REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
June 24, 1996

3. REPORT TYPE AND DATES COVERED
Technical 6/95 - 5/96

4. TITLE AND SUBTITLE
Cure Characterization of Bisphenol A Dicyante by Fluorescence, UV and FTIR Spectroscopy

5. FUNDING NUMBERS
NR 413 m 011
N000 14-89-J-1145

6. AUTHOR(S)
Y.E. Xu and C.S.P. Sung

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Institute of Materials Science
97 North Eagleville Road
University of Connecticut
Storrs, CT 06269-3136

8. PERFORMING ORGANIZATION REPORT NUMBER
Technical Report No. 53

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
ONR
800 North Quincy Avenue
Arlington, VA 22219

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

19960723 049

11. SUPPLEMENTARY NOTES
Published in ACS Polymer Preprints, 36(2), 356, 1995

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Reproduction in whole or in parts is permitted for any purpose of the United States Government, this document has been approved for the public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Dicyanate ester resins are a relatively new class of high performance materials in electronic and composite applications. In this work we present fluorescence, UV and FTIR spectroscopic investigation of cure chemistry of bisphenol A dicyanate ester. FTIR in situ monitoring shows cure kinetics is very sensitive to phenolic impurity. Strong fluorescence and phosphorescence signals associated with cure species have been detected. Fluorescence excitation and emission peaks appear at approximately 280nm and 430nm respectively. The peak intensity initially increases and then decreases; at the same time the peak maxima in the spectra undergo a red shift with cure time. The fully cured polymer emits phosphorescence around 480 nm. UV-Vis cure characterization shows that the absorption at 340 nm increases as the reaction proceeds. A series of model compounds are under study to identify the origin of fluorescence and phosphorescence emission and the UV changes.

DTIC QUALITY INSPECTED 3

14. SUBJECT TERMS
Bisphenol A Dicyanate, Cure Characterization, FTIR, Fluorescence, UV Spectroscopy

15. NUMBER OF PAGES
2

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT

18. SECURITY CLASSIFICATION OF THIS PAGE

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT

to appear in *Polym. Prep.* **1995**, 36(2)

CURE CHARACTERIZATION OF BISPHENOL A DICYANATE BY FLUORESCENCE, UV AND FTIR SPECTROSCOPY.

Y. Eugene Xu and Chong Sook P. Sung, Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3136

Dicyanate ester resins are a relatively new class of high performance materials in electronic and composite applications. In this work we present fluorescence, UV and FTIR spectroscopic investigation of cure chemistry of bisphenol A dicyanate ester. FTIR *in situ* monitoring shows cure kinetics is very sensitive to phenolic impurity. Strong fluorescence and phosphorescence signals associated with cure species have been detected. Fluorescence excitation and emission peaks appear at approximately 280 nm and 430 nm, respectively. The peak intensity initially increases and then decreases; at the same time the peak maxima in the spectra undergo a red shift with cure time. The fully cured polymer emits phosphorescence around 480 nm. UV-Vis cure characterization shows that the absorption at 340 nm increases as the reaction proceeds. A series of model compounds are under study to identify the origin of fluorescence and phosphorescence emission and the UV changes.

ACS Polymer Preprints, 36(2), 356, 1995

Cure Characterization of Bisphenol A Dicyanate Ester by Fluorescence, UV and FTIR spectroscopy

Y. Eugene Xu and Chong Sook P. Sung
Institute of Materials Science, University of Connecticut
Storrs, CT 06269-3136

INTRODUCTION

Dicyanate ester resins are a relatively new class of high performance materials used in electronic and composite applications. Because of their thermal stability, low dielectric loss, high toughness and good adhesion, they have received intensive commercial and scientific attraction recently [1,2].

Many characterization techniques such as FTIR [3], DSC [4], TBA [5], NMR [6] and HPLC [7] have been applied to understand the cure kinetics and mechanisms. Curing is known to reach a full conversion after higher temperature cure. The reaction is known to be very sensitive to impurities and catalysts. For example, an impurity of phenolic OH group due to the synthesis of monomer is speculated to form an imidocarbonate. The intermediate can react with two OCN groups to generate the stable triazine ring and release the phenolic group.

Despite substantial efforts, the cure chemistry is not well understood. If one assumes a dendrite growth model for trimerization, the maximum cyanate conversion is predicted to be only 75%. In order to account for an almost complete reaction (>98%), Fang has recently proposed the presence of intramolecular oligomers [8]. The presence of reactive dimer was proposed, since probability of three cyanate groups to simultaneously merge is relatively small. Side reactions leading to linear cyanate oligomer formation are suspected during cure.

Because the physical and chemical properties of thermosets depend on their cure states, it is desirable to obtain the information that describes the network structure. Spectroscopic methods have been proven to be convenient and powerful tools to characterize cure reactions and probe reaction mechanisms [9,10]. In this work, we present fluorescence, UV and FTIR spectroscopic investigation of cure chemistry of bisphenol A dicyanate ester.

EXPERIMENTAL

Materials Bisphenol A dicyanate ester (BPADCY) with purity of 99.5% was supplied by Ciba-Geigy Corporation. BPADCY was recrystallized in acetone three times before use. To compare cure kinetics, unpurified BPADCY, purified BPADCY, and purified BPADCY containing 2.4% bisphenol A (BPA) were investigated, since phenolic type impurity is expected to be present in BPADCY [11].

Sample preparation For UV-Vis and fluorescence work, BPADCY was melted between two quartz plates for 3 minutes at 100 °C, and then cured in argon a. 200 °C. Samples were removed from the oven at certain time intervals and the spectra were recorded at room temperature using a Perkin Elmer Lambda 6 UV-Vis spectrometer and a Perkin Elmer LS50B luminescence spectrophotometer. For FTIR monitoring, BPADCY was melted between two NaCl disks for 3 minutes at 100 °C, and then cured in argon at 200 °C. FTIR spectra were obtained both *in situ* and at room temperature using Mattson Cygnus 100 FTIR spectrometer.

RESULTS AND DISCUSSION

The polymerization of BPADCY monomer is depicted in Scheme 1. Polycyclotrimerization to form triazine rings is believed to be the main curing reaction.

Cure kinetics investigation by FTIR in argon was carried out at 160, 200 and 240 °C. Cyanate conversion can be calculated by OCN stretching at 2270 cm^{-1} with CH valence band at 2970 cm^{-1} as an internal standard. Figure 1 shows cyanate conversion measured *in situ* as a function of cure time for unpurified, purified and 2.4% BPA added BPADCY systems under an argon atmosphere. It is very obvious that the curing is slower for the purified system than the unpurified system. Adding BPA accelerates the reaction greatly as expected.

Figure 2 shows the changes in ambient fluorescence emission following cure of purified BPADCY at 200 °C in argon. A very strong fluorescence emission was observed. Excitation and emission peak appeared approximately at 280 and 430 nm, respectively. The peak intensity initially increased and then decreased; at the same time the peak maxima in the spectra underwent a small red shift with cure time. The shape of the spectra implies that there may be more than one type of fluorophore involved at later stage of cure. Both purified BPADCY with added BPA and unpurified BPADCY systems showed similar fluorescence results with emission maxima at 430 nm as the purified monomer following cure at 200 °C. BPA has an emission at 300 nm which decreased with cure time. Therefore, the observed emission at longer wavelength is not due to BPA. Fluorescence intensity changes as a function of cure time are shown in Figure 3 for all three cases. Again, BPA added monomer reached the maximum fastest, followed by unpurified BPADCY. Purified monomer was slowest as in FTIR results.

These results indicate that fluorescent species are involved during polymerization of dicyanate ester resin. However, the question remains as to their origins on a molecular level. Experiments in argon and further purification of BPADCY suggest that the fluorescence is likely to come from cure species, and not from impurities, air oxidation or moisture induced hydrolysis. One possible origin of the fluorescence is *s*-triazine rings which are formed during polymerization. While *s*-triazine itself has been reported to have little fluorescence or phosphorescence emission [12,13], substituted triazine ring may exhibit fluorescence emission as in cured dicyanate resin. Another possibility is the formation of fluorescent intermediates and their subsequent consumption for the observed fluorescence behavior.

UV-Vis cure characterization of BPADCY at 200 °C in air is illustrated in Figure 4. The resolution at low wavelength was lost as the reaction proceeded, but absorption at 340 nm increased during polymerization. Experiment in argon showed that this absorption is not due to oxidation. The identification of the absorption at 340 nm is in the process.

Due to the energy difference between singlet and triplet states, compounds with the lowest transition of n-π*, such as *s*-triazine, should prefer an intersystem crossing transition. Therefore, moderate phosphorescence is expected for dicyanate ester polymers. Phosphorescence emission was detected for BPADCY polymer as shown in Figure 1 (spectrum 9). Phosphorescence emission maximum at 480 nm occurs at a much longer wavelength than the 430 nm emission maximum in fluorescence.

A series of substituted triazine compounds are under study to identify the origin of fluorescence and phosphorescence emission and the UV changes.

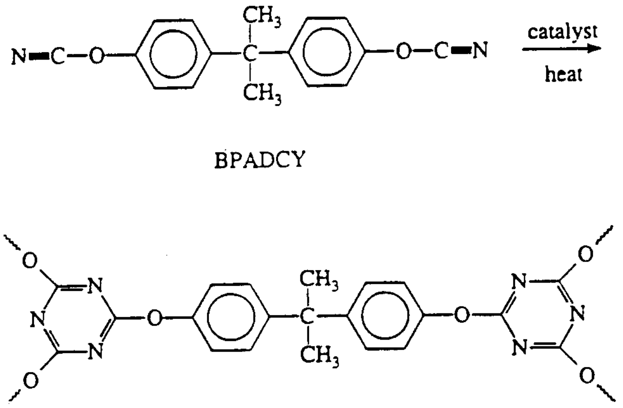
REFERENCES

1. *Chemistry and Technology of Cyanate Ester Resins*; Hamerton, I., Ed.; Blackie Academic and Professional: Glasgow, 1994.
2. Polycyanates: Chemistry and Application Symposium; Snow, A.W., Org.; *Polym. Mater. Sci. Eng. Prep.* **1994**, 71
3. Osei-Owusu, A.; Martin, G.C.; Gotro, J.T. *Polym. Eng. Sci.* **1991**, 31 1604
4. Simons, S.L.; Gillham, J.K. *J. Appl. Polym. Sci.* **1993**, 47 461
5. Simons, S.L.; Gillham, J.K. *J. Appl. Polym. Sci.* **1994**, 51, 1741
6. Fyfe, C.A.; Niu, J.; Rettig, S.J.; Burlinson, M.; Resdsema, C.M.; Wang, D.W.; Poliks, M. *Macromolecules*, **1992**, 25, 6289

7. Shimp, D.A. *Polym. Mater. Sci. Eng. Prep.* **1994**, 71, 813
8. Fang, T.; Moulinham, F.M. *Polym. Prep.* **1994**, 51, 1741
9. Song, J.C.; Sung, C.S.P. Sung. *Macromolecules* **1993**, 26, 4818
10. Sung, C.S P.; Sung, N.H. *Polym. Mater. Sci. Eng. Prep.* **1994**, 71, 425
11. Snow, A.W. In *Chemistry and Technology of Cyanate Ester Resins*; Hamerton, I., Ed.; Blackie Academic and Professional: Glasgow, 1994; pp7-54
12. Chowdhury, M.; Goodman, L. *J. Chem. Phys.* **1963**, 38, 2979
13. Gallivan, J.B.; Brinen, J.S.; Koren, J.G. *J. Mol. Spectrosc.* **1968**, 26, 24
14. Allen, N.S.; Binkely, J.P.; Parsons, B.J.; Philips, G.O.; Tennent, N.H. *Polym. Photochem.* **1982**, 2, 97 & 389

ACKNOWLEDGMENTS

We acknowledge the financial support in part by the Office of Naval Research and the Army Research Office (contract No. DAAL03-92-G-0267) and the National Science Foundation, Polymer Program (Grant DMR 94-15385).



Scheme 1. Polycyclotrimerization of BPADCY monomer

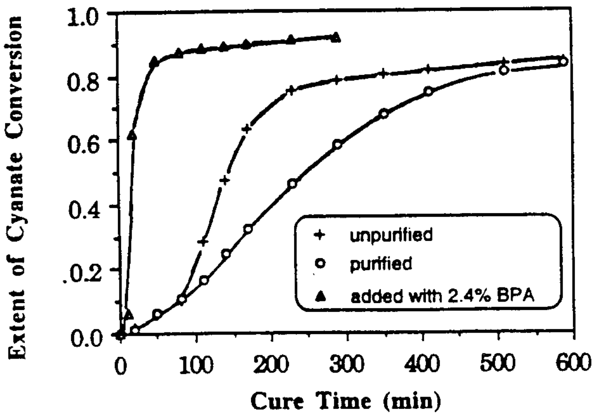


Figure 1. FTIR *in situ* cure kinetics of BPADCY during cure at 200 °C in argon

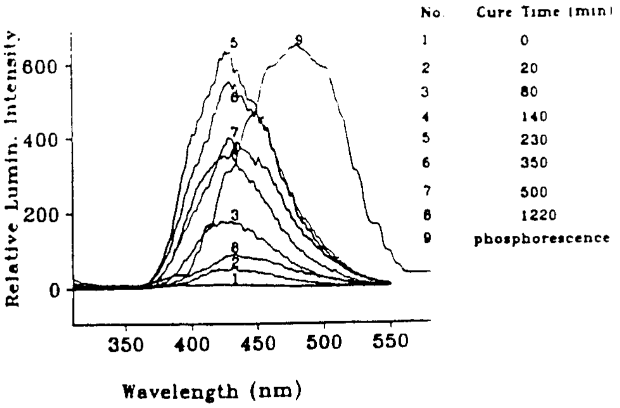


Figure 2. Ambient fluorescence emission spectra of purified BPADCY during cure at 200 °C (excited at 280 nm)

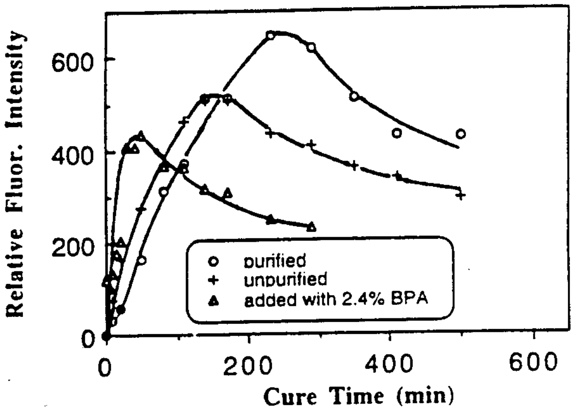


Figure 3. Fluorescence emission intensity at 430 nm as a function of cure time for BPADCY resins following cure at 200 °C (excited at 280 nm)

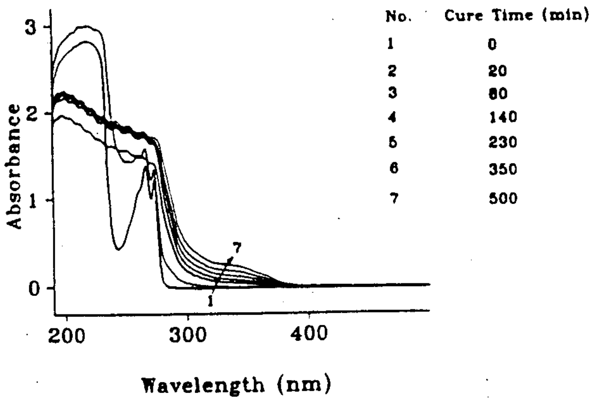


Figure 4. UV-Vis transmission spectra of unpurified BPADCY during cure in air at 200 °C