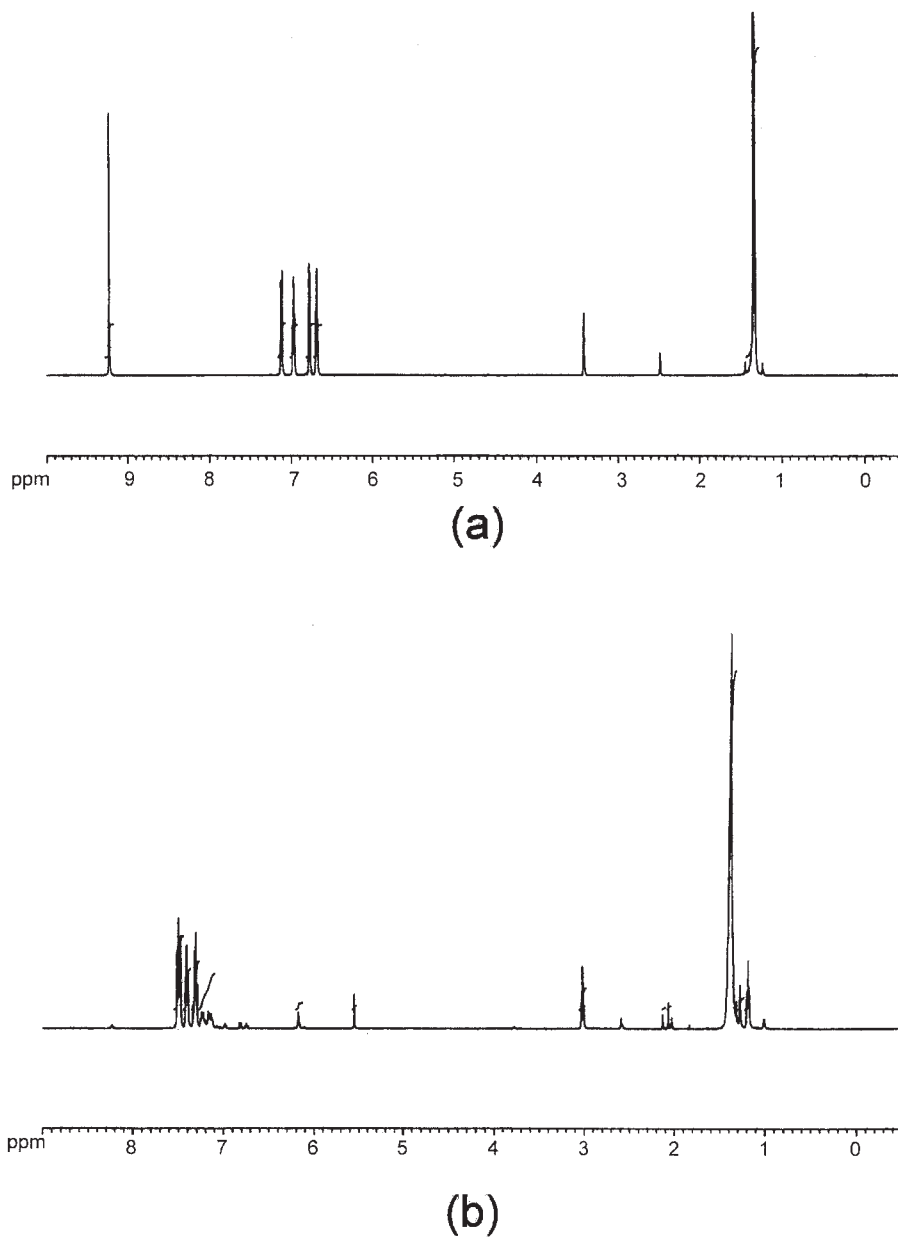


Figure 5 $^1\text{H-NMR}$ spectra of (a) 4-*tert*-butyl phenol and (b) 4TPCY.

which was much lower than that of the control BADCY (1.7%). The low moisture absorption may be attributed to the hydrophobic nature of the aliphatic DP structure and the tetramethyl group.^{31,32} Table II shows that the moisture absorption of the modified cured cyanate ester copolymers slightly increased with the 4TPCY content (0.91–1.17%). This may be attributed to the addition of the hydrophilic phenyl group of 4TPCY.

Dielectric constant and dissipation factor

Agilent 4291B was used to determine the dielectric constant and dissipation factor of a solid. Before the

testing, the cured cyanate ester samples (1 cm \times 1 cm \times 0.3 cm) were dried *in vacuo* at 100°C for 8 h. Table II shows that cured and pure DPCY-A (dielectric constant = 2.59 U, $\tan \delta = 0.0089$) had better dielectric properties than the control BADCY (dielectric constant = 3.03 U, $\tan \delta = 0.0117$). The dielectric constant and dissipation factor of the modified cured cyanate esters decreased slightly with an increase in the monofunctional cyanate ester (4TPCY) content in the products.

The dielectric constant could be reduced by an increase in the free volume of the molecule or by a decrease in the polarization.^{23,33,34} DPCY with low polar aliphatic DP linkages and four bulky methyl

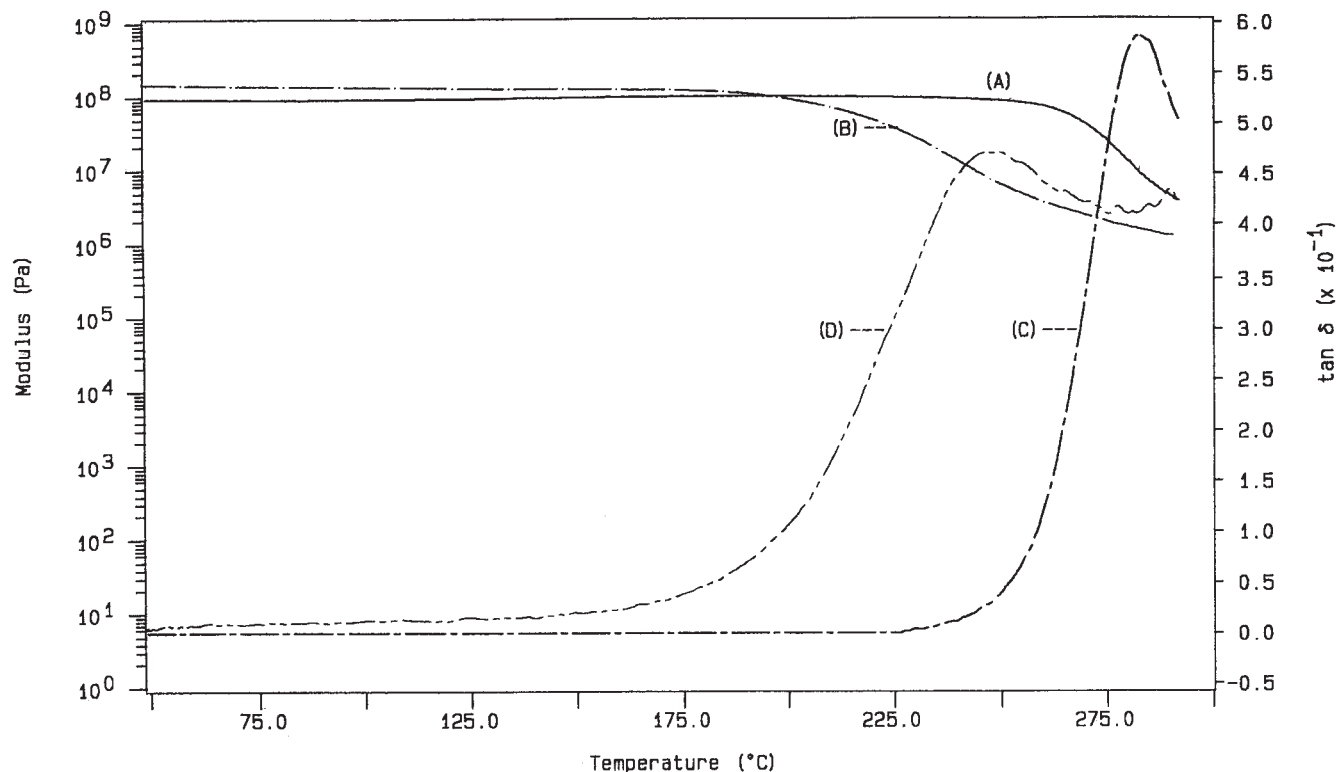


Figure 6 Dynamic viscoelastic analysis of cured cyanate esters of (A,C) BADCY and (B,D) DPCY-A.

groups led to more spacing between the polymer molecules, and this resulted in less efficient chain packing and an increase in the free volume of the cyanate esters, which reduced the dielectric constant of the cyanate esters. Furthermore, the presence of a low-polar, fully cured cyanate ester (triazine structure) might have increased the hydrophobicity and, therefore, reduced the dielectric constant and dissipation factor. The low dielectric constant and dissipation factor could also be interpreted as the reduction of unreacted —OCN groups, which resulted from increased mobility when 4TPCY took part in the curing process.

CONCLUSIONS

DPCY was successfully synthesized from 2,6-dimethyl phenol and DP in two steps. Because of the hydropho-

bic effect of the aliphatic DP structure and the substituted methyl groups, the cured DPCY resins exhibited low moisture absorption. Because of the higher free volume and low polarity of the aliphatic DP linkages, the cured DPCY exhibited a low dielectric constant and dissipation factor.

4TPCY was successfully synthesized and added to DPCY to form cured cyanate ester copolymers. The method increased the mobility of DPCY during the final stage of curing and resulted in a complete reaction of the cyanate groups. The cured cyanate esters with 4TPCY at a molar ratio of 0.05–0.1 (monofunctional/bifunctional) exhibited a lower dielectric constant (2.54–2.50 U) and dissipation factor (0.0078–0.0074) than the controls (for DPCY, dielectric constant = 2.59 U and $\tan \delta = 0.0089$; for BADCY,

TABLE I
Thermal Properties of the Cured Cyanate Ester Copolymers

Sample	TPCY/DPCY molar ratio	T_g (°C)	$T_{d5\%}$ (°C)	Char yield at 700°C (%)
BADCY	0.00	282	455.8	48.3
A	0.00	261	450.3	26.3
B	0.05	260	449.6	20.1
DPCY				
C	0.10	246	447.3	19.6
D	0.15	245	438.7	15.2
E	0.20	244	422.2	15.0

TABLE II
Moisture Absorption and Dielectric Properties of the Cured Cyanate Ester Copolymers

Sample	TPCY/DPCY molar ratio	Moisture absorption	Dielectric constant at 1 GHz	$\tan \delta$ at 1 GHz
BADCY	0.00	1.73	3.03 U	0.0117
A	0.00	0.91	2.59 U	0.0089
B	0.05	0.98	2.54 U	0.0078
DPCY				
C	0.10	1.03	2.50 U	0.0074
D	0.15	1.11	2.52 U	0.0055
E	0.20	1.17	2.55 U	0.0069

dielectric constant = 3.03 U and $\tan \delta = 0.0117$). Dynamic mechanical analysis measurements showed that the cured cyanate esters had T_g 's greater than 244°C, and TGA measurements showed $T_{d5\%}$ values greater than 420°C for the copolymer system. This combination of a low dielectric constant, a low dissipation factor, and outstanding resistance to moisture absorption makes the modified cyanate ester an excellent electrical laminate material.

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