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# Notes

## Fluorescence Characterization of Model Compounds for Cyanate Monomers, Cure Intermediates, and Cure Product

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### Introduction

High-temperature and high-performance thermosetting polymeric materials such as polycyanate resins have been widely used in composites, adhesives, coatings, and electronic industries. The development of the techniques for real-time monitoring of the cross-linked polymers has been growing because of the increased demand for improved productivity and quality. Our laboratory has developed UV−vis and fluorescence cure monitoring techniques to characterize cure reaction and water uptake in epoxy,[1] polyurethane,[2] polyimide,[3] bismaleimide,[4] and vinyl polymers.[5]

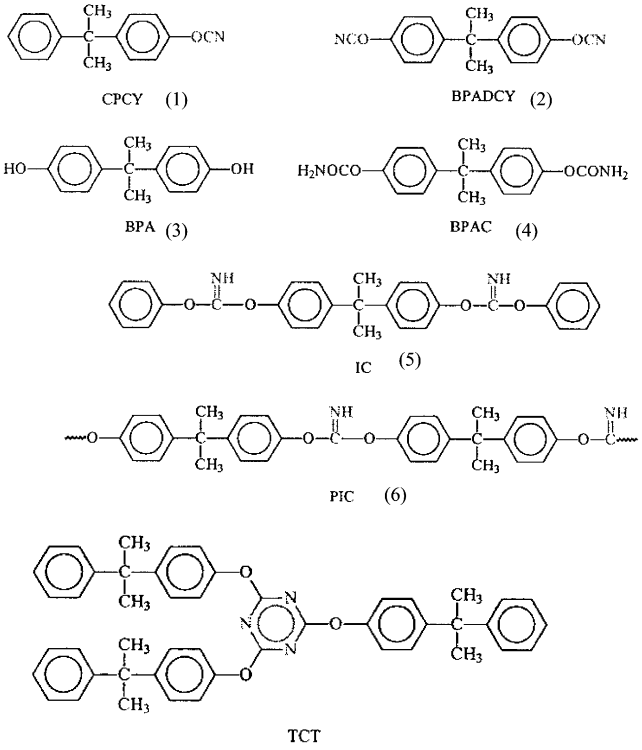
In our studies, we observed the changes in fluorescence, UV, and FTIR spectra as a function of the cure reaction of bisphenol A dicyanate ester (BPADCY).[6] Very strong luminescence emission has been detected during the cure reaction. Fluorescence excitation and emission peaks appeared at approximately 280 and 420 nm, respectively. The maximum of phosphorescence emission occurred at about 20 nm longer than that of fluorescence maximum. Although polycyclotrimerization to form *s*-triazine rings is considered to be the main cure reaction by IR, the origin of UV spectral change and fluorescence has not been elucidated before.

The fluorescence behavior of substituted s-triazines, especially aromatically substituted *s*-triazines, is not well documented. Since the aromatically substituted *s*-triazine is expected to be produced as cross-linkers in the cure of polycyanate due to cyclotrimerization, we decided to investigate the fluorescence behavior of substituted *s*-triazines to understand the observed fluorescence during cure.

Several mechanisms have been proposed for the cure reaction of polycyanate resins. Although controversy remains, the key product proposed during cyclotrimerization of cyanate ester in the absence of a catalyst is expected to be an intermediate called iminocarbonate as a result of reaction with bisphenol A (BPA), an impurity present in the monomer. This intermediate may react with two additional cyanate groups to form triazine ring and release BPA.[7] Therefore, the iminocarbonate was included as one of the model intermediates to study.

Other model compounds are bisphenol A (BPA) and BPA carbamate (BPAC) which are the suspected impurities in monomers.[7e] To identify the origin of fluorescence observed during cure of cyanate ester, seven model compounds are chosen to represent monomers, impurities, cure intermediates, and cure product as shown in Scheme 1. In this work, we report fluorescence spectroscopic characterization of these model compounds as well as a soluble oligomer mixture and the trimer from the monofunctional cyanate monomer.

**Scheme 1. Chemical Structures of Model Compounds; Numbers Correspond to Fluorescence Spectra in Figure 1a**



### Experimental Section

Cumylphenyl cyanate ester (CPCY) was synthesized and purified according to the literature.[8] Difunctional BPADCY monomer with the purity greater than 99.5% was supplied by Ciba-Geigy Corporation. The monomer was recrystallized in acetone three times before use. BPA was purchased from Aldrich and was recrystallized in water/acetone before use. BPAC was synthesized and purified according to the literature.[9a]

The proposed intermediates, phenol−iminocarbonate (IC) and poly(BPA−iminocarbonate) (PIC), were synthesized and purified by reacting BPADCY with a stoichiometric amount of phenol and BPA, respectively, according to the literature.[10] The model cure product, tricumylphenoxyl-*s*-triazine (TCT), was synthesized by heating cumylphenyl cyanate ester (CPCY) at 200 °C for 2 h. The presence of unreacted CPCY[9b] in TCT is below the detection limit of FTIR. All the synthesized compounds were characterized, and their structures were confirmed by FTIR, $^{1}$H NMR, and $^{13}$C NMR spectra.

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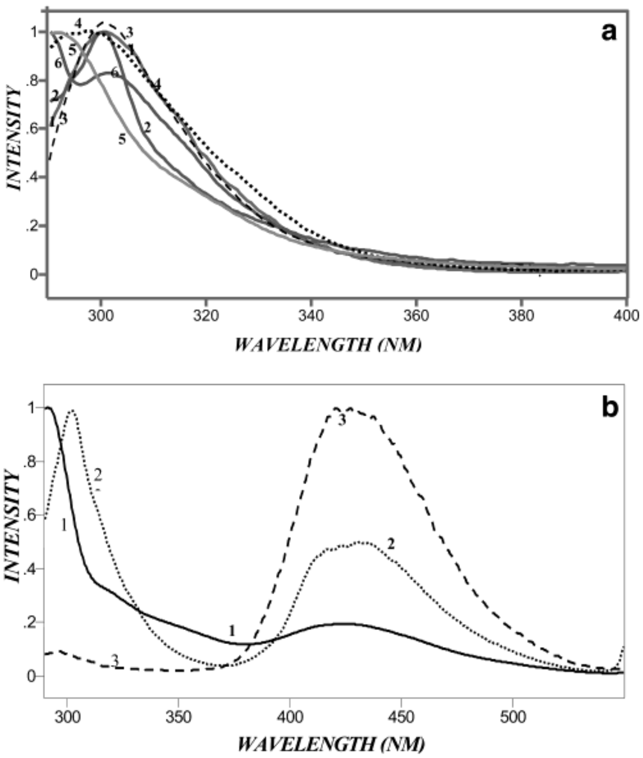

**Figure 1.** (a) Fluorescence emission spectra of monomers, suspected impurities, and cure intermediates in THF (excited at 265 nm: 1, CPCY, $1.84 \times 10^{-5}$ M; 2, BPADCY, $9.60 \times 10^{-6}$ M; 3, BPA, $2.76 \times 10^{-6}$ M; 4, BPAC, $1.91 \times 10^{-5}$ M; excited at 280 nm: 5, IC, $1.07 \times 10^{-5}$ M; 6, PIC, $6.64 \times 10^{-3}$g/mL). (b) Fluorescence emission spectra of triazine model compound and BPADCY oligomer in THF and solid state (excited at 280 nm; 1, TCT: $3.9 \times 10^{-4}$ M; 2, oligomer: $2.8 \times 10^{-5}$ g/mL; 3, solid oligomer film).

The soluble BPADCY oligomer was prepared by heating recrystallized BPADCY monomer at 200 °C for 60 min in argon, since the reaction was stopped before the gelation. The monofunctional monomer CPCY was melted between two quartz plates for 3 min at 100 °C and trimerized in argon at 200 °C. All model compounds were dissolved in spectrophotometric grade THF.

For fluorescence studies, a Perkin-Elmer LS50B luminescence spectrophotometer was used at room temperature. A Mattson Polaris 100 FTIR spectrometer was used for FTIR measurement with samples mixed with KBr powder. NMR spectra were collected in either $CDCl_3$ or $d_6$-acetone solution with a Bruker AC-270 NMR or DMX-500 NMR spectrometer.

## Results and Discussion

**Fluorescence Spectroscopic Characterization of Model Compounds and Soluble Oligomer.** Fluorescence emission spectra in THF are shown in Figure 1a for model compounds except the model cure product TCT. The benzene ring usually exhibits fluorescence emission around 275 nm.[11] Therefore, BPA fluorescence emission is typical of substituted benzene and similar to that of phenol,[12] with a emission maximum at 305 nm (curve 3 in Figure 1a). Fluorescence usually is weak in molecules with an $n-\pi^*$ state as the lowest excited singlet state such as cyanate ester moiety.[13] Consequently, the results show that BPA is about 500 times more fluorescent than BPADCY, which has an emission maximum at 295 nm (curve 2 in Figure 1a) when excited at 265 nm.

The emission peak of BPAC is between those of BPA and BPADCY and appears at 301 nm (curve 4 in Figure 1a). Fluorescence behavior of CPCY (curve 1 in Figure 1a) is very similar to that of BPADCY (curve 2 in Figure 1a), as expected. The emission of bulk CPCY and BPADCY is very similar to that in solution. Fluorescence emission is usually detected for a concentration in the range $10^{-5}-10^{-9}$ M depending on the characteristics of the fluorophores. In this concentration range, both IC and PIC in THF solutions only show emission around 295 and 302 nm (curves 5 and 6 in Figure 1a), respectively. All of these model compounds exhibit the emission typical of substituted benzene, and there is essentially no emission observed around 400 nm. Therefore, fluorescence emission from these species (monomers, impurities, and intermediate cure products) cannot account for the emission observed at 420 nm during the cure reaction of BPADCY monomer.

The fluorescence spectra of TCT, the model for cure product, is shown as curve 1 in Figure 1b. For TCT, the broad emission around 420 nm as well as a peak near 290 nm is clearly shown. Even the possible presence of small amount of unreacted CPCY cannot account for the broad emission observed around 420 nm in TCT. The soluble oligomer mixture has an emission at 295 nm and another very strong one at 430 nm in the solid state (curve 3 in Figure 1b). After dissolving in THF, the emission peaks (curve 2 in Figure 1b) show up at 302 and 432 nm, which are similar to the emission from TCT model compound. Cyanurate resin from BPADCY develops an amber color after cure with increasing broad UV absorption near 340 nm.[6c] When excited near 340 nm, little fluorescence is observed at 420 nm, indicating that the side reaction responsible for the amber color is not mainly responsible for the observed fluorescence during cure.

**Fluorescence Spectroscopic Characterization during Trimerization of CPCY.** Cumylphenoxy cyanate ester (monofunctional monomer, CPCY) has been reported to undergo a quantitative cyclotrimerization uncomplicated by side reactions.[8] In the current study, the formation of triazine rings has been confirmed by FTIR spectroscopy. With increasing reaction time, ambient fluorescence emission spectra during bulk reaction of CPCY in argon at 200 °C emerges with a maximum around 415 nm, which is also similar to that of the model compounds, TCT and BPADCY oligomer. Therefore, this result further supports that the emission around 420 nm in polycyanate resins comes from substituted triazine rings, which is the cross-linker in the resin.

## Summary

To elucidate the origin of the spectral changes observed in fluorescence emission during the cure reaction of a bisphenol A dicyanate ester monomer, seven model compounds representing monomers, impurities, cure intermediates, and cure product have been investigated. Fluorescence spectroscopic characterization indicate that aryl cyanate esters, aryl carbamate, and aryl iminocarbonate compounds exhibit a characteristic fluorescence emission at around 300 nm from substituted benzene rings. However, in the model cure product, tricumylphenoxyl-*s*-triazine, the emission was observed near 420 nm, which is similar to the fluorescence observed during cure of cyanate ester monomer. The soluble oligomer in the solid state and the trimer from a monofunctional cyanate monomer also exhibit the observed fluorescence emission near 420 nm. Therefore, it is concluded that the origin of the observed fluorescence during resin cure is mainly due to the cross-linker which is similar to tricumylphenoxyl-*s*-triazine.

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