ELSEVIER

S0032-3861(96)00407-7

Polymer Vol. 37 No. 21, pp. 4869–4872, 1996

0032-3861/96/\$15.00 + 0.00

Triazine formation in cyanate-based resin systems at room temperature conditions

A. Osei Owusu*
3M Corporate Research Laboratories, 3M Center 201-BS-08, Maplewood, MN 55144, USA

and G. C. Martin
Department of Chemical Engineering and Materials Science, Syracuse University, Syracuse, NY 13244, USA

and J. T. Gotro
Allied-Signal Laminate Systems, Lacrosse, WI 54602, USA
(Received 12 September 1995; revised 8 March 1996)

The reactivity of uncatalysed and catalysed cyanate ester resin in solvent was investigated under room temperature conditions. At room temperature, the uncatalysed resin was non-reactive in the solvents while a triazine reaction leading to the polymerization of cyanate monomer occurred in the catalysed systems. The extent of reaction and the relative amounts of triazine depends on the time in solution, the concentration and type of catalyst, and the type of solvent. These reactions, that occur in solution at room temperature, can significantly reduce the glass transition temperature of the fully cured material. Copyright © 1996 Elsevier Science Ltd.

(Keywords: cyanate ester; cyclotrimerization; reactivity)

Introduction

There is agreement in the literature that the cyclotrimerization reaction is the dominant reaction pathway during the cure of cyanate-based resins to form a highly crosslinked polytriazine network[1–10]. The reaction can be catalysed by co-ordination metal catalysts and an active hydrogen initiator or thermally induced at temperatures greater than 190°C. At lower temperatures the reaction rate for the uncatalysed systems is extremely slow to achieve any significant level of conversion.

During processing operations, resin systems are typically formulated in solvents and stored at room temperature. Clearly, an understanding of the behaviour of the resin under processing conditions is essential for process optimization. While previous studies have focused on the effects of catalysts and cocatalysts on the final properties of the network[2,4,6,8], little work has been done on the behaviour of the catalysed systems in solvents under room temperature conditions[11,12].

The objective of this work was to investigate the nature of reactions that occur in solvents for catalysed bisphenol A-based cyanate esters under room temperature conditions and to determine their effects on the glass transition temperature of the resin. Fourier transform infrared spectroscopy (*FT*i.r.), nuclear magnetic resonance (n.m.r.), and size exclusion chromatography (s.e.c.) were used to monitor the reactions. The glass transition temperature (T_g) of the network was determined using differential scanning calorimetry (d.s.c.) and the extent of reaction was measured from *FT*i.r. experiments.

Experimental

The bisphenol A dicyanate (BADCy) monomer, with the trade name AroCy B-10 and 99.9% purity, was supplied by Ciba-Geigy. The catalysts, 18% zinc octoate and 6% manganese octoate dissolved in mineral spirits, were obtained from Pfaltz and Bauer and technical grade nonylphenol was supplied by Eastman Kodak. Spectroscopic grade solvents, methyl ethyl ketone (MEK) containing 5×10^{-2} mol% water, tetrahydrofuran (THF) with 3×10^{-2} mol% water, and chlorobenzene (CB) with 5×10^{-3} mol% water, were obtained from Fisher Scientific and were used as received.

Solutions containing different catalyst concentrations (ppm of metal per cyanate equivalent weight) ranging from 0 to 750 ppm and 4 phr (parts per hundred by weight) nonylphenol (OH) were prepared by dissolving the components in methyl ethyl ketone (MEK), tetrahydrofuran (THF), or chlorobenzene (CB). The homogeneous mixture, at a concentration of 0.25 mol of BADCy/l, was stored at 25°C for various periods of time. Part of the sample was recovered by solvent flashing in a vacuum oven for d.s.c. analysis.

*FT*i.r. studies were performed using an IBM Instruments IR/32S. The spectra were taken using 0.05 mm fixed thickness and 32 mm NaCl cells. The fixed thickness cell was used to obtain the spectra of the pure solvent and the mixture, immediately after sample preparation, under a constant nitrogen-purged atmosphere. The spectrum of the resin was obtained by subtracting the spectrum of the pure solvent from the spectrum of the mixture using spectra subtraction software.

Spectra were also obtained for samples stored for various periods of time by preparing thin films of the resin on 32 mm diameter NaCl cells. The samples were

---

* To whom correspondence should be addressed

then placed in a vacuum oven to eliminate residual solvent prior to the analysis. Peak areas were calculated for the carbonyl at 1750 cm^{-1} and the triazine ring vibration at 1560 cm^{-1}. The C–H stretching peak at 2950 cm^{-1} was used as the reference peak.

^{13}C n.m.r. spectra were recorded on a Bruker/IBM AF-100 spectrometer at 25.18 MHz. 25 wt% solutions were prepared using deuterated chloroform from Aldrich. Chromium (III) acetylacetonate, 0.5 wt% in chloroform, was used to accelerate the relaxation process of the ^{13}C nuclei in the sample. All spectra were recorded without contribution from proton NOE. 8000 scans were averaged using a 2 s relaxation delay.

S.e.c. studies were performed using a Waters Associates 150 C ALC/GPC equipped with an RI detector. Tetrahydrofuran was used as the solvent. The column was operated at 30°C and a solvent flow rate of 1.0 ml/min was maintained. Polystyrene standards were used for the column calibration.

Both dynamic and isothermal d.s.c. experiments were performed using a Mettler DSC-30 equipped with a low temperature cell. Isothermal studies were conducted by ramping the sample at 100°C min^{-1} from 25°C to the isothermal temperature and holding for 1 h. The sample was then scanned at 10°C min^{-1} to determine the T_g. The temperature corresponding to the endothermic deflection of the baseline was taken to be the T_g.

Results and discussion

The *FT*i.r. spectra for BADCy/750 ppm Zn/4 phr OH in MEK taken immediately after sample preparation and after 24 h at 25°C are shown in *Figure 1*. The initial spectrum (a) shows a peak at 2270 cm^{-1} which is due to the cyanate vibration. After 24 h, new absorption bands are observed at 3450, 1750, and 1560 cm^{-1} as shown in spectrum b. The band at 3450 cm^{-1} is due to N–H stretching; the band at 1750 cm^{-1} is due to C=O stretching; and the peak at 1560 cm^{-1} is due to the triazine ring vibration. These results indicate that a trimerization reaction leading to the formation of triazine and a reaction resulting in the formation of a compound with N–H and C=O vibrations occur under these conditions. Cyanate/metal systems have previously been regarded as stable at temperatures less than 90°C[9].

Further evidence on the reactivity of the cyanate systems in solution was obtained from ^{13}C n.m.r. studies. The ^{13}C n.m.r. spectrum for BADCy/750 ppm Zn/4 phr OH formulated in MEK and stored for 24 h at 25°C is shown in *Figure 2*. The signal at 108 ppm is due to the cyanate group and the signal at 174 ppm is due to triazine formation. The signal at 155 ppm is characteristic of a carbonyl carbon attached to a NH_2 group.

The extent of polymerization under these conditions was verified from s.e.c. experiments. The s.e.c. chromatograms for uncatalysed samples of BADCy monomer and BADCy/750 ppm Zn/4 phr OH, prepared in THF and stored for 48 h at 25°C are shown in *Figure 3*. The chromatogram for uncatalysed BADCy shows a single peak at a retention time of 36.6 min, indicating that the uncatalysed systems are stable under these conditions. The chromatogram for BADCy/750 ppm Zn/4 phr OH shows, in addition to the monomer peak, a variety of peaks at retention times ranging from 30 to 36 min which correspond to higher molecular weight species.

The *FT*i.r., s.e.c. and the n.m.r. results suggest that polymerization of cyanate occurs in catalysed systems at room temperature leading to the formation of triazine and compounds that contain carbonyl and NH_2 groups. The reactions leading to the formation of compounds containing the carbonyl and NH_2 groups will be discussed in the next publication[13].

Effect of solvent

The effect of solvents on the reactions was investigated

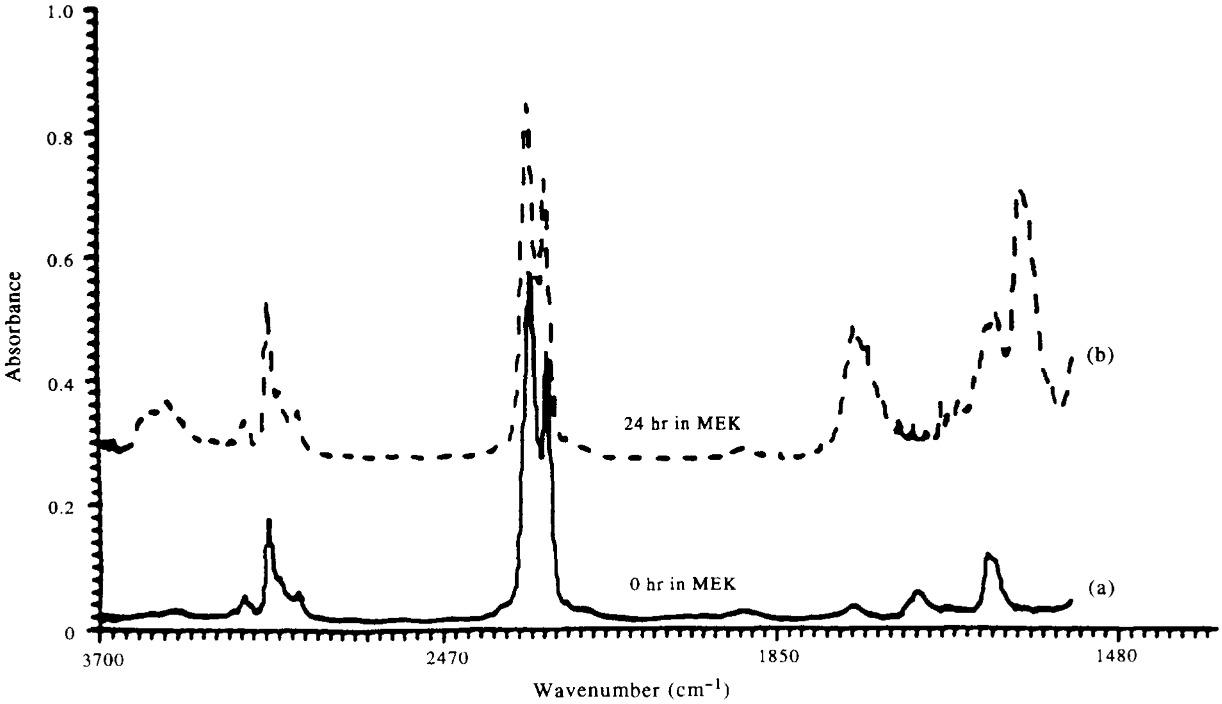

Figure 1 *FT*i.r. spectra for BADCy/750 ppm Zn/4 OH in MEK: initial spectrum (a); 24 h in solution (b)

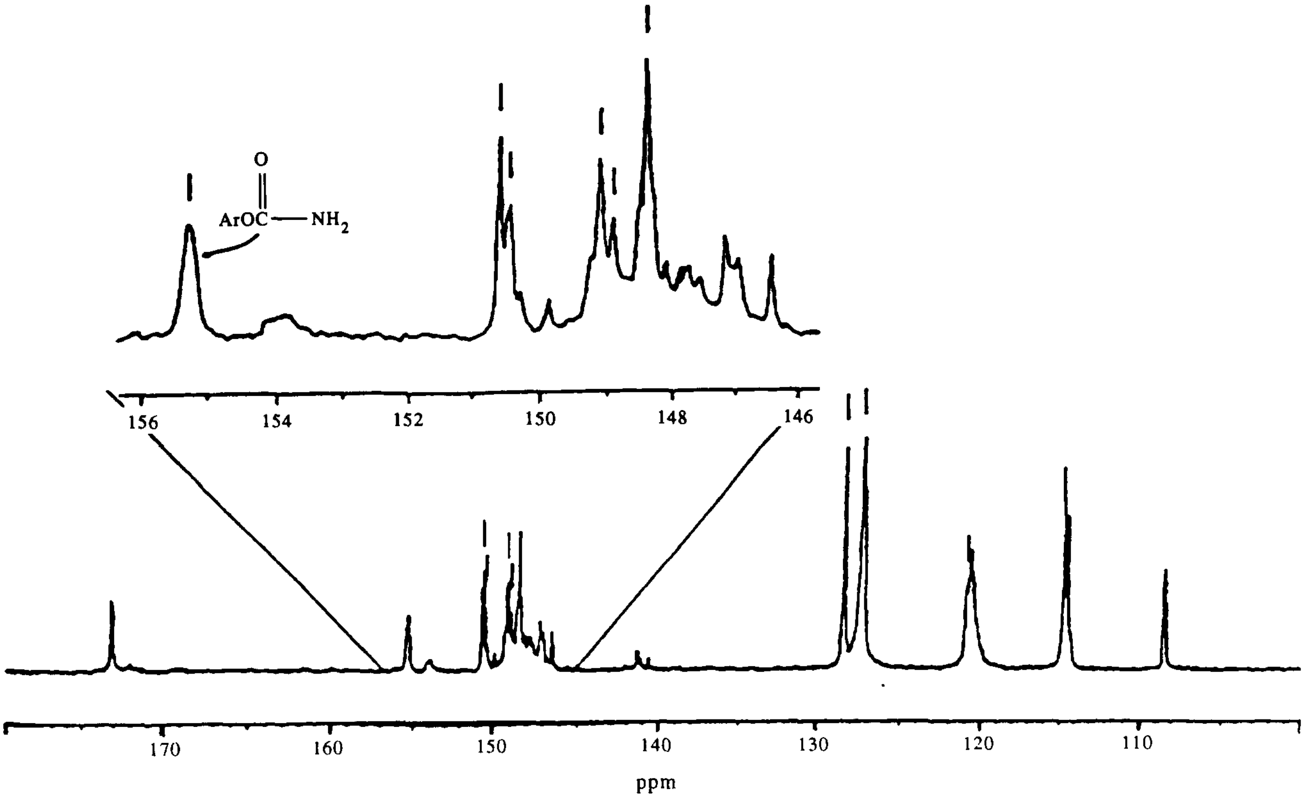

Figure 2 ^{13}C n.m.r. spectrum for BADCy/750 ppm Zn/4 OH samples formulated in MEK and stored for 24 h

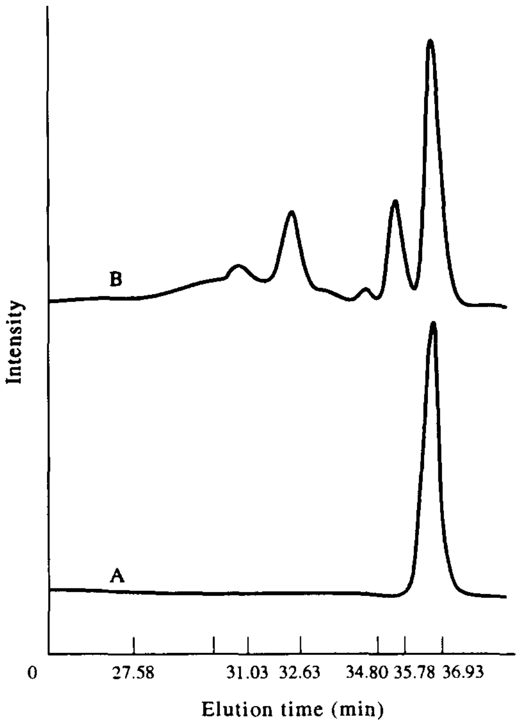

Figure 3 S.e.c. chromatograms for samples formulated in THF and stored for 48 h: uncatalysed BADCy (A); BADCy/750 ppm Zn/4 OH (B)

using *FT*i.r. for BADCy/750 ppm Zn/4 phr OH system formulated in THF, MEK, and chlorobenzene and stored for 24 h at 25°C. *Table 1* shows the extent of reaction in the solvents and the ratio of the intensities of the carbonyl and the triazine peaks to the reference band at 2950 cm^{-1}. The highest extent of reaction was attained in the samples formulated in THF. The extent of reaction was 17.2% in THF, 14.3% in MEK, and 6.5% in chlorobenzene.

The relative intensity of the triazine ring vibration is highest for the sample prepared in chlorobenzene while the intensity of the carbonyl absorption band is highest in the sample formulated in THF. This indicates that the extent of reaction depends on the type of solvent. Studies are currently underway to determine the effect of solvent hydrophobicity on these reactions.

Effect of catalyst

The extent of the trimerization reaction varies with the type and concentration of catalyst, and with the time the resin system remains in solution. The solvent-based conversions determined from *FT*i.r. experiments for BADCy/100 Zn/4 phr OH and BADCy/100 ppm Mn/4 phr OH in MEK for various periods of time are shown in *Table 2*. For the Zn-catalysed samples, the conversion increases from 2% after 24 h in solution to 9.5% after aging for 126 h. For the Mn-catalysed samples, 3.2% of the cyanate groups react after 126 h in solution. This result may be due to differences in the reactivities of the two metal catalysts since Zn-catalysed systems are more reactive than Mn-catalysed samples[2,6,8].

In order to elucidate the effect of the room temperature reactions on the final network structure, the T_g was measured on fully cured samples prepared from solutions aged for different times. *Table 2* shows the fully cured T_g values for BADCy/100 ppm Zn/4 phr OH and BADCy/100 ppm Mn/4 phr OH systems formulated in MEK. For the Zn-catalysed samples, the T_g decreases by 51°C from 258°C for samples prepared by immediate

Table 1 The extent of reaction in the solvents and the area ratio of the carbonyl and triazine peaks to the reference band at 2950 cm^{-1}

Solvent	% Conversion	$C=O/CH_3$	Triazine/CH_3	% Triazine
THF	17.2	0.84	0.16	16
CB	6.5	0.06	1.25	95
MEK	14.3	0.59	0.41	41

solvent evaporation to 207°C for samples aged for 126 h. The T_gs for the Mn-catalysed samples do not change after 72 h in solution and decrease by 17°C for samples stored for 126 h. The decrease in the T_g may be due to the incorporation of less stable structures in the network which endcaps the chains, thereby reducing the effective cyanate functionalities and the crosslink density of the network.

Summary

The reactivities of catalysed and uncatalysed cyanate ester resin systems under room temperature conditions were investigated. The results suggest that triazine formation occurs in solution for the metal-catalysed systems at 25°C. The extent of reaction and product distribution depends on the solvent and the type and concentration of the catalyst. The uncatalysed cyanate systems were stable at room temperature.

Table 2 The solvent-based conversions and the fully cured T_g for BADCy/100 ppm metal/4 phr OH systems prepared in MEK and stored for various periods of time at 25°C

Time in MEK (h)	Zn		Mn	
	% conversion	T_g(°C)	% conversion	T_g(°C)
0	0.0	258.0	0.0	261.4
24	2.0	—	0.0	259.4
48	3.5	245.8	1.2	257.3
72	5.2	237.0	1.8	256.0
126	9.5	207.4	3.6	244.3

Acknowledgements

The authors wish to thank G. Kohut and M. Poliks (IBM) for performing the n.m.r. experiments and D. A. Shimp (Ciba-Geigy) for the supply of the cyanate ester resin.

References

1. Shimp, D. A., Christenson, J. R. and Ising, S. J. 'Hi-Tek Polymers Publication', 1989
2. Osei Owusu, A., Martin, G. C. and Gotro, J. T. *Polym. Eng. Sci.* 1991, **31**, 1604
3. Shimp, D. A. *Proc. ACS Div. Polym. Mater. Sci. Eng.* 1986, **54**, 107
4. Osei Owusu, A., Martin, G. C. and Gotro, J. T. *SPE Tech. Papers* 1991, **49**, 727
5. Gupta, A. and Macosko, C. W. *Makromol. Chem., Macromol. Symp.* 1991, **45**, 105
6. Osei Owusu, A., Martin, G. C. and Gotro, J. T. *Proc. ACS Div. Polym. Mater. Sci. Eng.* 1991, **65**, 304
7. Bauer, M., Bauer, J. and Kuhn, G. *Acta Polym.* 1986, **37**, 11
8. Osei Owusu, A., Martin, G. C. and Gotro, J. T. *Polym. Eng. Sci.* 1992, **32**, 535
9. Wertz, D. H. and Prevorsek, D. C. *Plast. Eng.* 1984, **40**, 31
10. Osei Owusu, A. and Martin, G. C. *Polym. Eng. Sci.* 1995, **35**, 1
11. Osei Owusu, A., Martin, G. C., Poliks, M. D., Balko, J. W. and Gotro, J. T. *Proc. ACS Div. Polym. Mater. Sci. Eng.* 1992, **66**, 449
12. Shimp, D. A. *Proc. ACS Div. Polym. Mater. Sci. Eng.* 1992, **66**, 504
13. Osei Owusu, A. and Martin, G. C. (to be published)