

## Polar interaction in a cyanated poly(ether sulfone)-modified polycyanurate

Jer-Yuan Chang\* and Jin-Long Hong

Department of Materials Science and Engineering, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, ROC

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Low molecular weight cyanated poly(ether sulfone) (CPES,  $M_n = 3200$ ) was prepared, and cured with bisphenol A dicyanate (BPADCy). The resulting polycyanurates of different compositions show an S-shaped  $T_g$ -composition curve. This unexpected S-shaped curve is interpreted in term of the polar interaction between poly(ether sulfone) and *s*-triazine rings formed by polycyclotrimerization of aromatic dicyanates. Separate study on u.v. spectra of mixture model compounds suggests that this polar interaction belongs to an  $n-\pi^*$  interaction between the lone pair electrons of the N-atoms in the *s*-triazine ring and the  $\pi^*$ -orbital of the phenylene rings neighbouring to the sulfone linkage. I.r. study on the cured polycyanurates indicates that this polar interaction causes the shift of the  $—C=N$  stretching from 1564 to 1580  $\text{cm}^{-1}$ . © 1998 Elsevier Science Ltd. All rights reserved.

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### Introduction

Chemical interactions such as hydrogen bonds (H—bonds), strong dipoles, charge transfer complexes and ionic interactions in ionomers are specific, strong and orientation-dependent<sup>1,2</sup>. These specific interactions in a polymer blend are especially related to the mutual miscibility between the constituent polymers. However, most examples, like poly(vinyl phenol)-poly(2-vinyl pyridine)<sup>3</sup>, poly(ethylene-co-methacrylic acid)-poly(2-vinyl pyridine)<sup>4</sup>, poly(glutamate)-poly(vinyl phenol)<sup>5</sup>, illustrated previously concerned systems involving H—bonds. Few cases like poly(vinyl nitrate)-poly(vinyl acetate)<sup>6</sup> that the force between the polymer pair is the strong polar interaction between nitrate and acetate groups.

For polymer blends exhibiting miscibility over the entire composition range, four generalized  $T_g$ -composition curves of the linear relationship, minimum and maximum deviations from linearity and S-shaped curve crossing over the linear relationship are possible<sup>7</sup>. Among them, the S-shaped curve had been observed for polymer blends with specific interactions. With a modified Gordon–Taylor equation, Kwei successfully described the S-shaped  $T_g$ -composition curve<sup>7,8</sup>. Kwei equation had been further applied to thermosets to empirically correlate the resulting S-shape curve observed in the cured products from tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) and bisphenol A polycarbonate (PC)<sup>9</sup>. The positive deviation from linearity was interpreted by the intermolecular reactions between PC and the epoxy derived from TGDDM.

Polycyclotrimerization of aromatic dicyanates is unique in considering that this reaction brings three cyanate groups to form a six  $\pi$ -electron *s*-triazine ring as cross-linking points in the resulting polycyanurate network<sup>10</sup>. Generally, the polycyanurates are brittle due to their high cross-linking density. To increase the toughness of the polycyanurate network, poly(ether sulfone) had been introduced as reinforced component<sup>11–13</sup>. Previously, we synthesized cyanated poly(ether sulfone) (as CPES in Figure 1) of different molecular weights<sup>14</sup>, and to use them to toughen

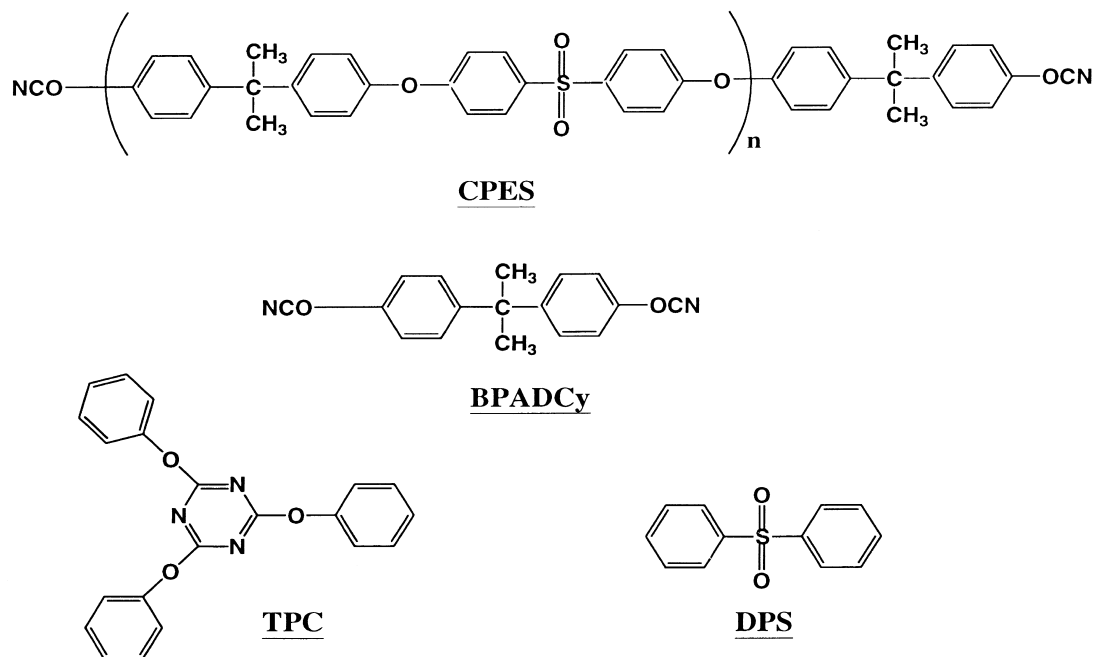
the polycyanurate derived from bisphenol A dicyanate (as BPADCy in Figure 1). During the study, we found the existence of polar interaction in the cured products. This specific polar interaction is between the CPES component and the *s*-triazine ring formed through polycyclotrimerization of BPADCy (or CPES); that is to say, the polar interaction enhances gradually during the curing reaction. To prove the existence of the polar interaction, infrared (i.r.) and ultraviolet (u.v.) spectroscopies were applied in this study.

### Experimental

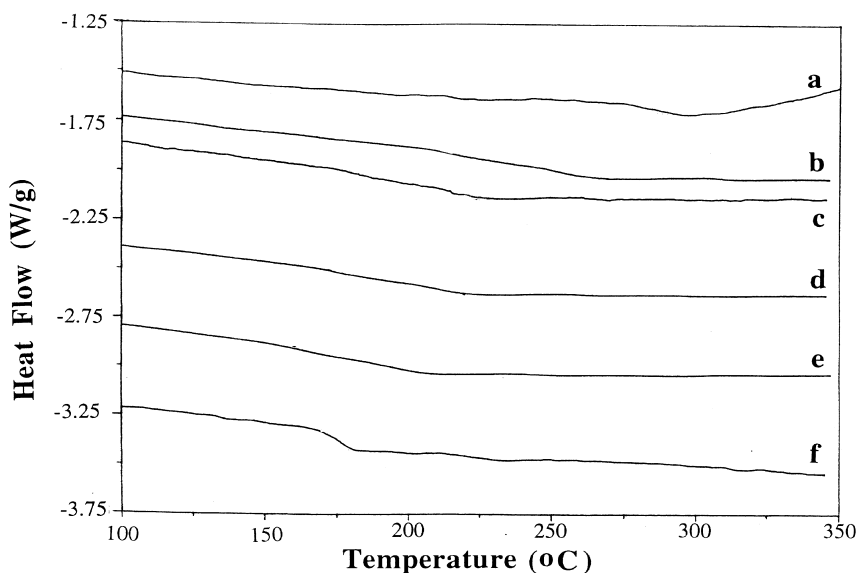
**Materials.** Preparation procedures for cyanated poly(ether sulfone) (CPES) were previously described<sup>14</sup>. Bisphenol A dicyanate (Tokyo Chemical Inc.) was used directly without purification.

**Instrumentations.** A DuPont DSC 910 cell connected to a DuPont 9900 data station were used to determine  $T_g$ . The cured samples of approximately 5 mg were sealed in a hermetic aluminium pan and heated with a scanning rate of 10°C  $\text{min}^{-1}$ . The cured samples were prepared by through mixing two components (BPADCy and CPES) at 130°C before further curing at 200°C for 90 min and 280°C for 30 min. The resulting samples were then rescanned to detect the  $T_g$ s. The infrared spectra were obtained from a Biorad Digilab FTS-40 FTIR spectrometer. A KBr pellet was used for the solid, organic compounds. For the cured products, BPADCy/CPES mixtures of different compositions were dissolved in  $\text{CH}_2\text{Cl}_2$  before deposited on a KBr disc. After removal of  $\text{CH}_2\text{Cl}_2$ , the disc was then placed on a hot plate and heated at 200°C for 90 min and 280°C for 30 min before i.r. measurement. A Hitachi U-3501 u.v. spectrometer was used to obtain u.v. spectra. Triphenyl cyanurate (TPC, structure shown in Figure 1) or diphenyl sulfone (DPS; shown in Figure 1) was dissolved in  $\text{CH}_2\text{Cl}_2$  before being put into a quartz cell for measurement. Mixtures of TPC/DPS were prepared with a constant TPC concentration of 0.5  $\text{mmol l}^{-1}$ . The relative molar ratios of TPC/DPS ranged from 1:0.5 to 1:5.

\* To whom correspondence should be addressed



**Figure 1** Chemical structures of CPES, BPADCy, TPC and DPS



**Figure 2** DSC thermograms of the cured BPADCy/CPESs obtained from a CPES weight percentages of (a) 0; (b) 10; (c) 40; (d) 70; (e) 90; and (f) 100

### Results and Discussion

To test the miscibility of the cured BPADCy/CPES system, the  $T_g$ s of the cured products were recorded as a function of compositions. The resulting DSC thermograms for both systems were shown in *Figure 2*. The single  $T_g$ s shown in all thermograms indicate all products contain no heterogeneous large domains (for domains larger than few hundreds angstroms). The homogeneity of this cured system can be further ensured by their corresponding fractographs from SEM. The fractured surfaces in the cured BPADCy/CPES show no sign of any dispersed second phase, indicating the absence of small-scale heterogeneity in the cured products.

The  $T_g$ s shown in *Figure 2* are all intermediate between those of the cured BPADCy and CPES and vary systematically with composition. The relationship between  $T_g$  and

composition in the cured BPADCy/CPES can be clearly demonstrated by *Figure 3*. The resulting S-shape curve indicates the presence of strong interactions in the cured products of all compositions. With a low content of CPESs, the cured BCs exhibited large, negative deviation from the linearity; however, as the CPES component exceeds 40 wt%, the corresponding cured products have their  $T_g$ s increased to approach the linear line. The rise of the  $T_g$ s suggests certain interactions between CPES component and the *s*-triazine formed during polycyclotrimerizations.

To identify the possible interactions existing in the constituent components of the cured BCs, u.v. study on model compounds with the inherent *s*-triazine ring (i.e. triphenyl cyanurate, TPC in *Figure 1*) and sulfone linkage (i.e. diphenyl sulfone, DPS in *Figure 1*) was performed. Pure DPS has an u.v. absorption at 267 nm while TPC shows featureless pattern above 250 nm (*Figure 4a*). To

compare, spectra of mixtures of different ratios were given in Figure 4b. Obviously, one extra shoulder at 274 nm was observed for mixtures of all compositions. Careful examination suggests that this interaction shoulder at 274 nm increases from a molar ratio of 1:1 to 1:3, and then keeps almost constant in the ranges of 1:3 to 1:5 molar ratios. This may suggest that amounts of interactions increase from molar ratios of 1:1 to 1:3 and become saturated if the ratio is less than 1:3. Reasonably, the ratio of 1:3 is related to the number of N atoms in one *s*-triazine ring to the sulfone linkage. The shift of wavenumber ( $\Delta\lambda$ ) in relationship to the

molar ratio provides information for the origin of the interaction. With the increasing interaction pairs (TPC:DPS ratio increases from 1:1 to 1:3), the corresponding bands shift to lower wavenumber (red shift). The red shift indicates that this interaction belongs to a  $n-\pi^*$  mode, which is mostly contributed by the lone-pair ( $n$ ) electrons on N-atoms of the *s*-triazine ring and the excited  $\pi$  orbital of the phenylene rings neighbouring to the sulfone groups.

The red shift observed in u.v. study can be qualitatively correlated with wavenumber shift of the  $-\text{C}=\text{N}$  stretching in the i.r. spectra. Although there are two  $-\text{C}=\text{N}$  stretching bands at around 1380 and 1560  $\text{cm}^{-1}$ , we are concentrating on the absorption at the higher wavenumber one since it showed certain variations on different cured products. The cured BPADCy exhibited a characteristic  $-\text{C}=\text{N}$  stretching at 1564  $\text{cm}^{-1}$  (Figure 5a). Interestingly, the partially-cured ( $\sim 50\%$  conversion of the BPADCy component) product from a 1:1 molar ratio of CPES and BPADCy has two  $-\text{C}=\text{N}$  stretching bands at 1564 and 1580  $\text{cm}^{-1}$  (cf. Figure 5b). These two absorption peaks became one broad peak at 1580  $\text{cm}^{-1}$  (Figure 5c) as the corresponding BPADCy/CPES system was completely cured. It is therefore suggested that both the BPADCy-rich and CPES-rich polycyanurate oligomers were generated in the partially-cured sample. As the reaction proceeds further, inter-reaction between these two oligomeric species became prevalent and this resulted in a network with most of its *s*-triazine cross-linking points closed by the neighbouring diphenylsulfone moieties in the chain segments of the poly(ether sulfone) and therefore, the shift of the  $-\text{C}=\text{N}$  stretching to a higher 1580  $\text{cm}^{-1}$  band. A separate i.r. study shows that only the band at 1580  $\text{cm}^{-1}$  peak (Figure 5d) was observed during cure of the pure CPES.

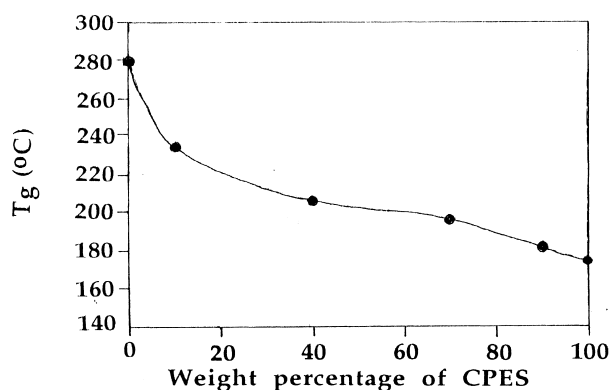


Figure 3 Relationship between  $T_g$ s and composition for the cured BPADCy/CPES products

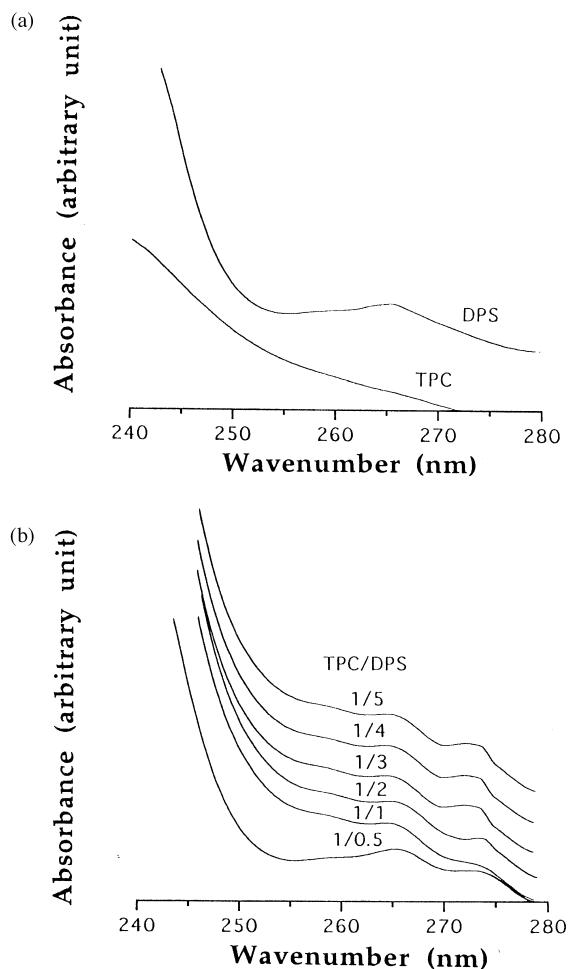


Figure 4 U.v. spectra of (a) pure TPC (triphenyl cyanurate) and DPS (diphenyl sulfone); and (b) TPC/DPS mixtures of different molar ratios

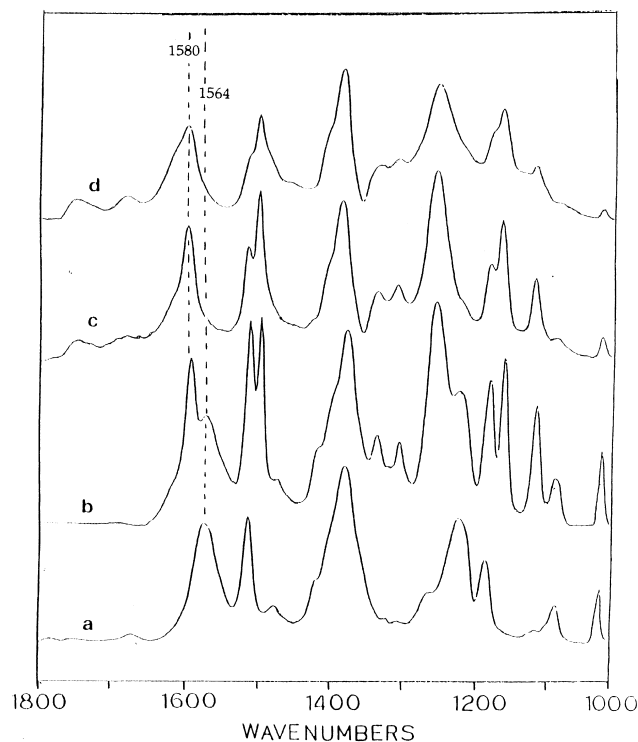


Figure 5 I.r. spectra of (a) the cured BPADCy; (b) the partially cured BPADCy/CPES (1:1 molar ratio); (c) the fully cured BPADCy/CPES (1:1 molar ratio); and (d) the cured CPES

### Conclusion

The  $T_g$ s of the cured BPADCy/CPESs exhibit an S-shaped dependence on their compositions. This S-shaped  $T_g$ -composition relationship can be explained by the strong polar interactions (an  $n-\pi^*$  interaction) between the lone-pair ( $n$ ) electrons on N-atoms of the  $s$ -triazine ring and the excited  $\pi$  orbital of the phenylene rings neighboring to the sulfone groups. This interaction can be further demonstrated by u.v. spectra of model TPC and DPS; and i.r. spectra of the cured BPADCy, CPES and BPADCy/CPES blend.

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