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High temperature ^{1}H NMR studies of epoxy cure: A neglected technique

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Summary

By reference to the reaction of a copper complex of phenyl glycidyl ether and 2-ethyl-4-methylimidazole, and Bisphenol A diglycidyl ether, ^{1}H nuclear magnetic resonance spectroscopy at high temperature is shown to be an excellent and under-utilized method for measuring the degree of cure, enabling kinetic parameters to be obtained.

Introduction

Reactions are usually investigated in the presence of solvent and often under conditions where the reactant concentrations are low so that a range of experimental methods can be employed to follow the kinetics. With the increasing interest in being able to model reactions (1), particularly those of an industrial nature, the presence of the solvent can be a complicating factor and extrapolation of the data to the 'real' conditions introduces an additional and unnecessary source of uncertainty. Unfortunately the experimental methods initially chosen are invariably no longer applicable. One or both of the reactants may be solids, in which case heating to above the melting temperature may be necessary. The purpose of this communication is to show that under these circumstances ^{1}H nmr spectroscopy, with a variable temperature probe in which temperatures as high as 450°C can be achieved, is a valuable, and as yet, neglected technique, particularly in the area of epoxy cure.

The use of imidazoles as curing agents for epoxy resins is well-established (2-4) and known to produce cured products with good physico-mechanical properties, although they suffer from poor storage stability. Elsewhere we report (5,6) the use of copper complexes of phenyl glycidyl ether and 2-ethyl-4-methylimidazole (*1*) (Figure 1) as curing agents for epoxy resins which display improved storage stability enabling their formulation in one-pot compositions. While remaining stable at ambient and low temperature, the complex (*1*) dissociates at *ca.* 120°C to produce the adduct (*2*). The reaction which we have chosen in order to exemplify the advantages of the nmr method is that between the adduct of phenyl glycidyl ether and 2-ethyl-4-methylimidazole (*2*) and a commercial prepolymer of Bisphenol-A diglycidyl ether (*3*).

Experimental

High temperature ^{1}H nmr spectra were obtained using a Bruker AC-300 spectrometer at pre-programmed time intervals using an automated routine. The ratio of the integrals of the epoxide methylene protons (doublet at *ca.* 1.56 ppm) and an internal standard, the methyl protons in the isopropylidene bridge (singlet at *ca.* 0.6 ppm) was determined and converted to epoxide concentration. Figure 2 shows a stacked plot of ^{1}H nmr spectra for a bulk sample containing 10 mole-% of curing agent, recorded at a temperature of 150°C over the course of 10 hours; the narrow lines and good resolution makes the calculation of epoxide concentration and the extent of cure simple and straightforward.

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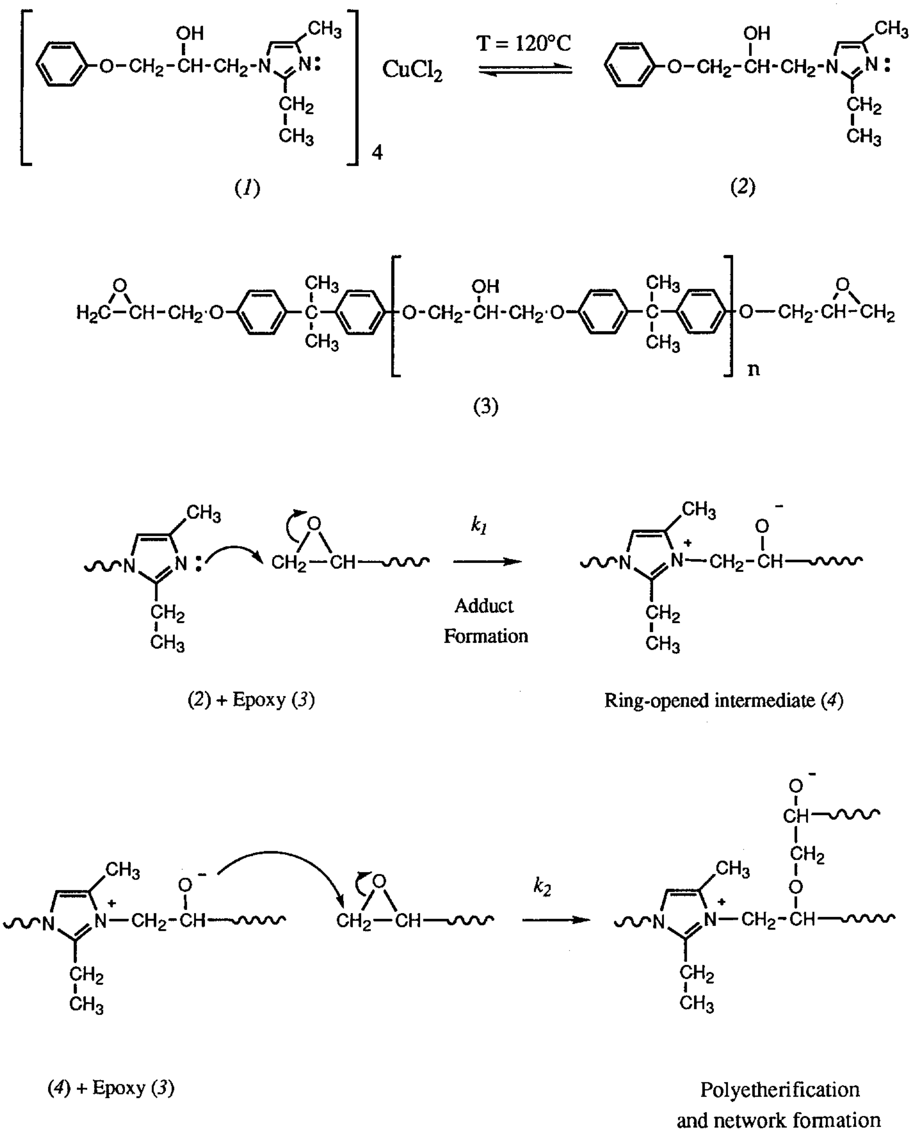

Figure 1. Structures of the compounds employed in this study and the proposed mechanism of cure

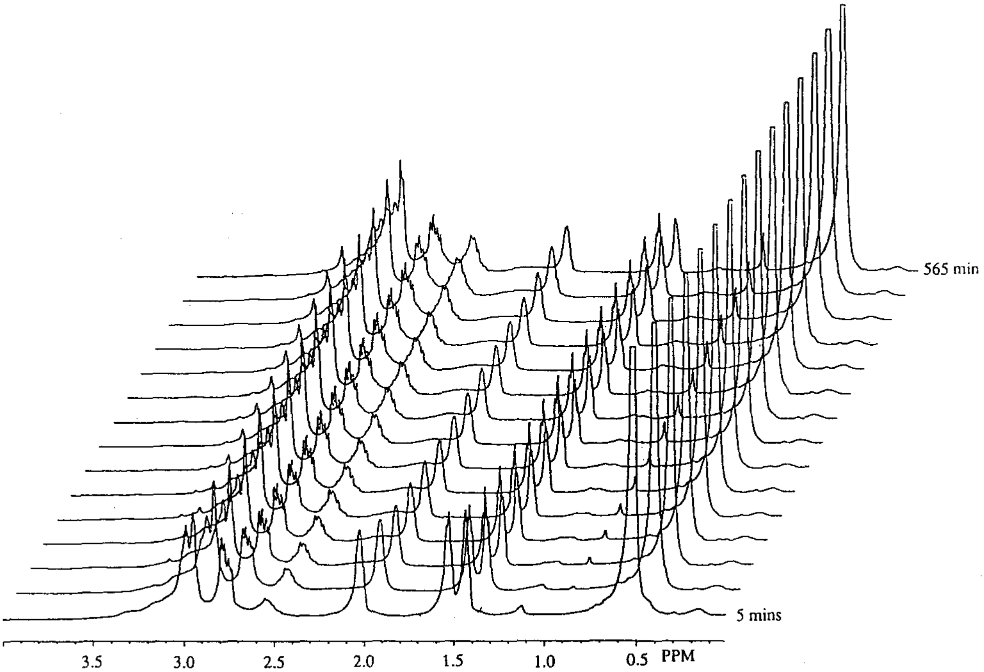

Figure 2. ^{1}H nmr spectra (showing expansion of oxirane ring region) of progressively cured MY750 (from 5 to 565 minutes at 150°C) containing 10 mole-% curing agent.

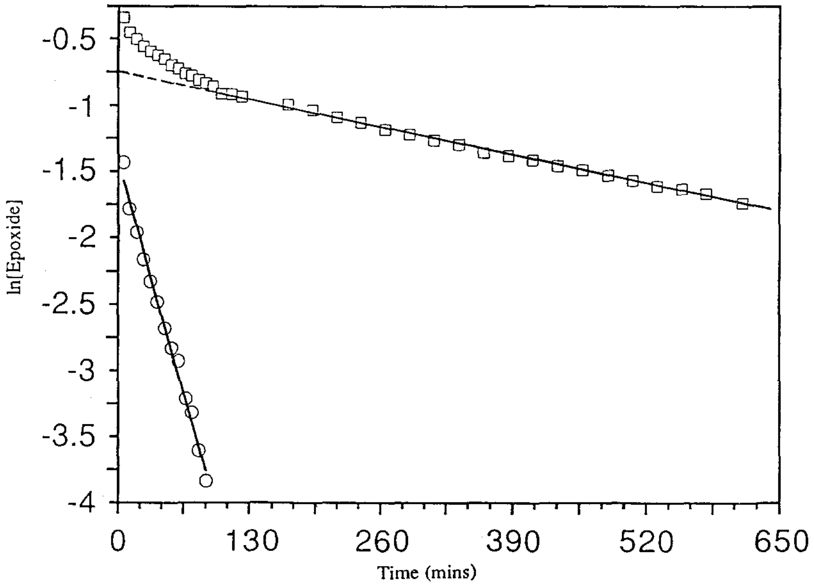

Figure 3. Plot of ln[Epoxide] against reaction time for MY750 cured with 10 mole-% curing agent, showing derivation of k_1 and k_2.

Results and Discussion

The imidazole-induced cure reaction is depicted in Figure 1; it involves two consecutive first order mechanisms: the activation of the lone pair of electrons on the imidazole ring to attack the oxirane ring results in the opening of the epoxy group (k_1) while the base (alkoxide) catalyzed homopolymerization of the epoxy ring (polyetherification) and subsequent network formation is also a first order reaction under the experimental conditions (k_2). When the logarithm of the epoxide concentration is plotted against time (Figure 3) the results appear as two consecutive first order processes whose rates are sufficiently different so as to be able to calculate both rate constants (the plot of k_1 was obtained from the differences between the extrapolation of the linear portion of the ln[Epoxide] plot and the points between t = 0 and 110 minutes). The upper curve in Figure 3 is the experimental data, and the lower data set is from the subtraction procedure. Another important advantage of the method (as it was not possible to obtain k_1 using the other techniques). These reactions have first order rate constants ($k_1 = 4.48 \times 10^{-4}\ s^{-1}$, $k_2 = 1.70 \times 10^{-5}\ s^{-1}$ at 150°C) that are conveniently slow so that the time taken for spectrum acquisition (109 seconds per spectrum) is relatively unimportant. The sharpness of the signals (linewidths < 8Hz) remains a feature of the spectra up to the stage when gelation starts to occur. The Arrhenius parameters are discussed in detail elsewhere (6).

Table 1 Curing reaction parameters obtained (6) from several analysis techniques

Monitoring Technique	Temperature (°C)	Curing Agent (mole-%)	k_1 (10^{-6} sec^{-1})	k_2 (10^{-5} sec^{-1})
^{1}H n.m.r. (D_6-DMSO)	150	13	-	4.03
^{1}H n.m.r. (fused state)	140	10	4.05	1.85
FT-IR	140	10	-	1.88

Conclusion

High temperature magnetic resonance spectroscopy for samples in a fused state (in the absence of solvent) has been shown to yield high quality spectra allowing the derivation of kinetic parameters which are in close agreement with those obtained from other spectroscopic techniques. Whilst we have illustrated the advantages of the technique to the problem of epoxy resin cure we have little doubt that the method is under-utilized and has potential application outside this immediate area.

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