Carbon-13 liquid- and solid-state nuclear magnetic resonance and infra-red studies of amine-cured epoxy resins

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The final network structure and the course of the reaction of bisphenol A diglycidyl ether with 1-cyanoguanidine dissolved in dimethylformamide in the presence of different accelerators have been studied by liquid-state ^{13}C nuclear magnetic resonance, solid-state ^{13}C cross-polarization/magic-angle spinning nuclear magnetic resonance and infra-red spectroscopies. Fractions of reactive groups such as oxirane rings, primary and secondary hydroxyl groups, imide and nitrile groups have been detected as functions of epoxy consumption and reaction conditions. Structural tautomerism of the hardener, the influence of water, the reaction of nitrile groups and other structural features of the curing system have been discussed.

(Keywords: bisphenol A diglycidyl ether; 1-cyanoguanidine; carbon-13 nuclear magnetic resonance; infra-red spectroscopy)

INTRODUCTION

The physical, chemical and ultimate mechanical properties of thermosetting polymers rely on their crosslinked structure. In particular, epoxy resin systems have been extensively studied using differential scanning calorimetry[1,2], Fourier-transform infra-red spectroscopy[3,4], high-performance liquid chromatography[5] and dynamic mechanical analysis[6]. However, none of these techniques allow us to identify directly the chemical structures of the epoxy network, whereas high-resolution ^{13}C nuclear magnetic resonance spectroscopy detects carbon resonances that directly reflect the chemical structures of the system.

This paper considers the usefulness of liquid-state ^{13}C n.m.r. in connection with solid-state ^{13}C n.m.r. and i.r. measurements for investigating the chemical structures and the course of the reaction of curing of the diglycidyl ether of bisphenol A (BADGE) with 1-cyanoguanidine (dicyandiamide, DCDA) in the presence of different accelerators such as *N,N*-dimethylbenzylamine (DMBA), monuron and imidazole.

CHEMICALS

Commercially manufactured and purified[7] BADGE, DCDA and dimethylformamide (DMF) were used in the investigated system.

Four series without any accelerator were prepared to study the course of the reaction up to the gel point by liquid-state n.m.r. The reaction was interrupted at different epoxy consumptions and the reaction products were stored at −20°C.

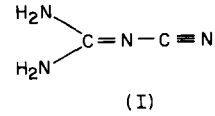
For solid-state n.m.r. and i.r. measurements, 20 samples were cured, varying the reaction conditions. For these conditions, see *Table 1*.

To get a homogeneous system, DCDA was dissolved in DMF (mole ratio 1:6 for all series). Signals at 162.4, 35.8 and 30.8 ppm were expected even in the cured state.

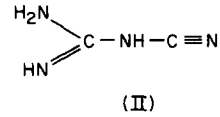
MONOMERS

The structure of monomeric BADGE is explained in many publications.

The i.r. spectrum of monomeric DCDA consists of a doublet in the nitrile range (2180 and 2160 cm^{-1}). The ratio of the two signals shifted by varying the chemical environment of the DCDA molecules. On the other hand, no shifts could be observed after heating of crystalline DCDA at 120°C for 1 h compared with untreated DCDA. Hence we assume the existence of two DCDA configurations:



(I)



(II)

Between these two configurations of DCDA, a chemical equilibrium exists, depending on the chemical environment and the temperature.

No splitting of n.m.r. resonances was detectable, probably owing to the comparatively high frequency of interchanging of the configurations.

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Table 1 Reaction conditions for the samples used

(a) Solid samples

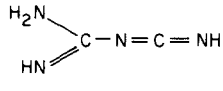
Mole ratio BADGE:DCDA	Temperature (°C)	Time (min)	Accelerator[a]
4:1	120	180	1, 2, 3, 4
2.5:1	120	180	1, 2, 3, 4
2.5:1	120	180	1, 2, 3, 4
4:1	150	90	1, 2, 3, 4
2.5:1	140	120	1, 2, 3, 4

[a]1, DMBA, 1 mol%; 2, imidazole, 1 mol%; 3, monuron, 2 mol%; 4, without accelerator

(b) Liquid samples (without accelerator)

Mole ratio BADGE:DCDA	Temperature (°C)
2.5:1	120
2.5:1	140
4:1	120
1:1	120

The carbonyl band at 1745 cm^{-1} in the i.r. spectra of the cured samples and the vanishing of the nitrile resonance at 118.5 ppm in liquid-state n.m.r. are in good agreement with the supposition of a third DCDA configuration originating during reaction (analogous to the tautomerism of cyanamide[7]):



(III)

ANALYSIS

Liquid-state ^{13}C n.m.r. spectra were collected on a Bruker HX 90 R spectrometer operating at a frequency of 22.635 MHz using dimethylsulphoxide (DMSO) as solvent. About 10 000 free induction decays (FIDs) were accumulated at a temperature of 31°C with the following parameters: spectral width, 4500 Hz; repetition time, 2.0 s[8,9]; pulse width, 4.7 μs (corresponding to 53.5° pulses); proton decoupling power, 3 W.

Computer integrals were used for the intensities. The conditions for quantitative analysis are fulfilled because the pulse repetition rate is larger than $3T_1$ for the carbons of interest.

The solid-state ^{13}C n.m.r. spectra were measured on a Bruker MSL 200 spectrometer at a temperature of 30°C using cross-polarization (CP) and magic-angle spinning (MAS). All solid samples were measured in Al_2O_3 rotors.

The contact time was adjusted to 0.7 ms, and the spinning frequency to 5 kHz. Some 2400 scans were accumulated for one spectrum at a resonance frequency of 50.3 MHz and a repetition time of 3 s.

Decoupling field strength was 50 kHz in frequency units, and spectral width was 20 kHz.

Computer software was used for the separation of the signals and for intensity determination.

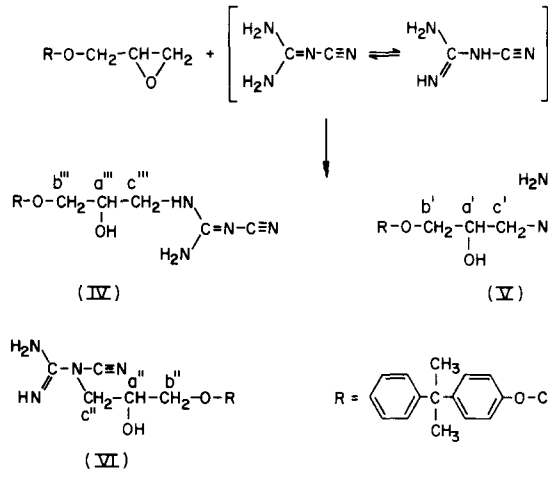
All solid samples were also measured on a Perkin–Elmer 580B i.r. spectrometer in the range between 4000 and 350 cm^{-1} at 25°C, connected on-line with a multichannel analyser (Tracor-Northern TN-4000).

For preparation, 1.3 mg substance and 0.35 g KBr were pressed into pellets.

Computer integrals were also used for the intensities.

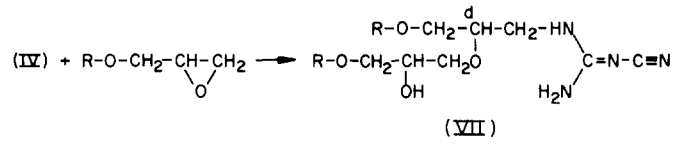
RESULTS AND DISCUSSION

Zeppenfeld *et al.*[10] described the main reaction between DCDA and phenyl glycidyl ether (PGE) as the addition of an amino group to an epoxy group, but it is not quite clear which amino group is preferred:



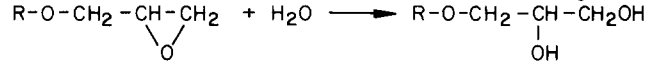
(IV) (V) (VI)

A secondary hydroxyl group, as a result of the main reaction, is able to open up a further epoxy group (etherification). This is the basic step for crosslinking:



(VII)

Unlike the main reaction, during etherification the total number of hydroxyl groups remains constant. However, it is difficult to obtain the ratio of both reactions because of the hydrolysis of BADGE, where primary and secondary OH groups appear:



(VIII)

A liquid-state ^{13}C n.m.r. spectrum (b) and the corresponding solid-state ^{13}C n.m.r. spectrum (a) are shown in *Figure 1*. Known structures and the assigned signals are marked. The signals of BADGE $C(CH_3)_2$ and DMF $N(CH_3)_2$ are not exactly degenerate in solution. New resonances were found between 44 and 50 ppm, at 64 ppm, at about 70 ppm, at 118 ppm, at 126 ppm and at about 162 ppm in the liquid-state spectra.

In the range of 70 ppm seven signals were found, split into two subranges: three signals (70.9, 70.3, 69.7 ppm (range a)) are due to carbons with attached secondary OH groups; a further three should be caused by ether carbons (68.1, 67.8, 67.0 ppm (range b))[9,11]. However, the exact order of a′, a″ and a‴ in range a and b′, b″ and b‴ in range b could not be explained. The intensities of the six signals increase with epoxy consumption. At 69.1 ppm the ether nucleus of unreacted BADGE loses its intensity.

Two signals appear at 46 and 49 ppm, respectively, increasing with excess of DCDA (range c). Probably carbons corresponding to peak 12 that have already reacted to $-CH_2-N-$ groups during the main reaction are responsible for these signals.

Etherification (77 ppm, carbon d in (VII)) was, with one exception, not detectable in liquid-state samples. It

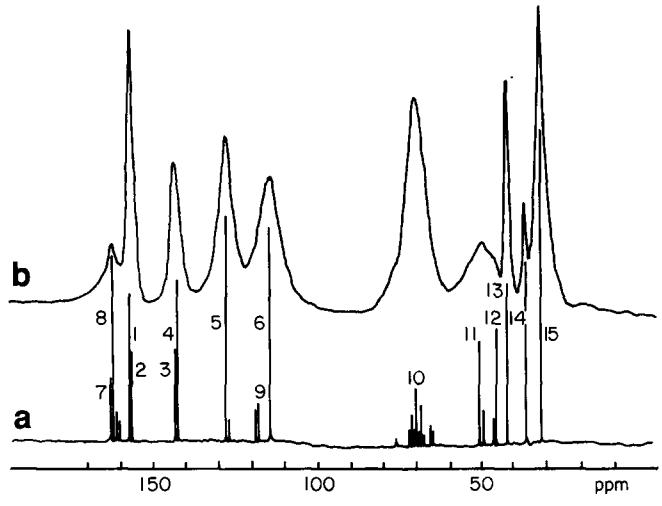
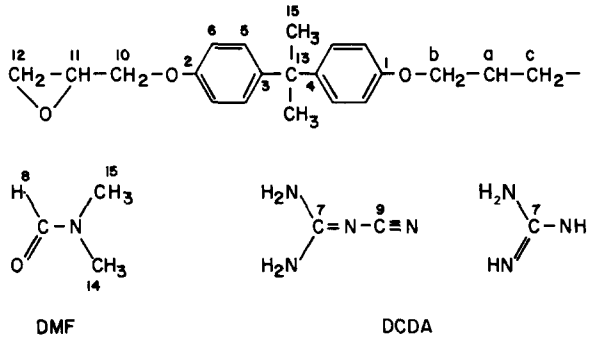


Figure 1 (a) Liquid-state ^{13}C n.m.r. spectrum of the sample 1:1, 120°C, 60 min, and (b) solid-state ^{13}C n.m.r. spectrum of the cured sample 2.5:1, 120°C, 120 min, without accelerator. Known structures and assigned signals are marked



is evident that the main reaction is strongly promoted below about 50% epoxy consumption.

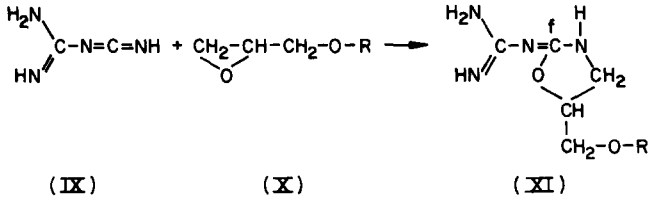
In one of the cured samples is an etherification signal clearly separable by solid-state ^{13}C n.m.r. Hence its proportion is less than 30% of the main reaction. Higher temperatures and an excess of BADGE favour etherification.

The resonances at 64 ppm have been assigned to primary hydroxyl groups carrying carbons e, as they arise from hydrolysis (see (VIII)).

The splitting of the nitrile signal (118.5 ppm) into a doublet could be due to the main reaction of DCDA. In this case the nitrile band shifts to 118.1 ppm. The intensities of both signals decrease with epoxy consumption. This process is accelerated with increasing temperature. It is evident that the nitrile group becomes more reactive at higher temperatures.

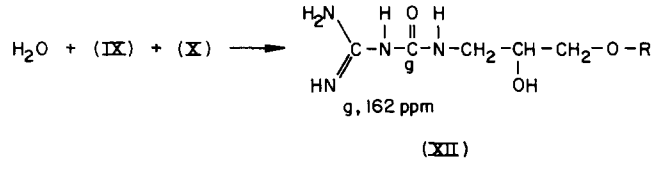
Figure 2 shows the behaviour of the imide intensities of DCDA (peak 7) *versus* curing time. The curves corresponding to higher hardener concentrations have a maximum that is higher than the initial fraction of the imide groups.

We assume that the third DCDA configuration could produce intramolecular cycles during reaction with the epoxy resin, with the destruction of the nitrile group:



The carbon f has the same chemical shift as carbon 7 of DCDA and therefore enhances its intensity. Furthermore, the ring in (XI) could cause the decrease of intensities in the liquid ^{13}C n.m.r. spectra of one series owing to high rigidity.

The two signals on the right-hand side of peak 8 can be traced back to reacted imide groups and to carbonyl structures. To build carbonyl structures, water and DCDA (III) play an important role:



This is in good agreement with the results of i.r. investigations, where we found a weak band at 1745 cm^{-1} due to carbonyl bonds. *Figure 3* shows the i.r. spectrum of sample 2.5:1 at 120°C for 180 min with 1 mol% imidazole accelerator. Because of evaporation of water, the abundance of carbonyl groups decreases with increasing temperature. The spectrum also shows the split nitrile resonance (2180 and 2160 cm^{-1}) corresponding to DCDA tautomerism.

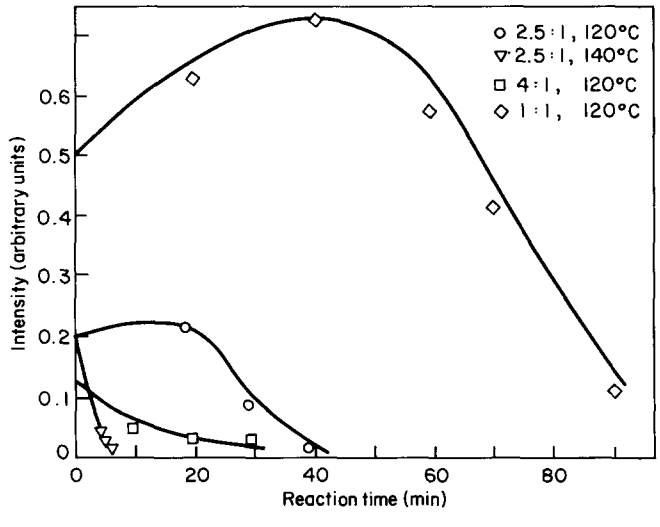


Figure 2 Imide intensities *versus* reaction time. Note the maximum in (◇) and (○) curves, which is higher than the initial fraction of imide bonds due to DCDA

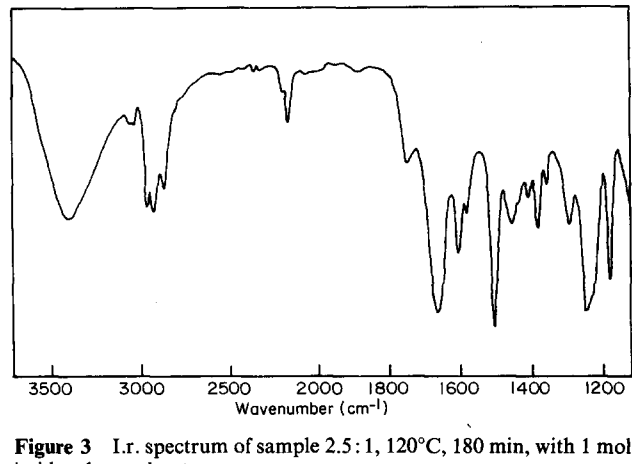
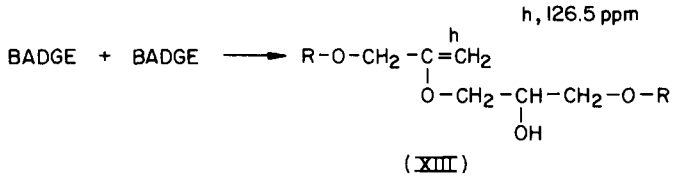


Figure 3 I.r. spectrum of sample 2.5:1, 120°C, 180 min, with 1 mol% imidazole accelerator

A weak signal at 126.5 ppm was detected in all liquid n.m.r. series, again vanishing above 20% epoxy consumption. The reason for this resonance is still unclear. Perhaps there is a relationship to double bonds if they exist after self-reaction of two BADGE monomers:



(XIII)

After tests on a model system (only PGE + 5 mol% DMBA, 120 min, 120°C), a signal at 126 ppm was detected with an epoxy consumption of about 95%.

Finally some remarks on the influence of the accelerators are necessary. Monuron, imidazole and DMBA accelerate the rate of curing. The gel point was reached after 2 min. Without accelerator, the samples were still soluble after 30 min of curing at 120°C. In contrast, the influence of the accelerators on the final structure of the network is very weak and not clearly detectable in solid-state ^{13}C n.m.r. and i.r. spectra.

CONCLUSIONS

The object of the investigation was the epoxy resin system comprising the diglycidyl ether of bisphenol A and 1-cyanoguanidine as the hardener dissolved in dimethylformamide. The course of reaction and the final structure of the network were studied as a function of the DCDA mole fraction, the reaction temperature and the reaction time. In addition, the influence of several accelerators on the curing mechanism was studied.

Using liquid-state ^{13}C n.m.r., different reactive groups were detected as a function of epoxy consumption. Initial investigations of the hardener led to the assumption of structural tautomerism. Intramolecular cycles and carbonyl structures were detected, owing to a third DCDA configuration formed during reaction.

The degree of etherification increased with excess BADGE and at higher temperatures. The reactivity of the nitrile groups increased at higher temperatures too.

Because of evaporation of water, carbonyl structures showed the inverse behaviour in their temperature dependence.

The accelerators used mainly acted on the reaction rate. No influence on the network structure is detectable.

High-resolution liquid-state and solid-state ^{13}C n.m.r. proved to be suitable methods for the investigation of the course of the reaction and the network structure of epoxy resin systems. In addition, important information was obtained by using i.r. measurements complementing the n.m.r. results.

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