

Triazine Networks Modified with Monofunctional Reactive Cyanate Ester Monomers

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SYNOPSIS

The preparation of cyanate ester thermosetting resins by coreacting a fluorinated bisphenol A dicyanate (6F-BADCY) monomer with a monofunctional reactive cyanate, namely, the dinonyl phenol cyanate (DNPC), is described in this paper. Our objective in this study was to modify the 6F-BADCY system with reactive diluents of a nonpolar nature and produce matrix resins processable at FR-4 epoxylike conditions. By introducing the monofunctional cyanate as a reactive diluent, it is expected that the molar crosslink density of the resulting network will be reduced. Highly branched triazine polymers will result from this approach. Dinonyl phenol cyanate was quantitatively synthesized by reacting dinonyl phenol with cyanogen bromide in the presence of triethylamine.

INTRODUCTION

Recently, cyanate esters have received a great deal of interest because they exhibit many features of particular importance to the electronic industry. Their excellent dielectric properties make them very attractive in the area of circuit board fabrication.¹⁻⁴ These materials, upon thermal curing, produce laminates with very low dielectric constants (E_r) compared to conventional epoxies. In addition, cyanate esters reinforced either with expanded polytetrafluoroethylene (PTFE) fabric or nonwoven film can result in composites with even lower dielectric constants.

Cyanates can be modified with a wide variety of thermosets such as epoxies, bismaleimides (BT), or acrylates and other monofunctional diluents to form compatible blends.⁵ Mixing with thermoplastics usually results in interpenetrating network-type structures.⁶⁻⁸ After being fully crosslinked, both cyanates and BT resins exhibit glass transition temperatures (T_g) of at least 250°C. Cyanates may be blended with brominated epoxies (up to 60% by weight) to modify the T_g and achieve flammability requirements. Curing of the cyanate/epoxy system

is influenced not only by the catalyst level but by the ratio of cyanate, epoxy, and hydroxyl groups in the resin mixture. Many heterocyclic ring structures have been proposed as the products of BT-epoxy resin reactions. Verification of such structures by spectroscopic methods has been very difficult.

In order to achieve complete conversion, bisphenol-A-based dicyanate networks require curing temperatures greater than 250°C. Similar results have been obtained for the fluorinated analogs. 6F-BADCY resins must be heat cured at elevated temperatures above their glass transition temperatures, i.e., about 320°C for 1 h. The resulting products have excellent properties for high temperature and/or electrical insulation uses. These properties include low dielectric constants, high T_g , and high thermal stability. However, the high glass transition temperatures require that the compositions be cured at high temperatures which, in the case of circuit board laminates, requires the use of high temperature lamination presses. This is viewed as an important disadvantage with respect to manufacturing time and expense. Improved processing and performance are thus required for these type of thermosetting resins.

Previously, we reported on the kinetics of the curing reaction of a bismaleimide/biscyanate/epoxy blend.⁹ In this paper, we wish to report, first, the synthesis of dinonyl phenol cyanate, a monofunc-

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tional aromatic cyanate having long aliphatic chains predominantly in the ortho-para position of the ring, and, second, its use in modifying the 6F-BADCY system to produce highly branched triazine polymers. The use of these modified products as a polymer matrix for composites is expected to give rise to systems with low dielectric loss properties and, most important, relatively low curing temperatures (180–200°C), as opposed to the 300°C needed for the pure cyanates. The thermal characteristics of these blends were studied using thermal analysis techniques.

EXPERIMENTAL

Preparation of Dinonyl Phenol Cyanate (DNPC)

Dinonyl phenol-flashed was purchased from Texaco Chemical Co. It is a viscous liquid possessing a slight phenolic odor and is a mixture of dinonyl phenols, predominantly ortho-para-substituted. The nonyl groups are random branched. It was used in the synthesis of the cyanate ester with no further purification.

Dinonyl phenol cyanate (Fig. 1) was prepared according to the procedure reported by Martin and Mauer.¹⁰ Distilled water (30 mL) and bromine (22 g) were introduced into a 500-mL three-necked round-bottom flask equipped with a low temperature thermometer, mechanical stirrer, and a 100 mL pressure equalizing dropping funnel. The mixture was stirred rapidly and cooled to -5°C in an ice-salt bath. Sodium cyanide (6.5 g) in water (30 mL) was then added dropwise over a period of 30 min; the temperature was maintained below 5°C during the addition. The solution turned gradually bright yellow. After 15 min, dinonyl phenol (44.6 g) in carbon tetrachloride (100 mL) was added all at once with vigorous stirring. Triethylamine (15 g) was then added over a period of 30 min; the temperature

was maintained below 10°C during the addition. The mixture was stirred for an additional 15 min. The organic layer was then separated, washed with water (2×100 mL), dried (Na_2SO_4), and concentrated. The resulting syrupy material was loaded on a short column of silica gel (150 g, in a sintered glass funnel) and the product eluted with hexane. The filtrate was concentrated to yield 26 g (54%) of dinonyl phenol cyanate as a light yellow liquid. Positive identification was made by the IR absorption peak at 2266 cm^{-1} , which is characteristic of the OCN vibration (Fig. 2).

Preparation of the 6F-BADCY/DNPC Blends

The 6F-BADCY monomer was supplied by Hi-Tek Polymers, Inc. as a powder with a purity greater than 99.5%. Blends of 6F-bisphenol A dicyanate, containing up to 20% dinonyl phenol cyanate, were dissolved in methyl ethyl ketone and catalyzed with zinc octoate (100 ppm zinc metal). Zinc octoate was purchased from Mooney Chemicals (Cleveland, OH 44113) as an 8% (zinc metal) solution in mineral spirits.

Samples to be analyzed by DSC were prepared by removing the methyl ethyl ketone using a vacuum desiccator for about 2–3 days at room temperature. The resulting sticky powders were extensively mixed to give homogeneous test samples and stored in a vacuum desiccator to minimize environmental effects.

A DuPont 912 dual sample DSC, coupled to the 9900 thermal analyzer, was used to examine the curing characteristics of this system. The instrument was purged with nitrogen at a flow rate of less than 50 cc/min during each run. The sample size was approximately 8 mg and the heating rate was $20^{\circ}\text{C}/\text{min}$.

Weight-loss experiments were performed using a Perkin-Elmer TGA 7 thermogravimetric analyzer. The sample size was approximately 15 mg. The dy-

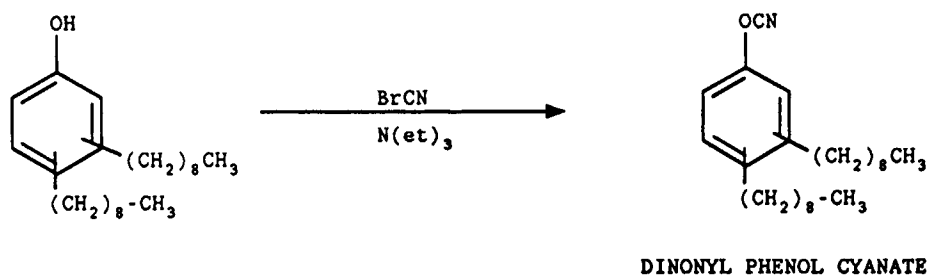


Figure 1 Synthetic route for preparing dinonyl phenol cyanate.

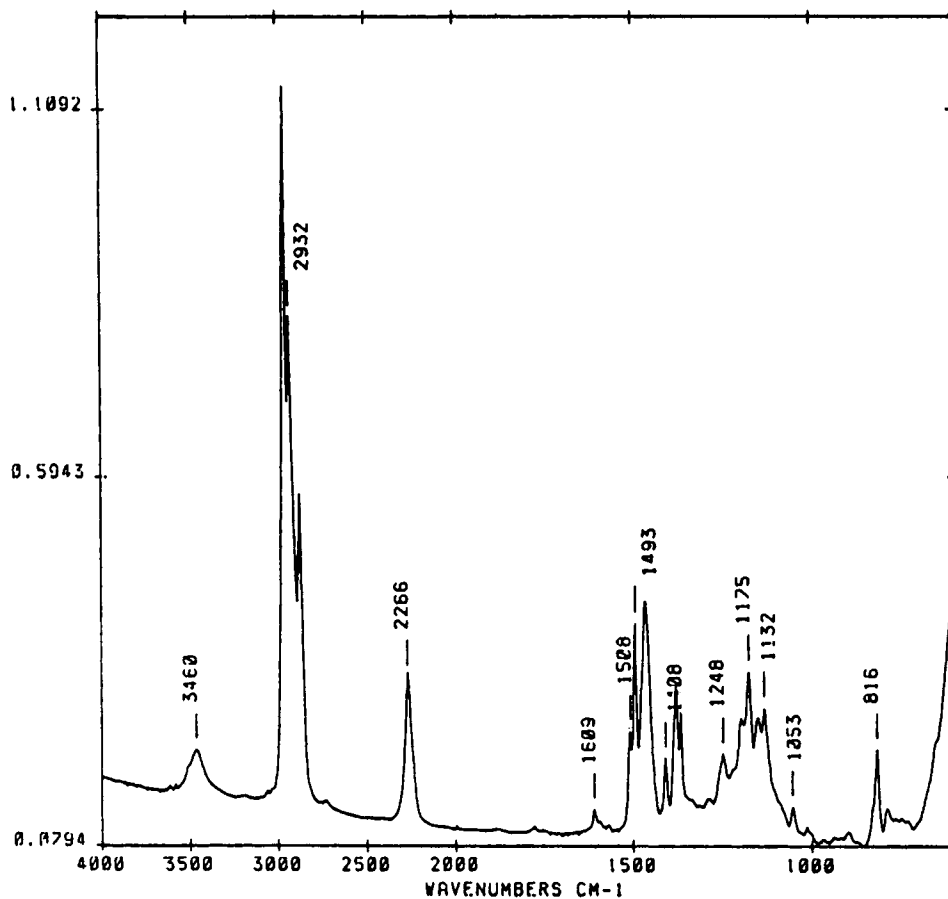


Figure 2 FTIR spectrum of the dinonyl phenol cyanate.

amic scans were made at a heating rate of 20°C/min under a nitrogen atmosphere. Various 6F-BADCY/DNPC blends were prepared by curing the samples at 180°C for 1 h followed by 210°C for 1 h. Pure 6F-BADCY was cured at 300°C for 1 h.

RESULTS AND DISCUSSION

Among several synthetic routes for preparing cyanates, the reaction of phenols with cyanogen halides is the most important and quantitative process.^{10,11} As an illustration, Figure 1 represents the synthesis of the dinonyl phenol cyanate from the corresponding phenol with cyanogen bromide, produced *in situ*, in the presence of triethylamine. As described in the Experimental section, a 54% percent yield was attained. The FTIR spectrum of the resulting light yellow liquid is shown in Figure 2. The absorption peak in the region of 2266 cm⁻¹ is characteristic of the —OCN functional group. The ¹³C-NMR spectrum of the same compound is very complicated due

to the presence of the various isomers in the starting material. The dinonyl phenol is mainly ortho-para substituted and was used as received from Texaco without any purification. This synthesis was used for the small quantities of material needed for preliminary screening and blending studies.

Triazine polymers having 3-dimensional structures are formed almost quantitatively by trimerization of the aromatic cyanates. This reaction could be promoted by acids, bases, or the addition of phenols. A typical example of such a reaction is that of 6F-bisphenol A dicyanate shown in Figure 3(a). The reaction involves the ring closure of three —OCN groups coordinated through the Zn metal. Total consumption of the —OCN groups, though, does not take place unless high curing temperatures are employed as previously reported.¹²

As a consequence, our focus here has been to utilize monofunctional aromatic cyanates for the modification of 6F-BADCY and produce systems processable at lower temperatures. In this case, since the reactive modifiers are of nonpolar character, it

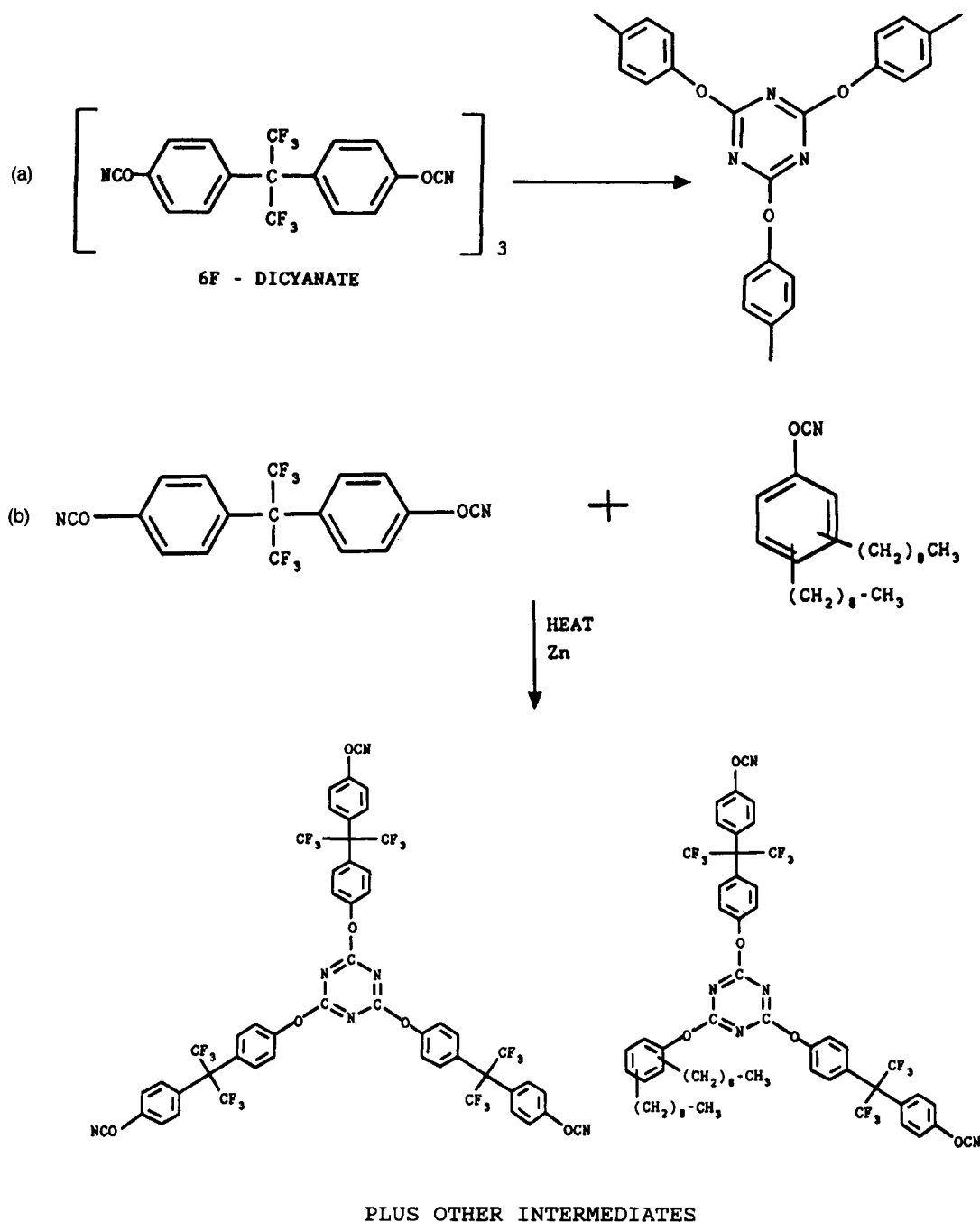


Figure 3 (a) Cyclotrimerization reaction of the 6F-BADCY and (b) 6F-BADCY with DNPC.

is expected that the excellent electrical properties of the modified products will be fully maintained contrary to the epoxy modifiers commonly used in circuit board laminate formulations that can alter the dielectric constant of the system significantly.

As shown in Figure 3b, dinonyl phenol cyanate can react with the 6F-BADCY and produce a num-

ber of possible reactive intermediates. Assuming that both monomers are equally reactive, the monofunctional cyanate would be added to the difunctional monomer and produce highly branched triazine polymers. As a result, the crosslink density can be drastically reduced by the introduction of monofunctional monomers. A remote possibility exists

that the difunctional cyanate may react by itself only. If this occurs, the DNPC would probably trimerize to a trisubstituted triazine ring and simply behave as a compatible diluent in the network. Formation of such product would most likely affect the solvent resistance and thermal stability of the modified products undesirably.

The thermal characteristics of these systems were evaluated using differential scanning calorimetry. A typical DSC scan for the pure fluorinated bisphenol A dicyanate catalyzed with zinc octoate (100 ppm zinc metal) is shown in Figure 4. The initial endothermic peak appearing at slightly below 86°C is due to the melting of the 6F-BADCY monomer. The exothermic peak with an onset temperature (T_{on}) of 128°C and T_{max} of 157°C is associated with the cyclotrimerization reaction of the monomer to form *s*-triazine polymers. Figure 5(a) represents a DSC scan of 6F-BADCY blended with 20% DNPC cured at 20°C/min from room temperature to 290°C and held at this temperature for 30 min. A rescan of the above sample is shown in Figure 5(b). The glass temperature shown in this figure is in the range of 140°C and seems to be rather diffuse.

By introducing the monofunctional cyanate, it is expected that the molar crosslink density of the resulting network will be reduced. This effect is clearly seen by measuring the glass temperature of the 6F-BADCY/DNPC blends. This is well represented by

the experimental findings plotted in Figure 6. The measured ultimate T_g 's for the various blends are shown here. A decrease in T_g , greater than 150°C, can be realized by simply incorporating 20% dinonyl phenol cyanate in the 6F-BADCY. T_g 's in the range of 140–190°C can be realized with 20–10% (wt) DNPC, respectively. Such T_g 's could be obtained by employing low laminating temperatures, as indicated by the 10 and 20% blends. These samples were cured at 180°C for 2 h and then rescanned to obtain the T_g . Blends with greater than 20% (wt) DNPC show very diffuse T_g 's in the range of less than 130°C.

The effect of DNPC content on the thermal stability of the blends was also evaluated using thermogravimetric analysis. The TGA thermograms shown in Figure 7 are characterized by a shallow weight loss followed by a steep degradation peak. The process of degradation starts around 310°C with significant weight loss above 380°C for all the samples irrespective of any level of DNPC present in the blend. No weight loss was observed for the 6F-BADCY polymer until around 445°C.

The percent weight loss of the samples during the thermal degradation in nitrogen between 40 and 300°C ranges between 1.2 and 2.3% as the amount of DNPC increases from 5 to 20%, respectively. The weight loss increase with increasing content of DNPC compared to the neat 6F-BADCY resin may be due to the high susceptibility of the aliphatic side

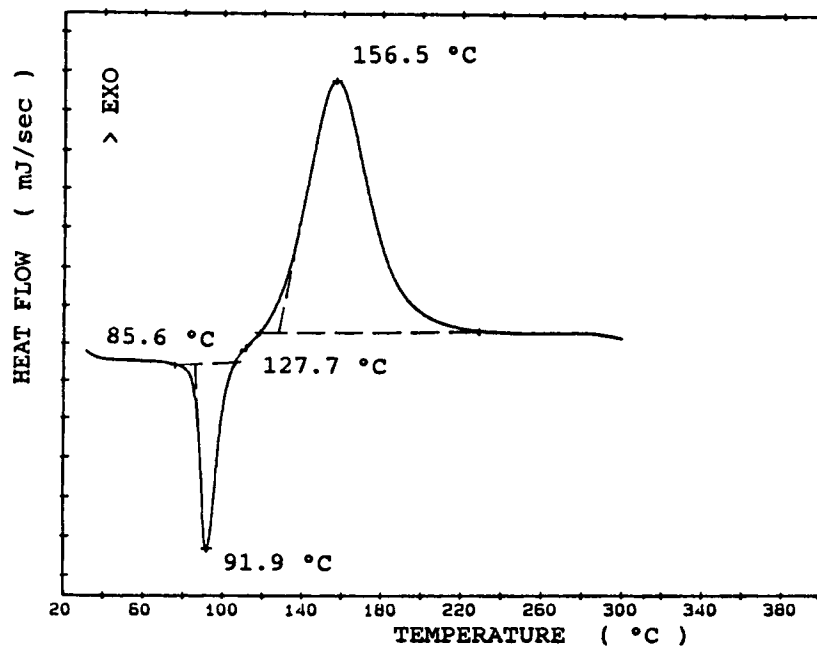


Figure 4 A typical DSC scan of the pure 6F-BADCY monomer catalyzed with 100 ppm of Zn; heating rate 20°C/min.

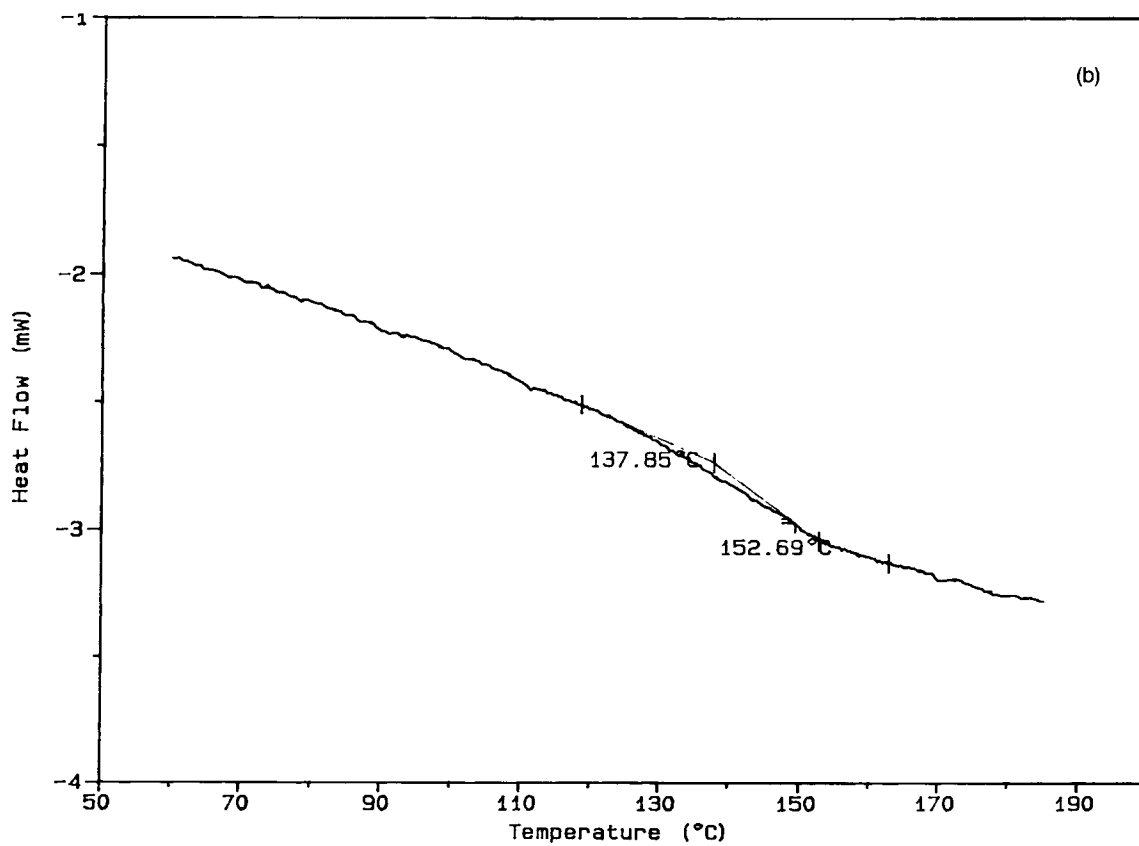
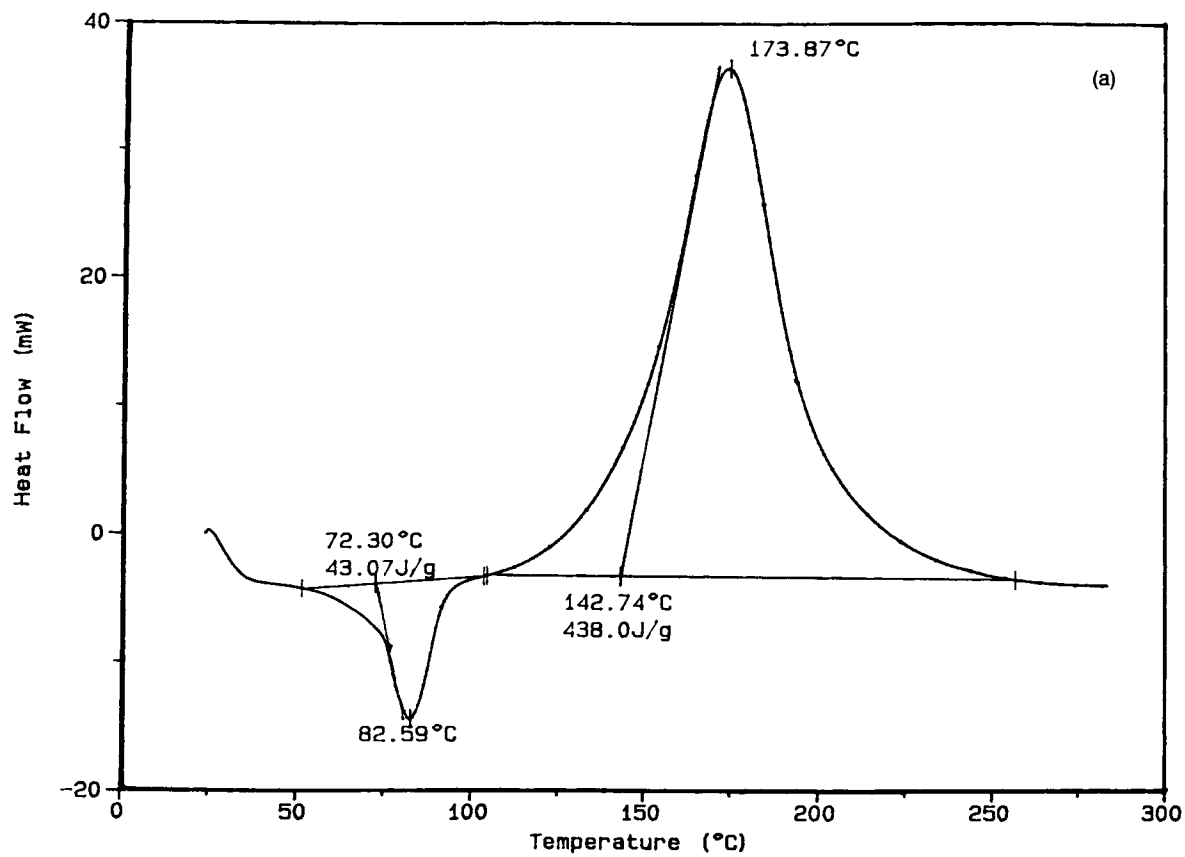


Figure 5 (a) DSC scan of the 80/20 6F-BADCY/DNPC blend; (b) rescan showing the glass temperature; heating rate 20°C/min.

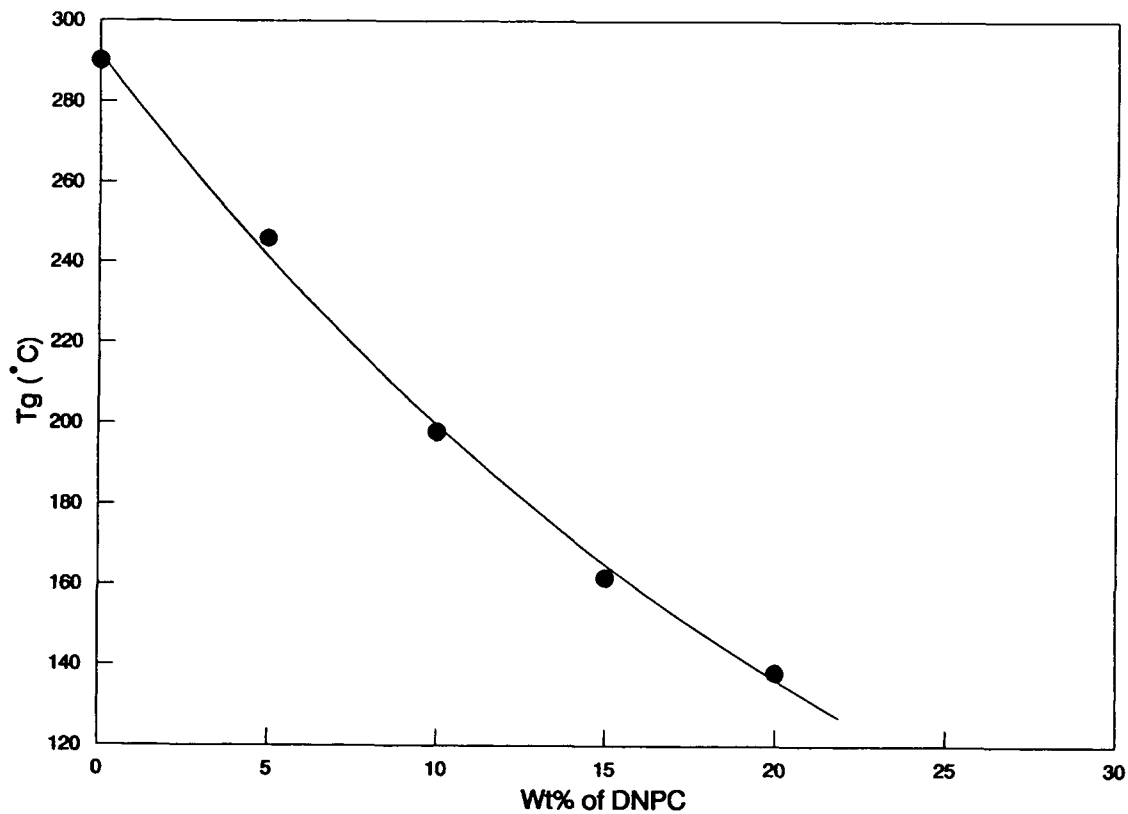


Figure 6 Effect of dinonyl phenol cyanate on the T_g of 6F-BADCY. Samples containing 10-20% DNPC were cured at 180°C/2 h.

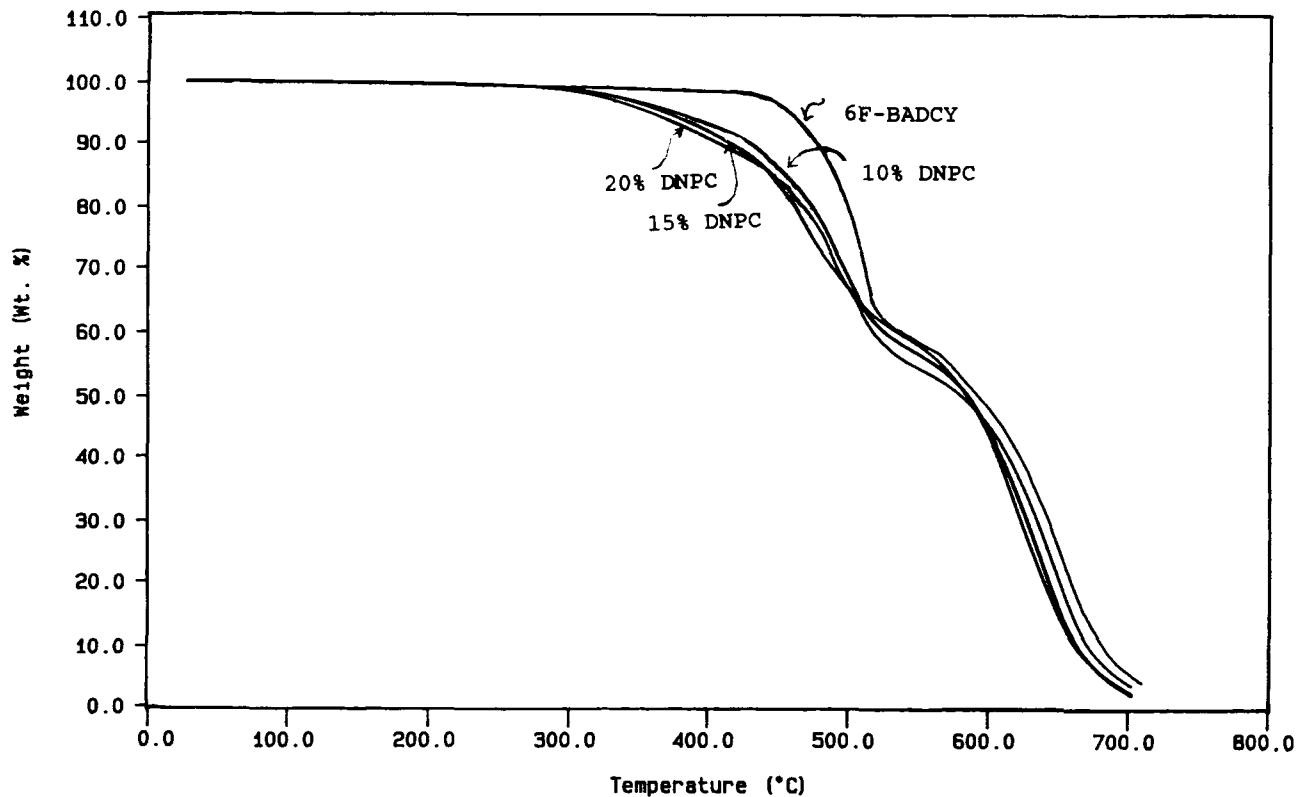


Figure 7 Weight loss as a function of the DNPC content in the network.

chains of the DNPC for thermal and oxidative degradation.

The 6F-BADCY based polymers have been reported to have excellent dielectric properties.⁴ The dielectric constant of the cured neat resin was measured to be in the range of 2.6–2.7. To modify the high temperature processing of such resins, reactive oligomers of the nonpolar nature such as hydrocarbons were selected.

Based on Clausius-Mossotti's equation,¹³ $\epsilon_r = (1 + 2\alpha)/(1 - \alpha)$, $\alpha = P_m/V_m$, where P_m is the molar polarization, V_m is the molar volume, and the α values are as reported by Takahashi et al.,¹⁴ it is expected that the dielectric constant of the modified resins not to be significantly altered. According to Takahashi et al., the relationship of the dielectric constant and α is monotonic, and, as a result, it is important to select modifiers that contain groups with small α values. The reported α values for the groups employed here are as follows: $-\text{CH}_3 = 0.24$, $-\text{CH}_2- = 0.29$, and phenyl ring = 0.38. When α values are less than 0.4, the dielectric constant of the resin that consists of these groups is expected to be less than 3.0.

CONCLUSIONS

The modification of the fluorinated bisphenol A dicyanate monomers and prepolymers with reactive monofunctional cyanates can be realized. Dinonyl phenol cyanate can be incorporated up to 20% by weight in the 6F-BADCY monomer and produces modified resin compositions that can be heat cured at temperatures between 180 and 220°C. Depending on the content of the dinonyl phenol cyanate, the

glass transition temperature of the useful modified products could range between about 140 and 190°C.

The authors will like to thank Professor O. Martin from the State University of New York at Binghamton for carrying out the custom synthesis.

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Received February 22, 1991

Accepted May 14, 1991