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The Curing of an Epoxy Resin as Followed by Carbon-13 NMR Spectroscopy

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Synopsis

Variable-temperature carbon-13 NMR spectroscopy was used to examine the curing reaction of DGEBPA with piperidine. An initial adduct was directly observed and the disappearance of monomer could be conveniently followed. Unreacted epoxide carbons were detectable in cured samples.

INTRODUCTION

Carbon-13 NMR spectroscopy has become an important tool in the study of polymer structure.[1] The mechanisms of polymerization reactions have been inferred from the tacticity of the final polymer by carbon-13 NMR measurements.[2] We report the in situ examination of an epoxy curing reaction by carbon-13 NMR spectroscopy and the subsequent insight gained into the reaction mechanism and final polymer structure. The use of carbon-13 NMR rather than proton NMR for this study has a number of definite advantages. For example, the larger carbon-13 chemical shift range enables very subtle structural and conformational changes to be discerned. In addition, the carbon-13 spectrum may be simplified by proton decoupling which makes all the carbon resonances appear as singlets. This is in contrast to proton NMR where spectra of large molecules are complex because of homonuclear spin-spin splitting and congested because of the small proton chemical shift range.

Curing of the diglycidyl ether of bisphenol A (DGEBPA) with piperidine was performed in a variable-temperature probe of a carbon-13 pulsed NMR spectrometer. Formation of an initial adduct was directly observed and the progress of polymerization was followed by recording carbon-13 spectra at time intervals. Unreacted epoxide carbons were detected in this sample as well as in a sample of DGEBPA cured by standard procedures.

EXPERIMENTAL

The DGEBPA used was of high purity (Dow D.E.R. 332 LC). Compound 5 was Epon 1001 (Shell). The resins and Fisher Certified piperidine were used without further purification. Carbon-13 NMR spectra were obtained at 25.15 MHz on a modified Varian HA-100 spectrometer equipped with pulse

TABLE I
Carbon-13 Chemical Shifts in ppm Relative to TMS

Compound	C-a	C-b	C-c	C-d	C-e	C-f	C-α	C-β	C-γ	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-4′
DGEBPA	69.4	50.2	44.3	—	—	—	—	—	—	157.0	114.5	128.0	143.8	42.1	31.5	—	—
Piperidine	—	—	—	—	—	—	47.9	27.9	25.9	—	—	—	—	—	—	—	—
Initial adduct																	
(1)	69.7	50.4	44.4	71.9	66.9	62.4	55.4	26.6	24.8	157.2[a]	114.9	128.1	144.0[a]	42.1	31.5	157.5[a]	143.5[a]
2	—	—	—	70.8	66.0	62.2	55.0	26.0	24.3	158.7	114.4	129.0	120.3	—	—	—	—
4	—	—	—	71.7	66.5	68.8	—	—	—	158.6	114.5	129.1	120.5	69.3	14.9	—	—
5																	
(Epon 1001)	69.2	50.1	44.0	69.5	68.9	69.5	—	—	—	156.8[a]	114.1	127.7	143.8[a]	41.7	31.5	156.6[a]	143.2[a]
Polymer[b] (6)	69.8	50.3	44.4	72.3	71.0	72.3	55.5	26.2	—	157.2	115.4	128.4	144.2	42.1	31.3	—	—

[a] The chemical shift assignments for C-1 and C-1′ and for C-4 and C-4′ may be interchanged.
[b] Unassignable shifts appeared at 48.8, 60.8, and 78.6 ppm.

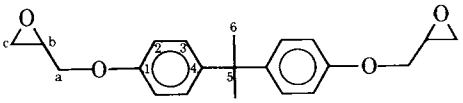
capability, external fluorine-19 lock, proton decoupling, and a 5-mm variable-temperature probe. A 90° pulse took 120 μsec. The time between pulses was 0.2 sec, and 1024 free induction decays were accumulated in a Nicolet 1074 Signal Averager before being Fourier transformed by a PDP-8/L computer. The spectral width was 250 ppm, and the computer resolution was 3 Hz. Chemical shifts were measured relative to the dimethylated carbon of DGEBPA. The shift of this carbon was independently determined to be 42.1 ppm from CCl_4. Chemical shift values were converted to the TMS scale using the relationship $\delta_{TMS} = \delta_{CCl_4} + 96.0$. Proton-coupled spectra were also obtained as an aid in chemical shift assignment. Samples of DGEBPA containing 4.76% piperidine were thoroughly mixed and immediately placed in the spectrometer probe. Spectra were obtained as a function of time and temperature. An authentic sample of 1 was made in the heated spectrometer probe by reacting equimolar amounts of DGEBPA and piperidine in dilute toluene solution.

1-Piperidinyl-3-phenoxy-2-propanol (2). To an ethereal solution of 15 g (0.1 mole) 1,2-epoxy-3-phenoxypropane was added 8.5 g (0.1 mole) piperidine. This mixture was stirred at room temperature for 2.5 days. The solvent was flash evaporated leaving 22.1 g (90%) 1-piperidinyl-3-phenoxy-2-propanol as a white solid: mp 50–52°; IR 3200, 1245, 1110, 1040 cm^{-1}; NMR (CCl_4) δ 1.5 (*m*, 6H), 2.4 (*m*, 6H), 3.9 (*m*, 3H), 4.87 (*s*, 1H), 6.8 (*m*, 5H).

1-Ethoxy-3-phenoxy-2-propanol (4). Sodium ethoxide was prepared by adding 2.3 g (0.1 mole) metallic sodium to ~100 ml EtOH. To this stirred solution was added dropwise 15 g (0.1 mole) 1,2-epoxy-3-phenoxypropane. After refluxing overnight, the reaction mixture was diluted with Et_2O and washed with H_2O. The organic layer was separated, dried over molecular sieves, and flash evaporated to leave ~13 g (64%) of a yellow oil: IR (neat) 3440 and 1250 cm^{-1}; NMR (TMS) δ 1.08 (*t*, *J* = 6 Hz, 3H), 3.34 (*q*, *J* = 6 Hz, 2H), 3.48 (*d*, *J* = 4 Hz, 2H), 3.92 (*d*, *J* = 5 Hz, 2H), 4.1 (*m*, 1H), 4.48 (*s*, 1H), 6.9 (*m*, 5H).

RESULTS AND DISCUSSION

Figure 1A is the carbon-13 spectrum of DGEBPA in CCl_4. Figure 1B shows the spectrum of DGEBPA containing 4.76% piperidine at a probe temperature of 30°C. The carbon resonances of monomer and piperidine are clearly visible in the latter. The lines appear broadened because of motional restrictions due to the high viscosity of the sample. Carbon-13 chemical shifts are given in Table I.



DGEBPA

The Initial Adduct. The probe temperature was raised to 90°, and the carbon-13 spectrum shown in Figure 1C was recorded. Clearly, a reaction occurred giving rise to new signals which were attributable to initial adduct 1. The adduct was identified on the basis of chemical shift similarity with model compound 2 and with an authentic sample of 1 obtained by reaction of

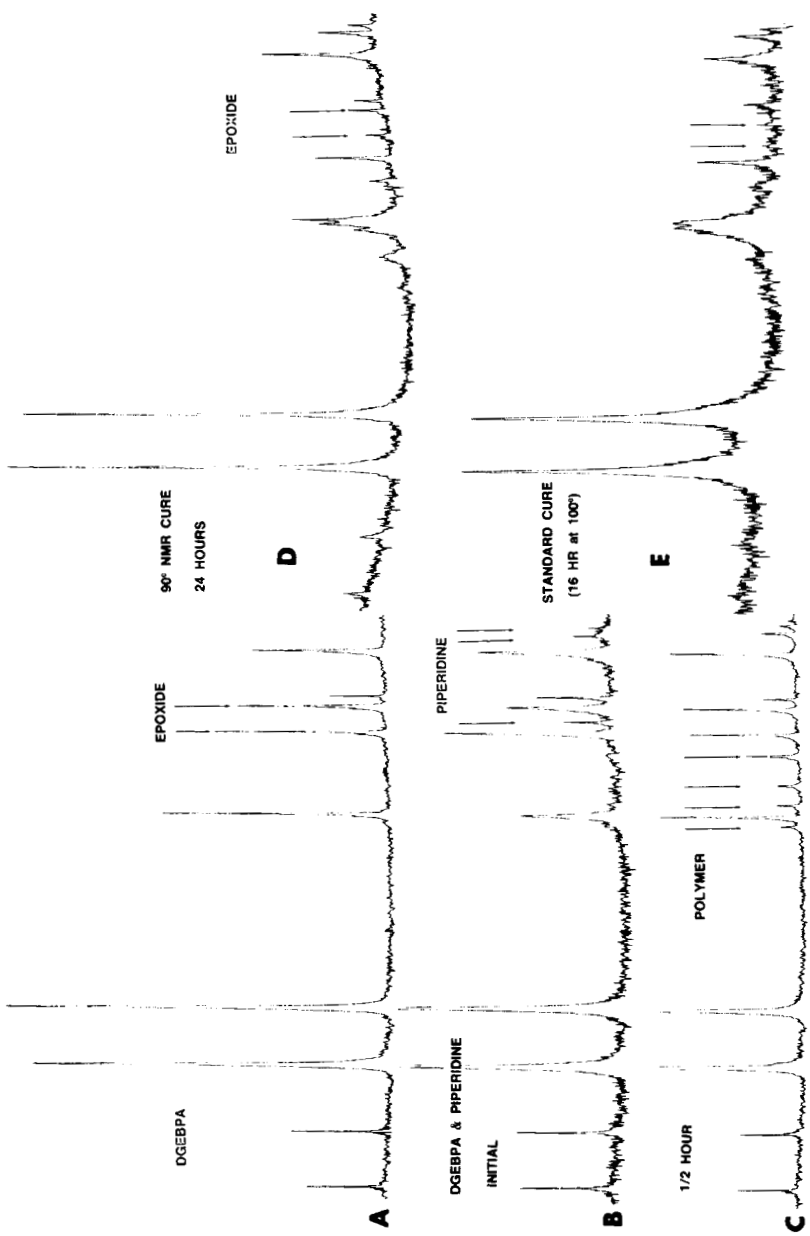
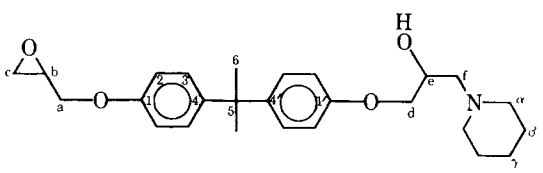


Fig. 1. Carbon-13 NMR spectra of DGEBPA piperidine system. The spectral width is 250 ppm: (A) DGEBPA + CCl_4; (B) DGEBPA + piperidine at 30°C; DGEBPA + piperidine at 90°C; (D) DGEBPA + piperidine cured at 90°C for 24 hr; (E) DGEBPA + piperidine cured at 100°C for 16 hr.

DGEBPA with an equimolar amount of piperidine in dilute toluene solution (Table I):



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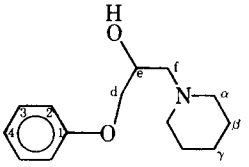

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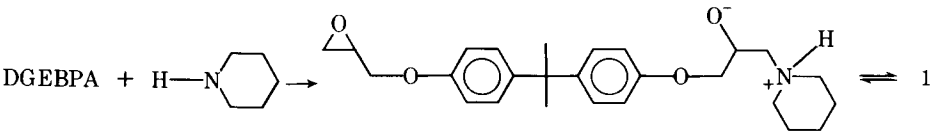
This indicates that the first step of the polymerization mechanism involves nucleophilic attack of the piperidine on the terminal epoxide carbon. The epoxide ring opens forming zwitterion 3,



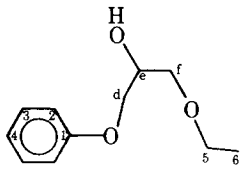
3

which is in equilibrium with the neutral adduct 1.

The Polymerization Reaction. Subsequent spectra obtained over a period of 4 hr showed a gradual broadening and diminishing of these new signals. This indicates additional reaction of 1 or its zwitterion form 3 with other monomer units and subsequent polymerization. As the molecule grows in size, the observation of carbon-13 resonances becomes more difficult with the present instrumentation. Under special conditions the observation of carbon-13 resonances in solids is possible. See, for example references 3 and 4.

The epoxide carbon resonances remained narrow and gradually decreased in intensity over the 4-hr observation period. In fact, zero-order plots were obtained when the relative epoxide carbon areas were plotted against time. Thus, carbon-13 NMR provides an alternative method of observing monomer disappearance during curing reactions.

Final Cure. The sample was cured at 90° in the spectrometer probe for 24 hr. In order to see carbon-13 signals, the probe temperature was raised above T_g to 180°C. Even at this temperature, the signals are noticeably broad (Fig. 1D). Unreacted epoxide carbons are still detectable. The chemical shifts of the polymer were assigned with the aid of model compounds 4 and 5,



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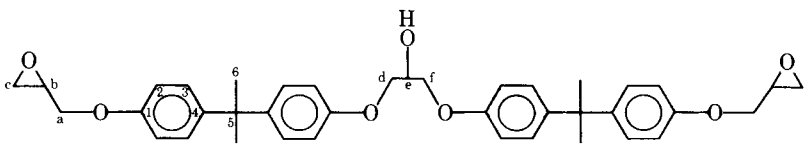

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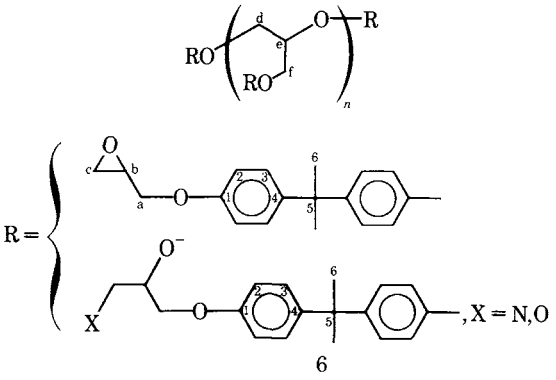
and are consistent with structure 6:



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The standard cure spectrum obtained at the same probe temperature (Fig. 1E) appears to be more fully cured by comparison because of additional line broadening and the disappearance of several signals. However, unreacted epoxide carbons are still visible even in this sample.

CONCLUSIONS

Carbon-13 NMR spectroscopy can be used to follow the progress of an epoxide curing reaction. The mechanism involves initial formation of an adduct which was directly observed. The disappearance of monomer was easily followed during the reaction. A generalized structure for the polymer was deduced. Carbon-13 spectra of cured samples heated above T_g revealed unreacted epoxide groups and the extent of cure.

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References

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